FUNCTIONAL POLYMERS DERIVED FROM 4-METHYLSTYRENE

by

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To my wife, Chimin

my father,

and my son, Yiqing

FUNCTIONAL POLYMERS DERIVED FROM 4-METHYLSTYRENE

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ABSTRACT

Novel procedures for the oxidation of 4-methylstyrene homopolymer and copolymers by a single step process have been developed. Poly(4-methylstyrene)s bearing a series of different functional groups (aldehyde, carboxylic acid, acetoxymethyl, nitrooxymethyl, trichloroacetoxymethyl, chloromethyl groups) have been prepared using these oxidation processes. As well, parameters that effect the reaction (molar ratio of oxidants to polymer, cosolvents, temperature, and reaction time) were investigated, and reaction mechanisms for these processes were proposed.

A common feature of the oxidations is a reduction in molecular weight of the resulting polymers. Mechanisms of degradation of poly(4-methylstyrene) by ceric (IV) under oxygen or nitrogen were proposed. This backbone cleavage was minimized by forming copolymers of 4-methylstyrene and alkyl methacrylates (methyl methacrylate, n-butyl methacrylate, and dodecyl methacrylate) or of 4-methylstyrene/α-methylstyrene. These copolymers are resistant to oxidative backbone cleavage, due to the steric effect of the α-methyl comonomer. the degree of backbone cleavage depends on the α-methyl comonomer content and sequences in these copolymers.

In addition, the thermal properties of functional polymers were studied by thermogravimetry and differential scanning calorimetry.

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PUBLICATIONS BASED ON THIS RESEARCH

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1. Quan Sheng, and Harald D. H. Stöver, **Selective modification of 4-methylstyrene polymers,** *ACS Polymeric Materials Science and Engineering*, **76**, 89, 1997.
2. Quan Sheng, and Harald D. H. Stöver, **Selective functionalization of poly(4-methylstyrene).** submitted to *Macromolecules.*
3. Quan Sheng, and Harald D. H. Stöver, **A new route to chlorination of poly(4-methylstyrene).** submitted to *J. Am. Chem. Soc.*
4. Quan Sheng, Harald D. H. Stöver, and I. J. De Souza, **Synthesis and oxidation of copolymer of 4-methylstyrene and methyl methacrylate**. to be submitted to *Macromolecules.*
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7. Quan Sheng, and Harald D. H. Stöver, **Thermal properties of functional poly(4-methylstyrene)**. in preparation.

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8. Quan Sheng, and Harald D. H. Stöver, **Selective Functionalization of poly(4-methylstyrene),** *35th IUPAC International Symposium on Macromolecules, Abstract Preprints*, p153, Akron, Ohio, July, 1994.

9 Quan Sheng, and Harald D. H. Stöver, **Oxidative Functionalization of 4-methylstyrene/alkyl methacrylate copolymers,** *78th Canadian Society for Chemistry Conference and Exhibition, Abstract Book*, No 261, Guelph, Ontario, May, 1995.

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LIST OF ABBREVIATIONS

AMA	Alkyl methacrylate
AIBN	2,2'-Azobisisobutyronitrile
BMA	Butyl methacrylate
CAN	Ceric ammonium nitrate
DMA	Dodecyl methacrylate
DMSO	Dimethylsulfoxide
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
EA	Elemental analysis
ESCA	Electron spectroscopy for chemical application
ESR	Electron spin resonance
GC	Gas chromatography
IR	Infrared spectroscopy
MEK	Methylethylketone
MMA	Methyl methacrylate
Mn	Number average molecular weight
MS	Mass spectroscopy
4MS	4-Methylstyrene

αMS	α-Methylstyrene
Mv	Viscosity molecular weight
Mw	Weight average molecular weight
MWD	Molecular weight distribution
NAA	Neutron activation analysis
NMR	Nuclear magnetic resonance
PBMA	Poly(butyl methacrylate)
PDMA	Poly(dodecyl methacrylate)
PMMA	Poly(methyl methacrylate)
P4MS	Poly(4-methylstyrene)
PαMS	Poly(α-methylstyrene)
PVA	Poly(vinyl alcohol)
PY-GC	Pyrolysis-gas chromatography
r.t.	Room temperature
SB	Styrene-butadine rubber
SBS	Styrene-butadine-styrene copolymer
SEC	Size exclusion chromatography
SEM	Scanning electron microscopy
SIS	Styrene-isoprene-styrene copolymer
TCA	Trichloroacetic acid
TEM	Transmission electron microscopy
TG	Thermogravimetry

TGA	Thermogravimetric analysis
Tg	Glass transition temperature
Tm	Melting temperature
UV	Ultraviolet spectroscopy
VBC	Vinyl benzyl chloride

CHAPTER 1

AN OVERVIEW OF THE SYNTHESIS AND CHARACTERIZATION OF FUNCTIONAL POLYMERS

1.1 INTRODUCTION

The study of functional polymers has received considerable attention in recent years, and many such polymers and materials have found applications in different areas of science and technology. The term 'functional polymers' includes two main categories: (a) polymers that perform certain functions, such as bearing loads or responding to light; and (b) polymers that incorporate chemical functional groups.[1]

Functional polymeric materials in the first sense include many engineering plastics such as polyester or polyamide. Also, uses of optically transparent polymeric materials increase rapidly. For example, optical fibers are widely used as substitutes for glass and quartz devices in various fields of technology, especially the biomedical and communication sciences.[1]

The functional polymers in the second sense are polymers incorporating chemical functional groups. This is a very exciting subject which has developed extensively in the past twenty years. Some of the highlights in this area include photo-sensitive polymers used for integrated circuit production, ion-exchange resins and membranes, and biomedical polymers. The chemistry of polymeric drugs, for example, is under continuous advancement, and the most effective anticancer agents incorporate functional polymers, both as supports and to help in targeting.[1]

In the area of chemically functional polymers, styrene-based systems continue to be exceedingly versatile and useful. This Ph.D. thesis focuses on novel chemical modifications of the homopolymer and copolymers of 4-methylstyrene. The review of functional polymers below will hence focus mainly on styrenic polymers.

1.2 SYNTHESIS OF FUNCTIONAL POLYMERS

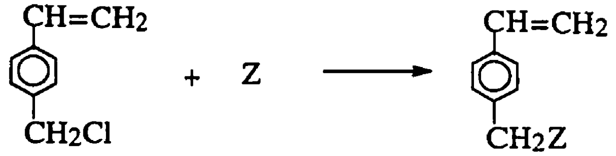
Functional polymers are produced either by direct (co)polymerization[2,3] of the desired functional monomers with suitably chosen structural and crosslinking monomers, or by chemical modification of preformed nonfunctional polymers.[4] In many instances, either of these two approaches can be employed for the synthesis of a given functional polymer, and the choice between the two alternatives is based on experience, availability of starting materials, convenience, and economic considerations.

1.2.1 Copolymerization of Functional Styrenic Monomers:

This route to functional polymers involves the synthesis and copolymerization of functional monomers. During the past twenty years, the research in this area has attracted considerable interest.[5]

1.2.1.1 Styrene-Based Functional Monomers

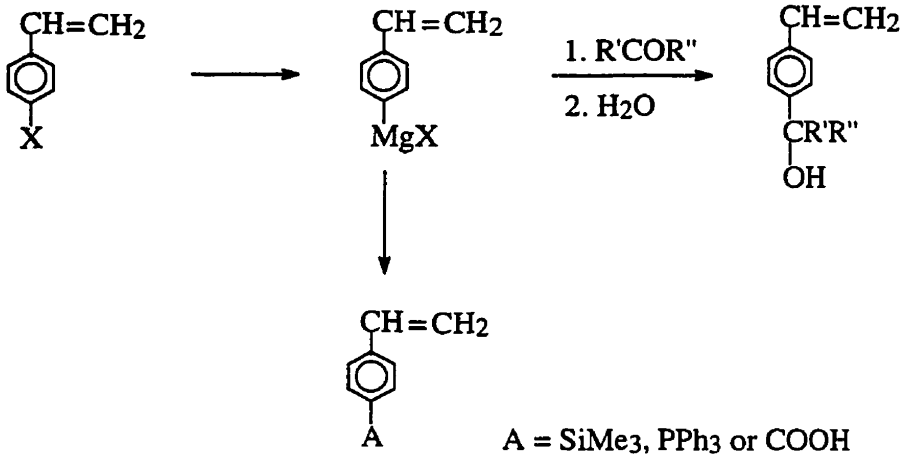
Provided a suitable ring-substituted styrene derivative is readily accessible, derivatization of such a monomer may provide a relatively straightforward route to other styrene-based functional monomers. This is particularly true in the case of chloromethylstyrene (vinyl benzyl chloride, VBC). Here, the chlorine atom in the monomer can be replaced by a variety of functional residues via nucleophilic substitution, as indicated in Figure 1.1.



$Z = OH, NMe_3, O(CH_2CH_2O)nMe, SCO_2CMe_3$, etc

Figure 1.1 Derivatization of chloromethylstyrene

Extensive compilations of patent literature on this topic are available in a pamphlet published by the Dow Chemical Company[6] and in a review by Camps *et al.*[7] Among other styrene derivatives which may, to a lesser extent, be suitable for further derivatization are 4-bromostyrene and 4-chlorostyrene (Figure 1.2)[8,9] and 4-hydroxystyrene. In the latter case, functional residues can be attached to the monomer through an ether or ester linkage.

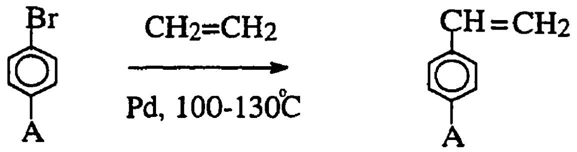


A = $SiMe_3$, PPh_3 or COOH

Figure 1.2 Derivatization of halostyrene via Grignard reaction

1.2.1.1a Direct Attachment of a Vinyl Function

Recently, Heiz and his colleagues[10] described an interesting one-pot synthesis of a variety of styrene-based functional monomers, as shown in Figure. 1.3. This new contribution by Heiz is a particularly welcome addition to the already known methods of styrene synthesis. In many instances these one-pot syntheses may be preferred over alternative methods.



A = CHO, COOH, $CONH_2$, NHCOMe, OMe, NO_2,

Figure 1.3 Synthesis of styrene derivatives via Heck reaction

1.2.1.1b Double Bond Formation via Wittig Reaction

There are two possibilities for styrene synthesis via the Wittig reaction, as illustrated in Figure 1.4.[11,12] These syntheses appear facile, but in practice they are often less convenient (and more expensive) than those shown in Figure 1.5 and Figure 1.6.

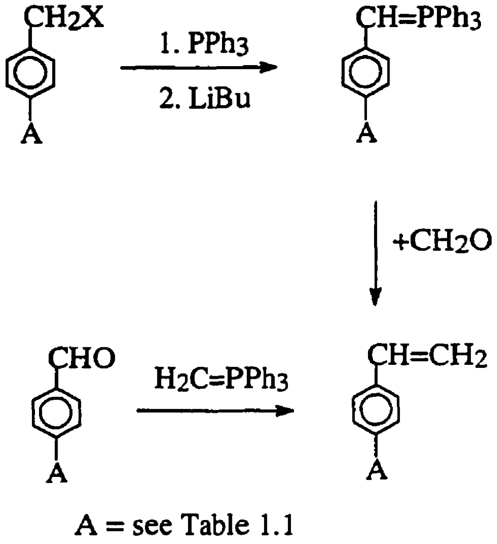
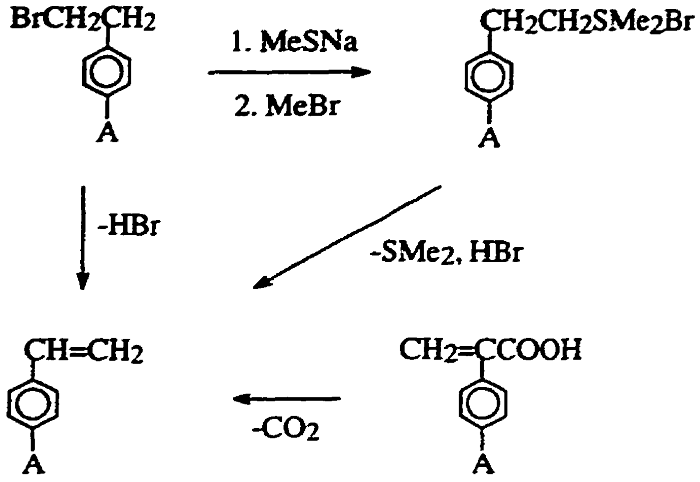


Figure 1.4 Synthesis of styrene derivatives via Wittig reaction

1.2.1.1c Double Bond Formation via Elimination

Examples of styrene derivatives produced via elimination reactions of carbon dioxide[13], aluminum alkoxide[14], hydrogen halides[15,16], or methylsulfonium bromide[17] are shown in Figure 1.5. Another important elimination reaction for the generation of a double bond is dehydration. This method is the one most frequently reported for the synthesis of styrene-based functional monomers, and it is described below in greater detail.

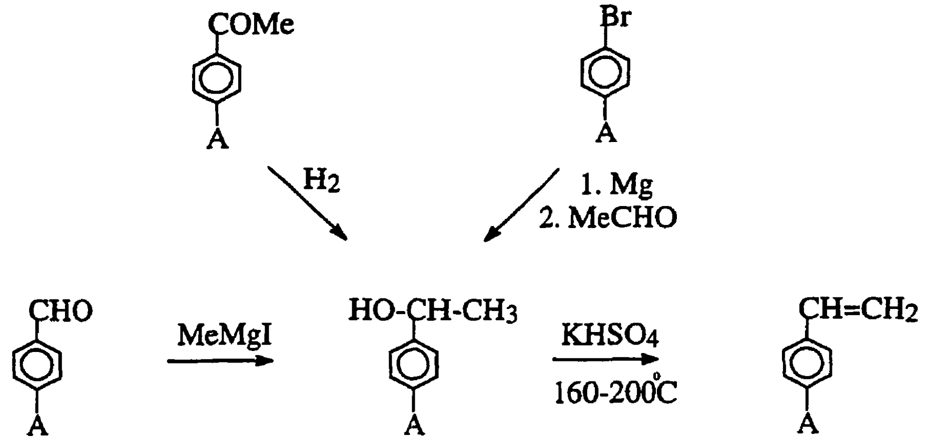


A = see Table 1.1

Figure 1.5 Synthesis of styrene derivatives via elimination reaction other than dehydration.

1.2.1.1d Styrene Synthesis by Thermal Dehydration

The immediate precursors for the synthesis of styrene derivatives by dehydration are 1-arylethanols. These can be produced from acetophenones[18], benzaldehydes[19], and halobenzenes[8,19], and they can be converted to the corresponding styrene derivatives by thermal dehydration, as indicated in Figure 1.6. The dehydration reaction is most conveniently carried out at 160 - 200°C, under which condition the dehydration product is collected by distillation as it is formed.



A = see Table 1.1

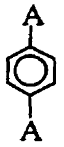
Figure 1.6 Synthesis of styrene derivatives via dehydration of 1-arylethanols

Commonly an acid catalyst and a free radical inhibitor are added. Several acid catalysts are known to effect alcohol dehydration,[21] but potassium hydrogen sulfate is more generally used for the synthesis of substituted styrene from 1-arylethanols. A free radical inhibitor (usually a phenol) is added to the dehydration mixture to prevent the polymerization of the resulting monomer. In this connection, it has been observed,[8] that the dehydration reaction proceeds more smoothly in the presence of a more acidic phenol such as trinitrophenol as compared to 2,6-di-*tert*-butylphenol.

1.2.1.1e Comments on the Synthesis of Styrene Derivatives

It is interesting to note that all of the syntheses shown in Figure 1.2-1.6 are aimed at 4-substituted styrenes. In principle, the corresponding 2- and 3- isomers, as well as di- and more highly substituted styrenes, can be produced by the same synthetic routes. However, in the case of the mono-substituted styrenes, the *para* isomer is generally preferred for the synthesis of polymer supports due to the greater accessibility of the functional groups on the polymer. In addition, 1,4-disubstituted benzenes are usually more readily accessible. Interesting examples of di- and tri-substituted styrenes include vinylsalicylaldehyde,[11] vinylsalicylic acid,[22] and the hindered vinylphenols.[23,24]

Among various benzene derivatives potentially suitable for the synthesis of 4-substituted styrenes, the symmetrically disubstituted benzenes appear to be particularly interesting.



A = Br, CH_2Cl, CHO.

For example, 1,4-dibromobenzene reacts with magnesium, in highly concentrated ether solution, to produce a mixture in which 4-bromophenylmagnesium bromide is the major component. The latter compound can then be used to synthesize either 4-bromostyrene[20] or 4-methoxymethylstyrene.[25] Similarly, 1,4-dichloromethylbenzene and 1,4-diformylbenzene have been used for the synthesis of, respectively, 4-divinylbenzene[11] and 4-chloromethylstyrene.[13]

In summary, most synthetic routes reported for the preparation of styrene-based functional monomers (**F1**) can be grouped under three main categories:

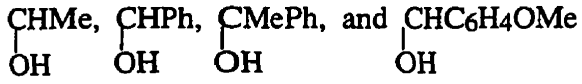
1. Direct attachment of the vinyl group ($CH=CH_2$) to the aromatic ring.
2. Generation of the double bond by a Wittig reaction.
3. Generation of the double bond by an elimination reaction.

Typical examples of styrene derivatives obtained by each of these routes are listed in Table 1.1.

Table 1.1 Example of 4-Substituted Styrenes ($CH_2=CH-C_6H_4-A$, F1) Prepared According to Figure 1.2-1.6

Monomer	A	Aromatic precursor	Method	Ref,
F1a	CH_2OH^a	4-Bromostyrene	Fig. 1.2	8
F1b	PPh_2	4-Chlorostyrene	Fig. 1.2	9
F1c	$COOH^b$	4-Chlorostyrene	Fig. 1.2	9
F1e	CHO^c	4-Bromobenzaldehyde	Fig. 1.3	10
F1f	$CH=CH_2$	Chloromethylstyrene	Fig. 1.4	11
F1g	$OCOCMe_3$	4-Hydroxybenzaldehyde	Fig. 1.4	12
F1e	CHO	Terephthaldicarboxyaldehyde	Fig. 1.5	13
F1h	Br	4-Bromocinnamic acid	Fig. 1.5	13
F1i	OMe	4-Methoxyacetophenone	Fig. 1.5	14
F1h	Br	2-Bromoethyl precursor	Fig. 1.5	15
F1	CH_2Cl	2-Bromoethyl precursor	Fig. 1.5	16
F1i	OMe^d	2-S-S-Dimethylethylsulfonium bromide precursor	Fig,.1 5	17
F1k	OCOMe	4-Hydroxyacetophenone	Fig. 1.6	18
F1l	Cl^e	Bromophenyl or benzaldehyde precursor	Fig. 1.6	19
F1f	$CH=CH_2$	4-Bromostyrene	Fig. 1.6	8
F1h	Br	4-Dibromobenzene	Fig. 1.6	20

[a] Also:



$\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{HMe}$, $\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{HPh}$, $\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{MePh}$, and $\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{HC_6H_4OMe}$

[b] Also: $SnPh_3$, and $SiMe_3$.

[c] Also: COOH, $CONH_2$, NHCOMe, OMe, and NO_2.

[d] Also: Br, Cl, and other substituent.

[e] Also: Dibromo- and dichlorostyrene.

1.2.1.2 Copolymerizability and Monomer Choice

When producing polymers by copolymerization, an important consideration is whether, and how, a particular functional monomer will copolymerize with a given structural monomer. Thus, in general, the copolymerization limits of a given monomer pair must be carefully assessed before attempting the synthesis of a desired functional copolymer. In homogeneous solution or bulk copolymerization, two different vinyl monomers copolymerize according to their reactivity ratios.[26,27]

Briefly, two monomers present may copolymerize in a random, alternate, or blockwise fashion. It is also possible that one of the monomers may homopolymerize with little or no incorporation of the other. The reactivity ratios of a large number of monomer pairs is known,[27] or it can be deduced from related information (i.e., *Q*-*e* values[28]).

The synthesis of crosslinked polymer supports usually involves a "terpolymerization" reaction, i.e., the simultaneous copolymerization of three monomers. Determination of terpolymerization reactivity ratios is more complicated,[29] and not many terpolymerization parameters are available. However, as a first approximation, relevant copolymerization reactivity ratios may be assessed to give an idea of the pattern by which a particular functional or crosslinking monomer may be incorporated into a three-component polymer matrix.

Another important consideration is that in heterogeneous polymerization systems, namely suspension, emulsion, dispersion, and precipitation techniques,[30] the copolymerizability of a given monomer pair may not necessarily follow the reactivity ratios found in homogeneous bulk (or solution) polymerization. This is due to the different partitioning of two monomers between the two phases present in the polymerization mixture. When this occurs, the composition of the resulting polymer may be different from that expected on the basis of the established reactivity ratios.

1.2.2 Modification of Polymers

Active functional groups can also be introduced into homopolymers and copolymers through chemical modification of pre-formed polymers.

1.2.2.1 Styrenic Polymers by Polymer Modification.

Linear polystyrene and cross-linked styrene-divinylbenzene resins have been subject to more chemical transformation than any other group of polymers, largely because they form the basis of water-treatment resins,[31] and have attracted wide interest as heterogeneous supports for reagents and catalysts.[32] Figure 1.7 shows some important reactions. Some of these, such as the chloromethylation and sulfonation reactions, are the basis of major industrial processes.

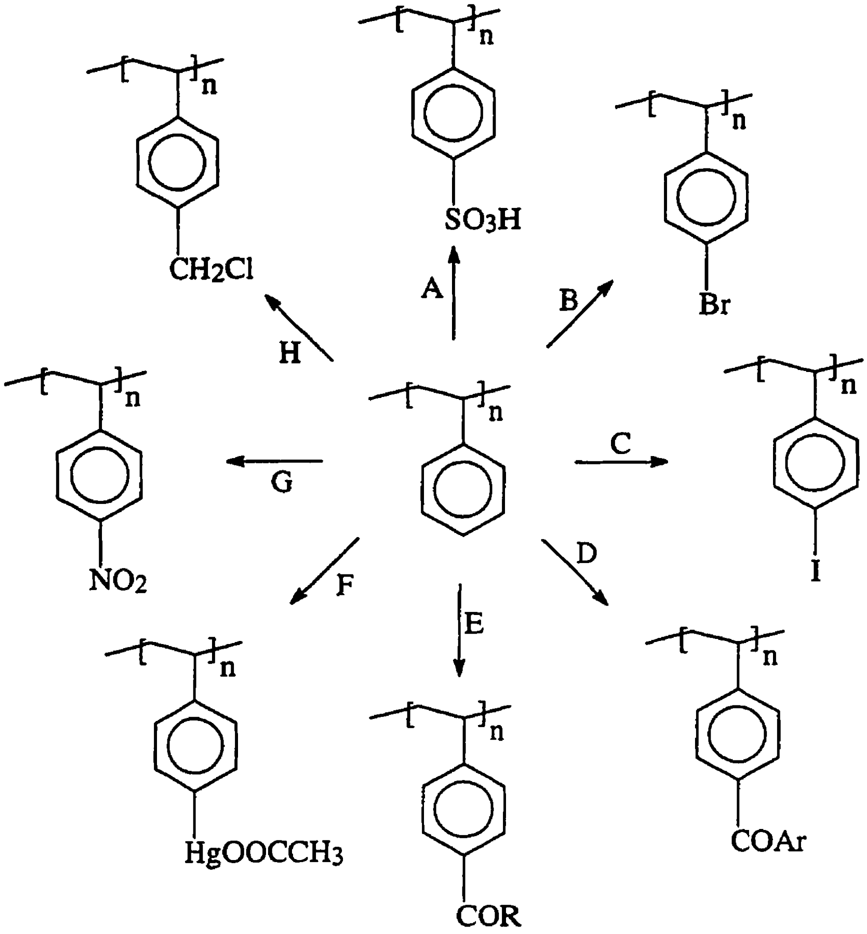


Figure 1.7 Electrophilic aromatic substitution reactions of polystyrene

A. Ref. 33; B. Ref. 34; C. Ref. 35; D. Ref. 36; E. Ref. 37; F. Ref. 38; G. Ref. 39, 40; H. Ref. 41.

Chloromethylated polystyrene provides a convenient starting point for many other chemical modifications, some of which are shown in Figure 1.8.

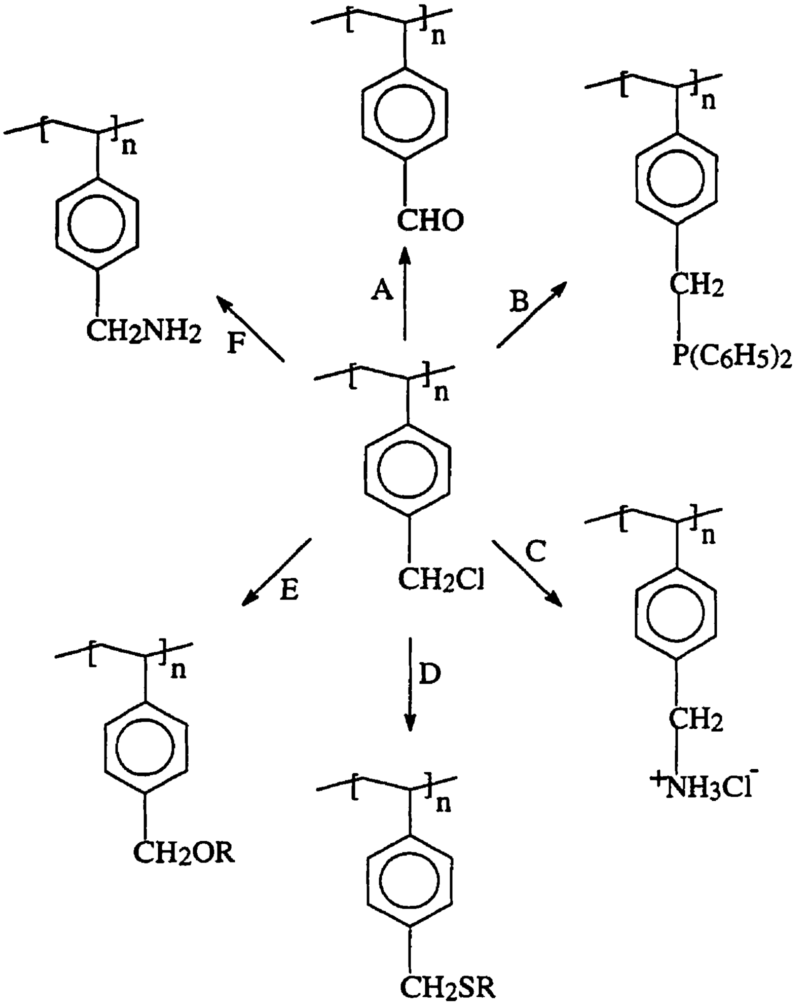
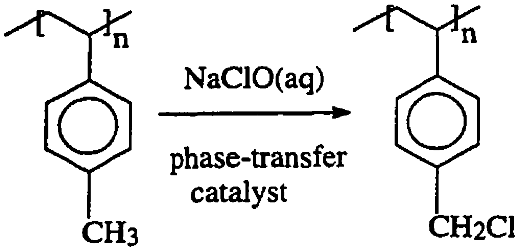


Figure 1.8 Reaction of chloromethyl polystyrene with nucleophiles

A. Ref. 42; B. Refs. 43, 44; C. Refs. 45, 46, 47; D. Ref. 48; E. Ref. 49; F. Ref.. 50.

The chloromethylation reaction has been widely studied and reviewed.[51] It is potentially hazardous, and recently much safer procedures employing long-chain haloalkyl ethers as the alkylating agent have been developed.[52,53] The mild monochlorination of the methyl group in poly(*p*-methylstyrene) and related styrene copolymers developed by Ford and others could represent a major step forward. In this procedure, sodium hypochlorite and a phase-transfer catalyst are employed.[54]



Groups that have been introduced into polystyrene by phase-transfer catalyzed nucleophilic displacement on the chloromethyl substituent include: $-CH_2CH(CN)_2$,[55] $-CH_2CH(COOR)_2$,[55] $-CH_2OH$,[55] $-CH_2OC_6H_4X$ (halogen),[56] $-CH_2OOCCH_3$,[56] $-CH_2SOCCH_3$,[56] $-CH_2SCN$,[57] $-CH_2SH$,[57] $-CH_2CH_2X$.[58]

Whereas chloromethylated polystyrene allows the attachment of a wide variety of nucleophilic species, lithiated polystyrene fulfills the complementary function of allowing facile attack on the aromatic ring by electrophilic species, even weak ones. Figure 1.9 summarizes the principal transformations using this approach. The lithiated species is probably best generated from the corresponding brominated derivative via a metal-halogen exchange using n-butyllithium.[59] However, direct lithiation of aromatic groups on polystyrene can be achieved using the same lithium alkyl in the presence of tetramethylethylenediamine.[60] The controlled functionalization of polystyrene using a process of metalation with a potassium superbase followed by reaction with electrophiles was described by Frechet.[61] The advantages of this methods are that the metalation is extremely efficient, occurring rapidly even at room temperature, and the degree of functionalization can be controlled over a very broad range.

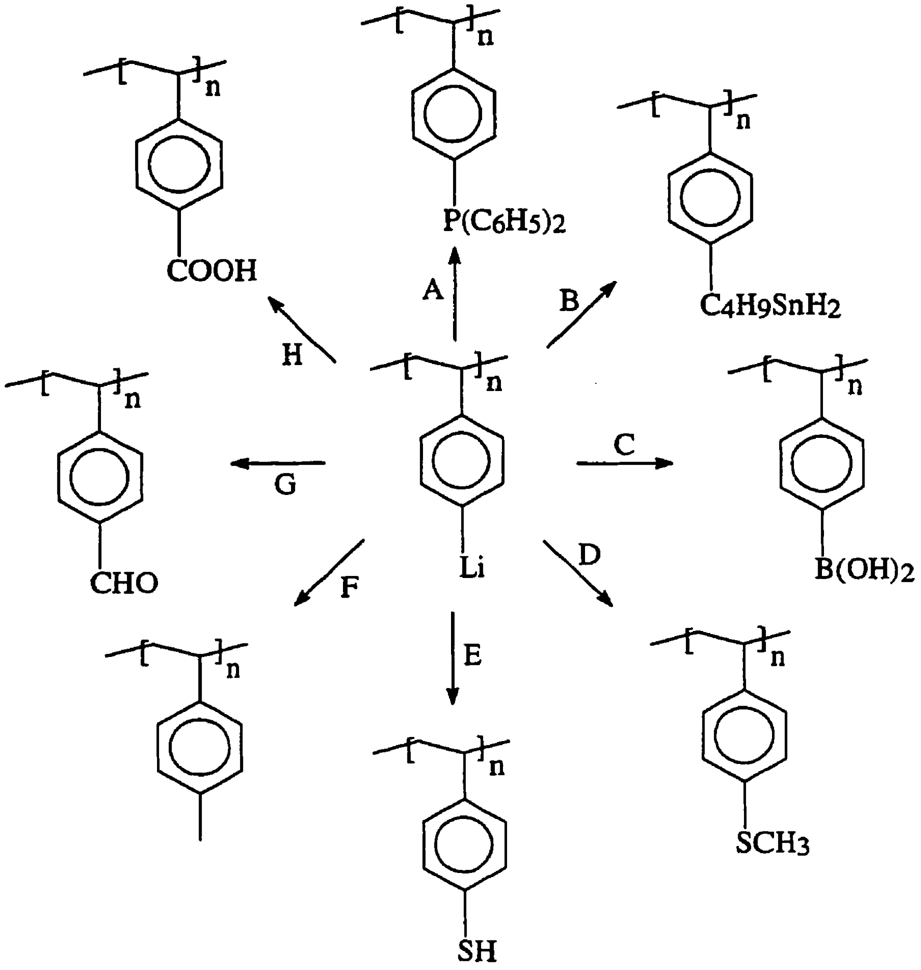
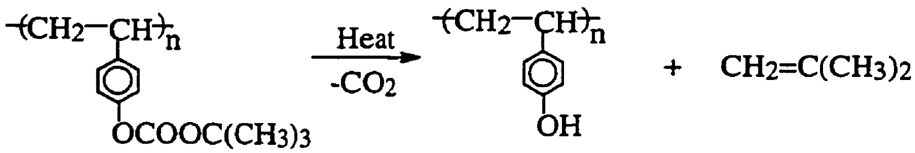


Figure 1.9 Reaction of lithiated polystyrene

A. Ref. 62, 63; B. Ref. 64; C. Ref. 59; D. Ref. 65; E. Ref. 66; F. Ref. 67; G. H. Ref. 59.

Sulfonation of polystyrene is a significant industrial process. Strongly acidic ion-exchange resins are prepared by sulfonation of solid resins using sulfuric acid.[33] Thus, careful use of the sulfuric acid-acetic acid mixture allows uniform sulfonation of the surface (only) of macroporous resins.[68] A number of hydrocarbon-soluble sulfonation agents have been developed for the modification of polystyrene.[69] These are essentially acyl sulfates, which are very reactive, readily substituting polystyrene.

Other functional groups substituted directly into the aromatic ring of polystyrene that might prove useful for further elaboration are the hydroxyl (phenolic) and amino groups. Amino groups are generally introduced by nitration and reduction.[70] Generation of phenolic groups is more difficult. In the past this modification has been achieved indirectly by copolymerization of styrene with *p*-acetoxystyrene followed by hydrolysis of the copolymer.[71] Using a similar approach, copolymerization of *p*-(*t*-butoxycarbonyl)styrene with styrene yields copolymers in which phenolic residues can be produced by a simple thermolysis reaction.[72]



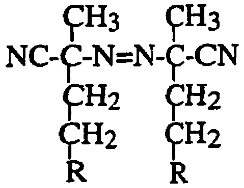
The process has the advantage of being extremely clean, causing the formation of gaseous coproducts only, carbon dioxide and isobutylene. Treatment of the benzyl ether derivative of polystyrene with HBr has also been used to generate the phenolic function.[73]

1.2.2.2 Styrenic Polymers with Telechelic or Pendant Functional Groups

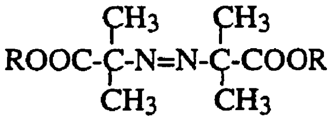
Telechelic polymers are low molar mass macromolecules with two reactive end groups. Telechelic polymers can be used for chain extension by means of bifunctional linking reagents, network formation by means of multifunctional linking agents, and synthesis of block copolymers by coupling of different telechelics. Industrial interest in telechelics was stimulated by the development of thermoplastic elastomers. Styrenic telechelic polymers can be prepared by either radical or anionic polymerizations.

1.2.2.2a Radical Polymerization

Telechelic polystyrene can be synthesized by radical polymerization.[74,75,76,77] AIBN has often been used as initiator, at times with modification at the methyl[78] and the nitrile groups.[79]



$$NC-\underset{\substack{CH_2\\CH_2\\R}}{\overset{CH_3}{C}}-N=N-\underset{\substack{CH_2\\CH_2\\R}}{\overset{CH_3}{C}}-CN$$



$$ROOC-\underset{CH_3}{\overset{CH_3}{C}}-N=N-\underset{CH_3}{\overset{CH_3}{C}}-COOR$$

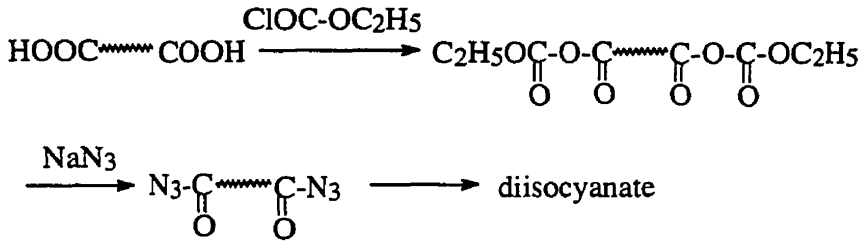
Where R = $-COOH$, $-CH_2OH$, $-NCO$.

Where R = $-CH_3$, $-(CH_2)_nOH$

In styrene polymerization, hydrolysis of the nitrile groups can yield carboxy-terminated oligostyrene. Isocyanate end groups may be introduced into polymer ends in two ways shown below as (a) and (b):[80]

(a) $H_2N\sim\sim\sim NH_2 \xrightarrow{COCl_2} OCN\sim\sim\sim NCO$

(b)



$$HOOC\sim\sim\sim COOH \xrightarrow{ClOC-OC_2H_5} C_2H_5O\underset{\parallel}{\underset{O}{C}}-O-\underset{\parallel}{\underset{O}{C}}\sim\sim\sim\underset{\parallel}{\underset{O}{C}}-O-\underset{\parallel}{\underset{O}{C}}-OC_2H_5$$

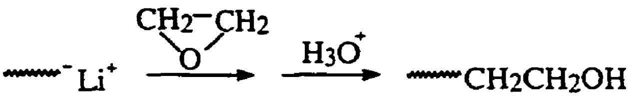
$$\xrightarrow{NaN_3} N_3-\underset{\parallel}{\underset{O}{C}}\sim\sim\sim\underset{\parallel}{\underset{O}{C}}-N_3 \longrightarrow \text{diisocyanate}$$

Methyl 2,2-azoisobutyrate initiates styrene polymerization yielding α, ω-bis(2-methoxycarbonylmethylethyl) oligostyrene.

3,3'-Azobis(3-cyanovaleric acid) or 4,4'-azobis(4-cyanopentanol) as an initiator for styrene oligomerization yields telechelics with COOH and OH end groups, respectively.[81,82,83]

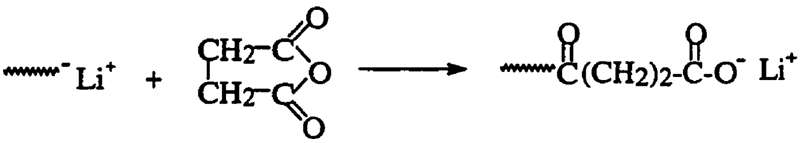
1.2.2.2b Anionic Polymerization

Hydroxyl End Groups. The direct reaction of poly(styryl)lithium with excess ethylene oxide in benzene solution produces the corresponding hydroxyethylated polymer in quantitatively yield without formation of detectable amounts of oligomeric ethylene oxide blocks.[84]



Recently, Peter et *al.*[85] reported the development of a new method, which is based on a termination reaction of living anionic polystyrene with chlorosilane derivatives containing protected functional groups, and introduced primary aliphatic amines and primary aliphatic alcohols. Also, the functionalization reaction of poly(styryl) lithium with styrene oxide forms the corresponding hydroxyl-functionalized polymer with a yield of 85%.[86]

Carboxyl End Groups. Termination of bifunctional living polystyrene by solid CO_2 yields polymers with carboxyl end groups.[87,88] The use of substituted 1,1-diphenylethylenes to prepare end functionalized polymers has been utilized to synthesize carboxyl-functionalized polymers. The functionalization reaction was effected in toluene/THF mixtures (4/1, v/v) at -78°C to produce the carboxyl-end polystyrene (Mn 2100) in quantitative yield after acid hydrolysis as shown:[89]

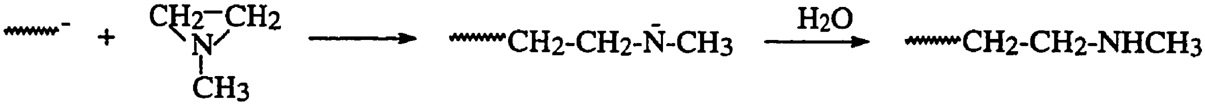


Polystyrene chains with terminal anhydride groups were synthesized by direct chain transfer reaction between poly(styryl) lithium and trimellitic anhydride chloride (TMAC) and by the alkoxy dehalogenation reaction between TMAC and hydroxy-terminated polystyrene.[90]

Halide End Groups. The most direct method of preparing halide terminal groups is the reaction of living polymer anions with a halogen, such as chlorine,[91] or iodine.[92]

Amine End Groups. Poly(styryl)lithium and α, ω-dilithium polystyrene can be aminated in 92% and 80% yields, respectively, using the reagent generated from the reaction product of methoxyamine and methyllithium at -78°C, i.e., utilizing the procedure of Beak and Kokko.[93, 94, 95, 96, 97] Difunctionality can be achieved by coupling with dimethyldichlorosilane.[98]

Secondary amine groups are generated by termination on N-alkyl aziridines.[92]

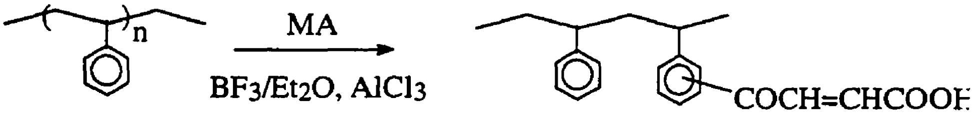


Tertiary amine-terminated polymers can be made by termination reaction with α, ω-alkylene chloroamines.[99]

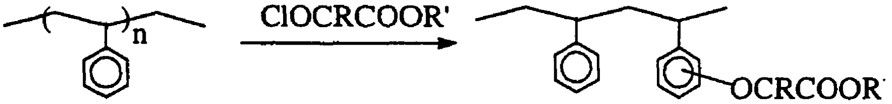
$$\sim\sim\sim^{-} + Cl\!-\!(CH_2)_n\!-\!N(R)_2 \longrightarrow \sim\sim\sim(CH_2)_n\!-\!N(R)_2$$

Also, poly(styryl) lithium reacts with dichlorosilane containing protected groups to yield primary end amine groups as discussed before.[85]

Side Chain Functionalization. The reaction of anionic polystyrene with maleic anhydride using the Lewis acid (BF_3/Et_2O, $AlCl_3$) as catalyst yields polymers containing COCH=CHCOOH groups on the aromatic rings.[100]



A method for the functionalization of polystyrene resins through long aliphatic spacers was established by Luis and his coworkers.[101] The acid chloride of a monoalkyl ester of an alkanedioic acid was used as acylation agent.



Polystyrene undergoes formylation in the treatment with 1,1-dichloromethyl methyl ether and titanium(IV) chloride in carbon disulfide.[102]

1.3 CHARACTERIZATION OF FUNCTIONAL POLYMERS

Adequate polymer characterization is essential in working with functional polymers. In newly synthesized materials, polymer composition, molecular weight, and physical properties are determined first. Then other information may be needed with respect to selection or qualification of polymers for specific purposes. In the following section, we will give a brief introduction to the characterization of polymers, and then discuss characterization of the functional groups.

1.3.1 General Characterization of Polymers

Molecular Structure. Many chemical and spectroscopic techniques are available for the characterization of primary molecular structure, i.e., the presence and sequence of monomeric units in a polymer chain.

Fractionation. This technique separates polymers based on molecular weight or chemical composition. In practice, partial separations by molecular weight and chemical composition are often achieved simultaneously. On the basis of solubility, fractionation can be achieved by precipitation, fractional dissolution, thin layer chromatography, and related methods.[103]

Size Exclusion Chromatography (SEC). The separation is based on the hydrodynamic volume of a polymer molecule. This volume, converted to a molecular weight or equivalent molecular weight, is compared to the hydrodynamic volume of a standard polymer by means of a calibration curve.[104]

Nuclear Magnetic Resonance. Both ^{13}C and ^{1}H NMR provide qualitative and quantitative analyses with respect to monomer composition, comonomer and the sequence stereochemical configuration (tacticity) present along the polymeric chain.[105,106]

Infrared and Raman Spectroscopy. Both techniques provide information on chemical, structural, and conformation aspects of polymers and polymer blends, and chemical reactions.[107, 108, 109] Both IR and Raman spectra are made up of bands that can be related to the presence of pairs or small groups of atoms present in the sample. Frequently, this can be directly translated into information regarding the qualitative and quantitative presence of functional groups. Infrared is the preferred spectroscopic tool in polymer characterization because of the availability and relatively low cost of the basic instrumentation.

Pyrolysis-Gas Chromatography. This is applied extensively to synthetic [110, 111, 112, 113] and natural polymers.[114] [115] In this technique the polymers are converted to low molecular weight products by flash pyrolysis inside a modified GC inlet port. The composition and relative abundance of the pyrolysis products are characteristic for a given polymer, and their determination allows identification of otherwise intractable material. PY-GC also can provide quantitative analysis of polymer structure, including monomer composition, stereochemistry, tacticity, and monomer sequence in homo- and copolymers. It is complemented by pyrolysis-mass spectrometry and pyrolysis-infrared.

UV Spectroscopy. This is often available, but is not well suited to the direct study of polymers. However, because of the inherently high sensitivity of UV, it is often useful in the identification or quantitative determination of additives, stabilizer, and minor contaminants.

Electron Spectroscopy for Chemical Application (ESCA). This is a useful technique for structural and chemical characterization of polymer surfaces.

Molecular Size

Average Molecular Weight. Many techniques are available for determining average molecular weight. For example, Membrane osmometry (Mn), Vapor pressure osmometry (Mn), end group determination (Mn), light scattering (Mw), dilute-solution viscometry (Mv), and SEC (Mw, Mn).

Molecular Weight Distributions (MWD). Size exclusion chromatography is mainly used for the study of MWD. The breadth of MWD is measured by the so-called polydispersity index, which is the ratio of the weight- to number-average molecular weight.

Other Properties

Thermal Methods. In thermal analysis the properties are measured as a function of temperature or of time at constant temperature. Methods include differential thermal analysis (DTA), differential scanning calorimetry (DSC), and thermogravimetry (TG).[116, 117, 118]

The glass transition temperature (T_g) and melting point (T_m) can be determined by many techniques, for example, DSC, NMR, and DTA.[119,120]

Solid state NMR, microscopy (optical SEM and TEM), inverse gas chromatography, neutron scattering are often used as well for specific purposes..

Mechanical Properties

Mechanical properties (including strength, stiffness, elongation, impact strength, hardness, etc) of polymers can be measured by different instruments.

1.3.2 Functional Group Analysis

Functional-group determination is widely used for the analysis of polymers having a chemically or spectroscopically active species.[121, 122] Most procedures involve direct measurement of an active function or utilize a chemical reaction to provide a readily measurable group or determine the amount of an active reagent remaining after reaction is complete. The specimens are usually handled in solution.

The most widely used techniques for functional-group analysis employ titrimetry, infrared spectroscopy, and some physical tests.

1.3.2.1 Titrimetry

Titrimetry is widely used for determinations of acidic and basic functions such as hydroxyl groups, [124, 125, 126, 127] carboxyl groups, [128] esters, [129, 130, 131] carbonyl groups, [132] epoxy groups, [133, 134, 135] alkoxy and peroxide groups, [136] amine groups and other nitrogen-containing functions, and unsaturated groups. [137, 138]

1.3.2.2 Ultraviolet-Visible Spectroscopy

Many of the colorimetric methods are adaptable to semiquantitative and quantitative procedures. For the latter, spectrophotometric methods are preferred to visual methods. Spectrophotometric techniques are particularly useful for determining small concentrations of elements or functional groups.

The AutoAnalyzer (Technicon) was developed for automated colorimetric analyses in the clinical laboratory and has been extended to a wide variety of methods, such as determination of NH_3, Cd, halides, HCHO, HCN, SO_4, and urea.[139]

Aldehyde and ketone groups have been determined by reaction with 2-methoxyphenol and H_2SO_4 using 2,2,2-trifluoroethanol as solvent to produce a red dye.[140] Absorbance is measured between 525 and 530 nm.

1.3.2.3 Other Methods

Atomic absorption spectroscopy, fluorescence spectroscopy, element analysis, and chemical methods (such as catalytic hydrogenation of unsaturated group, reduction reaction of hydroxyl groups of polymer with $LiAlH_4$, measurement of the formed hydrogen) are available to test the presence of functional groups.

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CHAPTER 2

SELECTIVE OXIDATION OF POLY(4-METHYLSTYRENE) BY CERIC AMMONIUM NITRATE (CAN)

2.1 INTRODUCTION

The selective conversion of commodity polymers into reactive polymers bearing a range of functional groups is interesting academically as well as industrially. Polymers and copolymers containing acetoxymethyl groups are very useful materials. They can be used as negative-tone resist systems,[18,19] as polymers having aromatic acetoxymethyl groups are easily cross-linked by acid catalyzed reactions. Also, the benzylic acetoxy group becomes a good leaving group upon protonation, and polymers having an acetoxy moiety can be functionalized further by nucleophilic substitution reactions to lead to other functional groups.

In general, there are two ways to prepare polymers containing benzylic acetoxy groups. One is the polymerization of 4-vinylbenzyl acetate which is prepared itself by a multistep synthesis.[17] Another is the functionalization of poly(vinylbenzyl alcohol). Both methods are costly, and limited to radical polymerization. A route to introduce acetoxymethyl groups directly into styrenic polymers would be of interest both theoretically and practically.

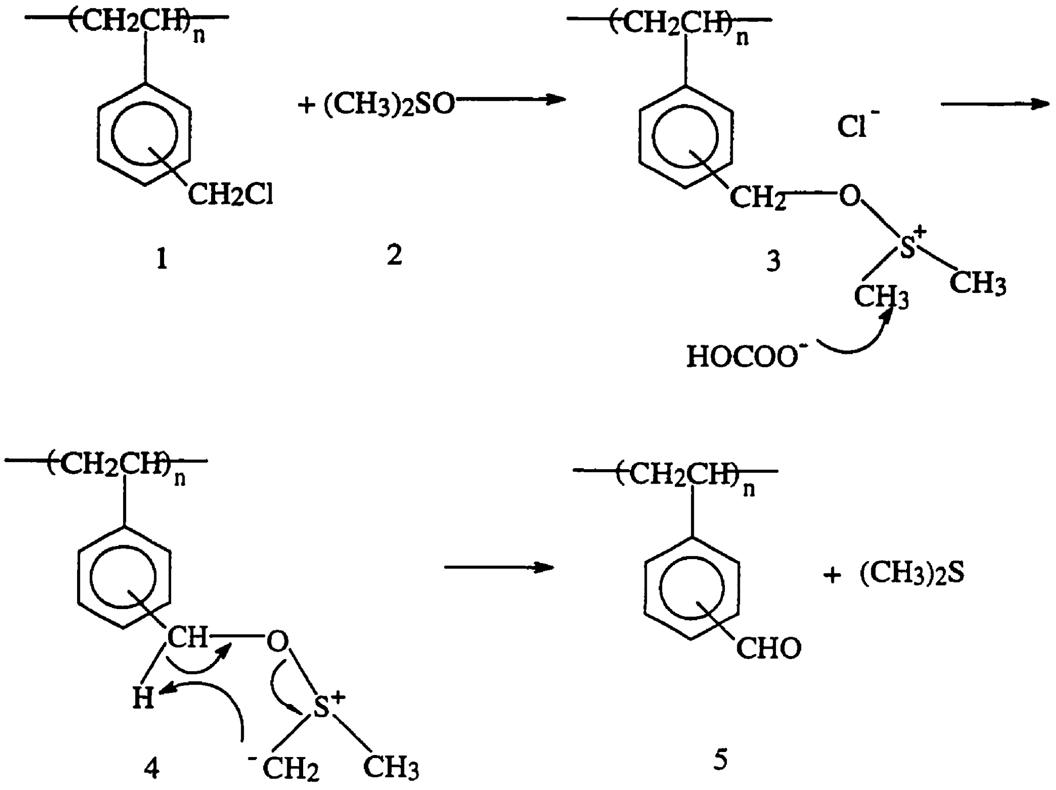
Our group recently reported the selective solution oxidation of poly(4-methylstyrene) in the presence of cobalt(II) acetate bromide and dioxygen or air, to give aldehydes and carboxylic acids.[1,2,3] This reaction is analogous to the widely used cobalt catalyzed oxidation of alkylbenzenes.[4,5,6] It proceeds through benzyl radicals on the polymer that subsequently quench with oxygen to form peroxy radicals. These peroxy radicals then decompose to produce aldehyde and, after a second oxidation step, form carboxylic acid. The final polymers contain aldehyde and carboxylic acid groups with a total degree of oxidation between 5 and 95 percent.[3,7] Competitive oxidation in the backbone causes some polymer degradation, which can be suppressed by using comonomers that sterically and / or electronically protect the backbone from oxidation.[7] The resulting highly oxidized polymers are base soluble, and may be further converted to polyols or acetoxymethylstyrene copolymers that are useful as acid crosslinkable resins.[8]

This chapter describes oxidation using ceric ammonium nitrate under nitrogen or oxygen/air to introduce acetoxymethyl and aldehyde groups respectively.

In the absence of oxygen, Ce(IV) complexes and other metal species are known to oxidize methyl benzenes by a two-step electron transfer process.[9,10] A benzyl radical is formed in the first step by electron transfer and proton loss (preferentially at the primary benzylic position in case of asymmetrically substituted dialkyl aromatics). In the absence of oxygen, these benzylic radicals are stable enough to encounter a second Ce(IV) complex, and to lose a second electron to form the corresponding benzylic carbocation species. These benzyl cations will then react with the best nucleophiles available. As reactions are commonly carried out in glacial acetic acid, benzyl acetates are usually the major products.[9]

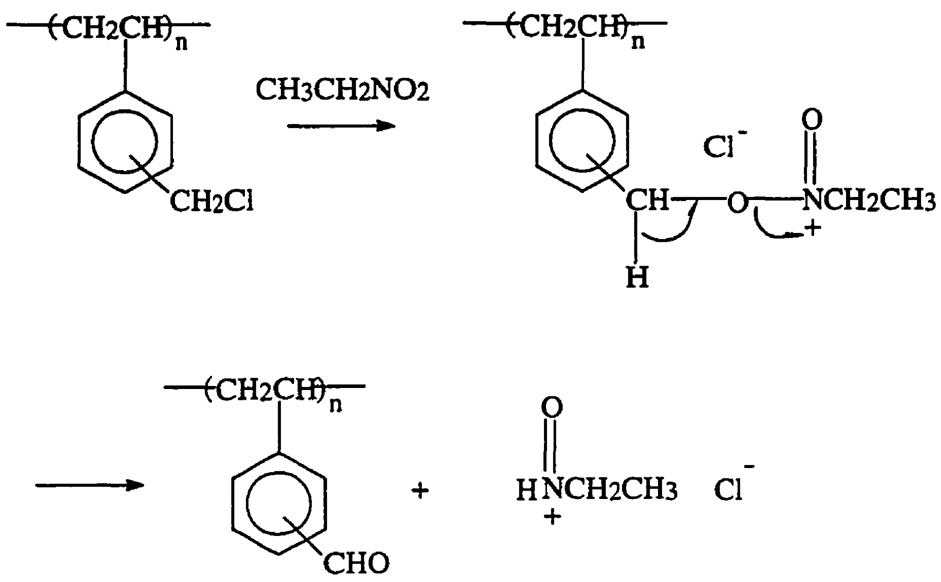
This chapter describes the selective oxidation of poly(4-methylstyrene) with a ceric (IV) complex (ceric ammonium nitrate, CAN) under nitrogen. Here, CAN oxidation leads initially to a mixture of benzyl acetate and benzyl nitrate groups on the polymer. This is due to the competition of nitrate anions with acetic acid or acetate anions for the intermediate benzylic cation. Treatment with hot glacial acetic acid converts these benzyl nitrate groups into benzyl acetate groups. This process then represents a new route to a series of functionalized polymers potentially useful as curing agents, and available for further modification.

Polystyrenes bearing pendant aldehyde groups, similarly have many applications. The reactivity of the aldehyde groups has for example been used to bind complex pyrazolines with an amine functional group[11] or sugars with an acetal group.[12,13] Polystyrene containing aldehyde functional groups can be prepared by chloromethylation of polystyrene, followed by oxidation of the chloromethylated polystyrene. There are two main oxidation reactions commonly used for chloromethylated polystyrene. One is the oxidation of chloromethylated polystyrene with dimethylsulfoxide(DMSO) in the presence of sodium bicarbonate. This technique is well known for monomeric alkyl halides.[14,15,16] The reaction proceeds through intermediate **3** via nucleophilic attack of the electron rich oxygen of DMSO on the halide. Abstraction of a proton by the bicarbonate would then lead to intermediate **4**. Elimination of dimethylsulfide finally yields **5**.



This process leads to some side reaction of crosslinking.

Another process involves the oxidation of chloromethylated polystyrene by nitroethane.[17]



The previous work of our group involved the selective oxidation of poly(4-methylstyrene). The oxidation reaction proceeds by selective oxidation with molecular oxygen or air in an acetic acid/organic cosolvent mixture in the presence of cobalt acetate and sodium bromide.[1,3] The aldehyde and carboxylic acid groups were introduced randomly along the backbone. This process leads to functional polymers containing a mixture of pendant aldehyde and carboxylic acid groups. The introduction of mainly aldehyde groups was difficult by this process, as some of the aldehyde immediately oxidized further to carboxylic acid.

In this chapter, we describe the selective functionalization of poly(4-methylstyrene) to produce novel poly(4-methylstyrene) polyals, with pendant aldehyde groups distributed along the polymer backbone. With the method that we employ, we can readily control the amount of formyl functionality on poly(4-methylstyrene).

2.2 AIM OF THE RESEARCH

In this chapter, we study the oxidation of poly(4-methylstyrene) with ceric ammonium nitrate under different conditions. In the first part, a ceric ammonium nitrate/benzene-glacial acetic acid/nitrogen system was employed to introduce acetoxymethyl and nitrooxymethyl groups into poly(4-methylstyrene). In the second part, a ceric ammonium nitrate-trichloroacetic acid/benzene-glacial acetic acid/oxygen or air system was used to introduce formyl groups into poly(4-methylstyrene).

We tested the effect of experimental parameters on oxidation yield with the following parameters being varied systematically:

1. the type of organic cosolvent,
2. the molar ratio of CAN/P4MS,
3. reaction time,
4. reaction temperature,
5. addition of sodium acetate.

Finally, we propose a possible oxidation mechanism for these two systems.

2.3 EXPERIMENTAL METHODS

2.3.1 Materials and Their Purification

In this study, reagent grade 4-methylstyrene (4MS) monomer was purchased from Deltech Corp. It was purified by passing it through an alumina column to remove inhibitors prior to polymerization.

2,2'-Azobisisobutyronitrile was purchased from Kodak and used as received. Glacial acetic acid, trichloroacetic acid, benzene, *n*-heptane, methylethylketone, and dimethyldigol were purchased from Aldrich and used as received. Ceric ammonium nitrate was purchased from Sigma. It was dried at 85°C for one hour and stored in a dessicator prior to use.

2.3.2 Free Radical Solution Polymerization of Poly(4-methylstyrene)

4-Methylstyrene (50 mL, 44.8 g, 0.378 mol), toluene 50 mL, and 2.2'-azobisisobutyronitrile (AIBN) (0.50 g, 0.0031 mol) were placed in a 100 mL beaker. The mixture was stirred until all of the initiator was completely dissolved. The contents of the beaker were then transferred into a 250 mL three-neck round bottom flask fitted with a condenser, nitrogen inlet, and magnetic stirring. The polymerization reaction was carried out under a nitrogen atmosphere at a temperature of 75°C for 24 hours.

The resulting polymer solution was diluted with 200 mL methylene chloride and precipitated into 1000 mL methanol. The ensuing methanol slurry was stirred for two hours. The polymer was filtered, washed with methanol and reprecipitated once from methylene chloride into a 4-fold excess of methanol. Typical yield: 38.5 g, 85%. Mn: 17,800. Mw/Mn: 1.75.

2.3.3 Selective Functionalization of Poly(4-methylstyrene) by a Ceric Ammonium Nitrate/Acetic Acid-Benzene/Nitrogen System

Poly(4-methylstyrene) 0.296 g (2.5 mmol) was dissolved in a mixture of 30 mL glacial acetic acid and 30 mL benzene (or other organic cosolvent) as described in a 100 mL three-neck flask fitted with a condenser, nitrogen inlet, magnetic stirring, and a thermometer reaching below the liquid level. The temperature was raised to 80°C, and 1.37 g (2.5 mmol) of ceric ammonium nitrate was added to the flask all at once. During the reaction, the color of the solid changed from orange to light yellow or colourless, and the color of the solution changed from yellow to pale yellow. After one hour the reaction mixture was cooled, and filtered, and the benzene component was removed on a rotary evaporator at reduced pressure. The remaining solution of oxidized polymer and ceric salts in acetic acid was precipitated into 200 mL of a mixture of methanol and water (4:1 v/v). After standing overnight, the colourless precipitate was filtered, washed with a 4:1 methanol/water mixture, and dried under vacuum at 60°C overnight. Yields were typically around 90%.

One 30 g batch of poly(4-methylstyrene) having a number average molecular weight (Mn) of 17,800 and a polydispersity (Mw/Mn) of 1.75, was used for all the following experiments of this project.

2.3.4 Displacement of the Nitrate Group by Acetoxy Group

A sample of 0.29 g of the oxidized polymer was dissolved in 35 mL glacial acetic acid and heated to reflux under nitrogen. Samples were removed at different times and precipitated into a 4:1 methanol water mixture as described above. After 3.5 hours reflux, most of the nitrate had been converted to acetoxy groups (according to the ^{1}H NMR spectrum). After 10 hours of reflux, all benzylic nitrate had been converted to benzylic acetate groups.

2.3.5 Selective Functionalization of Poly(4-methylstyrene) (P4MS) by a Ceric Ammonium Nitrate-Trichloroacetic acid/Acetic Acid-Benzene/Oxygen System

Poly(4-methylstyrene) 0.296 g (2.5 mmol) and trichloroacetic acid 4.085 g (25 mmol) were dissolved in a mixture of 30 mL glacial acetic acid and 30 mL benzene in a 100 mL three-neck flask with a condenser, oxygen inlet, and a thermometer reaching below the liquid level. Oxygen (flow rate 15.1 mL/min.) was bubbled into the system. The temperature was raised to 50°C, and 1.37 g (2.5 mmol) of ceric ammonium nitrate was added to the flask all at once. The color of solid and liquid were orange and yellow respectively. After 1 hour oxidation, the reaction mixture was filtered using glass wool, and the benzene component was removed on a rotary evaporator at reduced pressure. The remaining solution of oxidized polymer and ceric salt (about 5%) in acetic acid was precipitated into 200 mL of a mixture of methanol and water (4:1 v/v). After standing overnight, the white precipitate was filtered, washed with a 4:1 methanol/water mixture, and dried under vacuum at 60°C overnight. the products were obtained quantitative.

One 30 g batch of poly(4-methylstyrene) having a number molecular weight (Mn) of 16,760 and a polydispersity (Mw/Mn) of 2.06, was used for all the following experiments of this project.

2.3.6 Characterization of Functional Poly(4-methylstyrene)

The characterization of functionalized poly(4-methylstyrene) was carried out by nuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectroscopy, size exclusion chromatography (SEC), and elemental analysis (EA).

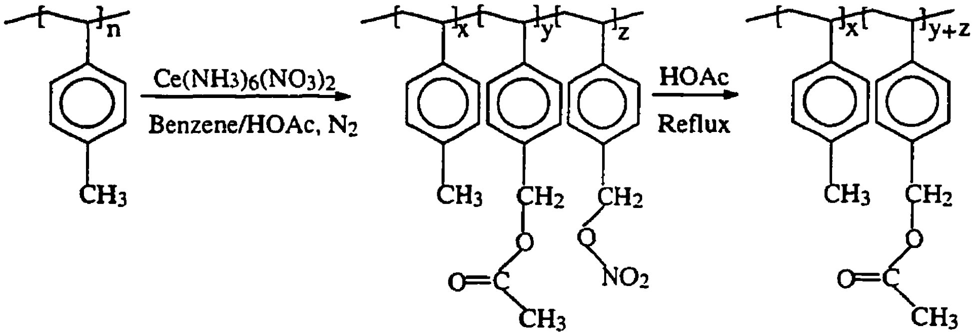
Most NMR spectra were measured in deuteriochloroform solution on a Bruker AC200 or AC300 NMR instrument. A 1:1 mixture of deuteriochloroform and deuterioacetone was used for highly oxidized poly(4-methylstyrene). Chemical shifts are in ppm relative to tetramethylsilane for proton chemical shifts, and to the solvent carbon (deuterio chloroform) signal at 77.0 ppm for carbon chemical shifts.

Molecular weights were determined on a Waters size exclusion chromatography (SEC) system using three Waters Ultramicrostyragel columns in series. It was calibrated using narrow-disperse polystyrene standards. The infrared spectra were obtained using a BIO-RAD FTS-40 instrument. The IR sample was prepared by dissolving the polymer in methylene chloride and then forming a thin film on a sodium chloride plate. The elemental analysis was carried out by Guelph Chemical Laboratories Ltd.

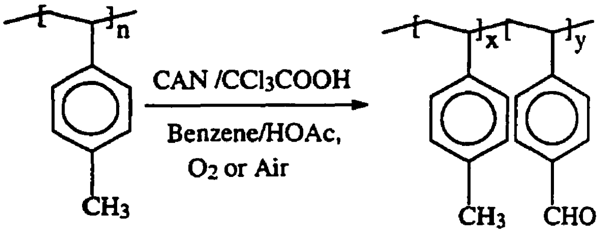
2.4 RESULTS AND DISCUSSION

In this chapter, ceric ammonium nitrate was used as an oxidant for poly(4-methylstyrene). A mixture of 50:50 (v/v) of glacial acetic acid and benzene was used as a solvent under nitrogen or air atmosphere to introduce different functional groups.

In the absence of oxygen (under nitrogen), terpolymers of acetoxymethylstyrene, nitrooxymethylstyrene, and 4-methylstyrene were obtained. However, nitrate groups were easily displaced by acetoxy groups by refluxing in glacial acetic acid.



In the presence of oxygen, trichloroacetic acid was used as a promoter, and formyl groups were introduced into poly(4-methylstyrene). If the oxidation reaction was carried out at high temperature, or for longer time, or higher oxygen pressure, mixtures of aldehyde and carboxylic acid were obtained.



2.4.1 Characterization of Functional Polymers

2.4.1.1 Confirmation of Structure of Functional Polymer by NMR

Figure 2.1 shows the NMR spectrum of poly(4-methylstyrene) before and after ceric ammonium nitrate/nitrogen oxidation. The proton NMR spectrum of poly(4-methylstyrene) produced can be found in Figure 2.1(A). Broad peaks are present because the polymer is atactic, such that there are different stereochemical environments around each carbon. The methyl hydrogens appear at 2.3 ppm, the aromatic hydrogens at 6.6 ppm and 6.9 ppm, the methylene hydrogens in the backbone at 1.4 ppm, and the methine hydrogens in the backbone at 1.9 ppm.

Oxidation converts a portion of the 4-methyl groups to acetoxymethyl and nitrooxymethyl groups. The 4-methyl peaks decreased in intensity, and the benzylic signal at 5-6 ppm appeared. Before oxidation by ceric ammonium nitrate/nitrogen, there were no peaks evident in the 5.00 ppm - 6.00 ppm region of the spectrum which is characteristic of the benzylic groups containing oxygen functionality. The peak at 5.00 ppm is characteristic of a benzyl acetate function and the peak at 5.29 ppm corresponds to benzyl nitrate groups.

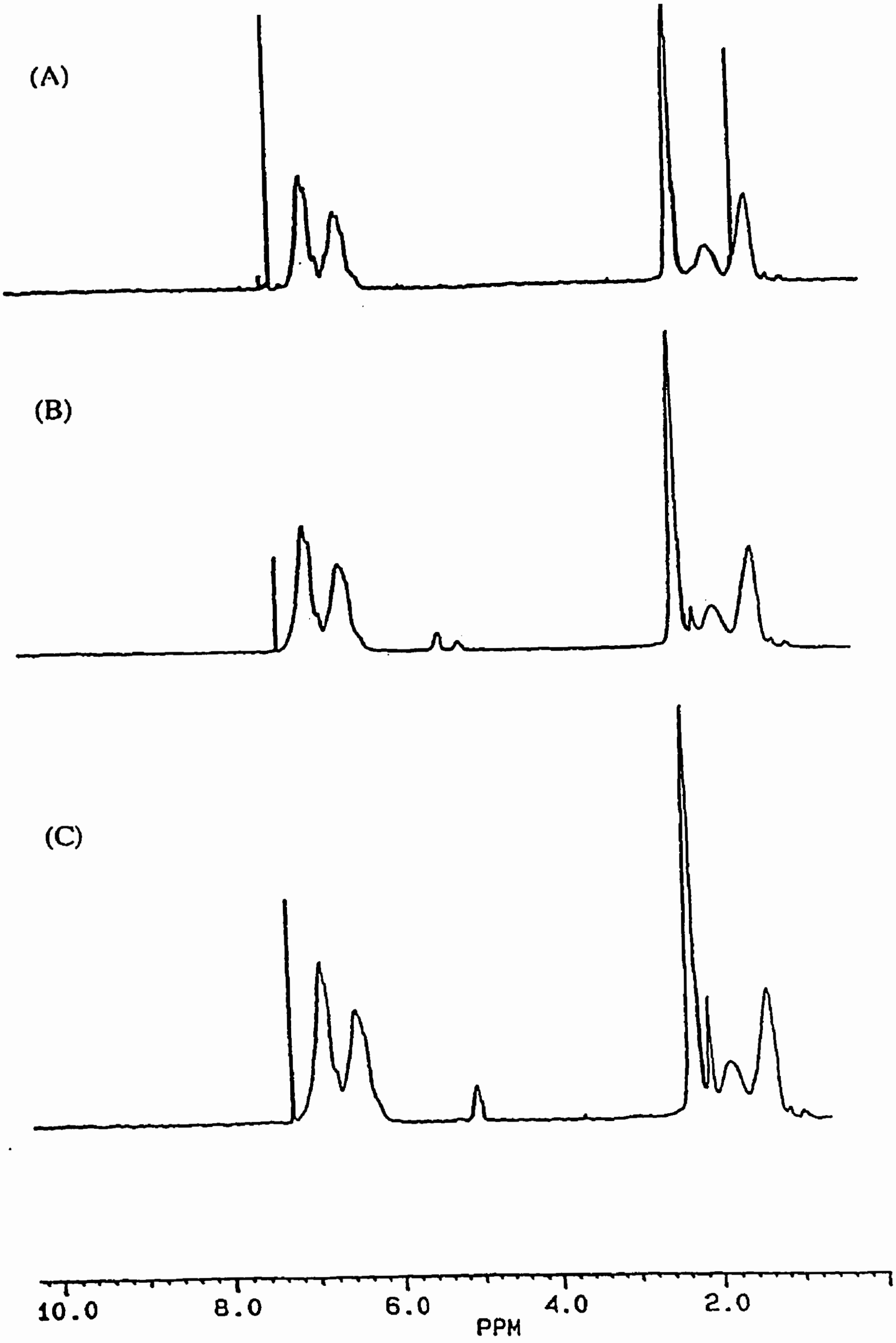


Figure 2.1 ^1H NMR spectrum. (A): Poly(4-methylstyrene), (B): after oxidation of poly(4-methylstyrene) by cerium ammonium nitrate, (C): after displacing the nitrate group.

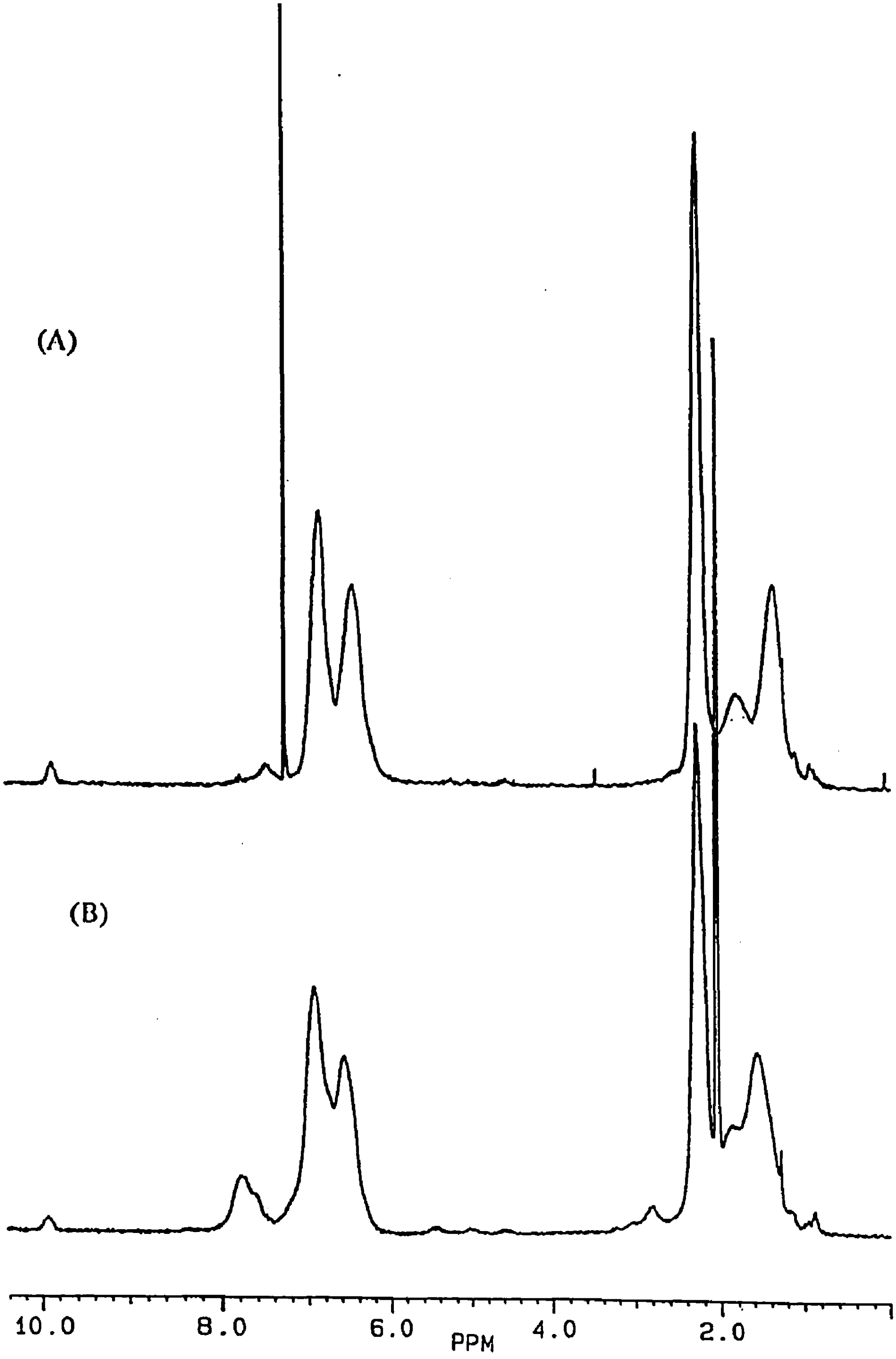


Figure 2.2 ^1H NMR spectrum. (A): oxidation product containing 9.2% aldehyde, (B): oxidation product containing 8.8% aldehyde and 18.7% carboxylic acid.

The oxidation of poly(4-methylstyrene) by ceric ammonium nitrate/oxygen converts a portion of the 4-methyl groups into aldehyde and carboxylic groups. In the proton NMR spectra, this results in a new peak at 9.9 ppm, corresponding to the aldehyde hydrogen. The carboxylic acid proton signal is usually too broad to be observed. However, the presence of carboxylic acid functional groups is evident as a downfield shift of the aromatic protons *ortho* to the carboxylic acid. The aldehyde as well causes a similar, though smaller shift of the aromatic protons *ortho* to it. Before oxidation there are only two peaks evident in the aromatic region from the 4-methylstyrene units of polymer. After oxidation, these peaks appear to be broadened due to overlap of all aromatic peaks (oxidized and unoxidized). The peak at 7.5 ppm is characteristic of protons *ortho* to an aldehyde group, and the peak at 7.8 ppm corresponds to protons *ortho* to a carboxylic acid group. This is outlined in Figure 2.2.

The degree of oxidation of poly(4-methylstyrene) by ceric ammonium nitrate/nitrogen can be determined by comparing the intensities of the benzylic methylene signals with those of the aromatic signals. Similarly, the degree of oxidation of poly(4-methylstyrene) by ceric ammonium nitrate/oxygen can be calculated from the area ratios of signals at positions *ortho* to an aldehyde, *ortho* to a carboxylic acid, and those of the remainder of the aromatic ring. The total degree of oxidation is represented by the number of methyl groups of poly(4-methylstyrene) that were oxidized to aldehydes or carboxylic acids.

2.4.1.2 Confirmation of Oxidation by Element Analysis

Elemental analysis was used to confirm the introduction of oxygen and nitrogen during the oxidation. For oxidation by ceric ammonium nitrate/nitrogen, acetoxy and nitrate groups were introduced into poly(4-methylstyrene), and the chemical composition was changed. Before oxidation there were no oxygen and nitrogen contained in the polymer. Due to oxidation oxygen and nitrogen could be detected.

The following is an example of elemental analysis of an oxidized polymer:

Sample No.	carbon(%)	Hydrogen(%)	Nitrogen(%)	Oxygen(%) (by difference)
a-11(found)	76.61	7.08	2.81	13.50
(calcd.#)	77.24	6.93	2.73	13.10

(# according to the NMR data).

2.4.2 Introduction of Acetoxy Groups into Poly(4-methylstyrene) by a CAN/Acetic Acid-Benzene/Nitrogen System

2.4.2.1 Study of the Oxidation Mechanism

Oxidation of alkylbenzenes with ceric (IV) ammonium nitrate in acetic acid under exclusion of oxygen is known to produce acetoxylated products. Controlled oxidation of toluene with CAN was reported by Walter S. Trahanovsky[9]. Using glacial acetic acid as a solvent, the acetoxymethylbenzene was the major product with a 90% yield; using 50%

aqueous acetic acid, the major product was benzaldehyde. The proposed mechanism was electron transfer.

The mechanism of oxidation of polymethylbenzene with CAN in acetic acid was reported by Baciocchi.[10] It was found that the reaction required 2 mol of CAN for 1 mol of hydrocarbon and led in each case to the formation of benzylic acetate and nitrate. The benzylic radical and Ce(IV) formed an alkyl-Ce(IV) intermediate which subsequently underwent competitive oxidative solvolysis (leading to acetate) and oxidative displacement (leading to nitrate). The following scheme shows the proposed mechanism:

$ArCH_3 + Ce(IV) \rightarrow ArCH_3^{+\cdot} + Ce(III)$

$ArCH_3^{+\cdot} \rightarrow ArCH_2\cdot + H^+$

$ArCH_2\cdot + Ce(IV) \rightarrow ArCH_2^+ + Ce(III)$

$ArCH_2^+ + AcO^- \rightarrow ArCH_2OAc$

$ArCH_2^+ + NO_3^- \rightarrow ArCH_2NO_3$

The same author studied the electronic and stereoelectronic effect of α-substituents in the deprotonation of α-Z-substituted *p*-xylenes.[21] It was found that when Z was a t-butyl group, the relative reactivity $K(CH_2Z)/K(CH_3)$ for the deprotonation reaction of α-Z-substituted *p*-xylene radical cation was less than 0.01 in the CAN oxidation. This negligible deprotonation rate was attributed to a stereoelectronic effect (the bulky t-butyl group does not allow the C-H bonds to be collinear with the π system). As described earlier,[1,7] the polymer backbone of poly(4-methylstyrene) appears to sterically interfere with resonance stabilization of the forming benzylic radical cation or benzyl radical in the methine position during the rate-determining step of oxidation.

From the above discussion, it can be concluded that after interaction of CAN with alkyltoluene to form radical cations, alkyl benzyl radicals are formed predominantly, because the loss of a proton is controlled by stereoelectronic considerations and not by the thermodynamic stability of the products.[22] For the same reason, when poly(4-methylstyrene) is oxidized by CAN, the selective oxidation of methyl groups might occur because of the very long backbone chain. Oxidation of poly(4-methylstyrene) might follow the same mechanism: first an electron transfer from benzene to oxidant, then loss of a proton to form the benzyl radical cation (either primary benzyl methyl position or tertiary benzyl methine position), which transfers a second electron to oxidant, leading to the formation of benzyl cation, which reacts with nucleophiles present in the system (acetic acid and nitrate). Finally a mixture of acetoxylation products and nitrooxy products of the side chain will be obtained.

For the selective oxidation of poly(4-methylstyrene), a ceric ammonium nitrate (CAN) system was used first. Figure 2.3 shows the oxidation reaction.

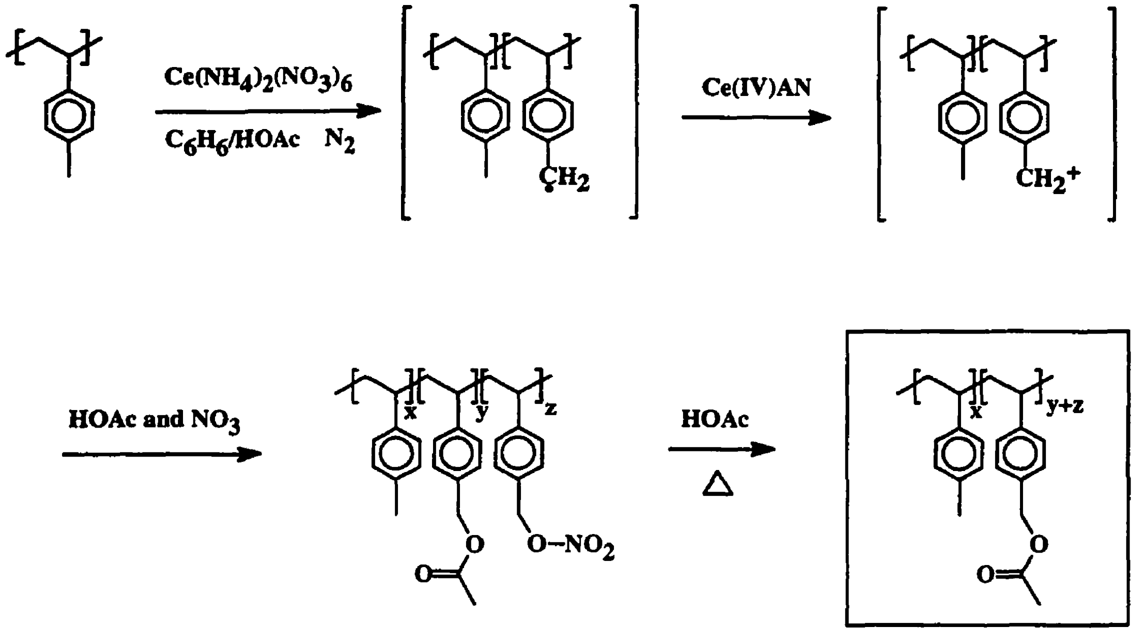


Figure 2.3 Oxidation of poly(4-methylstyrene) by ceric ammonium nitrate

Ceric ammonium nitrate (CAN) gave a very clean oxidation of poly(4-methylstyrene). The ^{1}H NMR spectra of poly(4-methylstyrene) and the oxidized polymer are shown in Figure 2.1(B). There are two benzylic methylene protons: at 5.00 ppm, as a characteristic of the benzyl acetate function; and at 5.29 ppm, as a characteristic of the benzyl nitrate function.

Integration of these benzylic methylene signals indicated a constant nitrate/acetate ratio of 1.7 ± 0.15 for all reactions. This ratio also did not drift during the reaction due to acetolysis of the nitrate, as had been observed in the case of the corresponding CAN oxidation of tri and tetramethylbenzenes.[24] Refluxing in glacial acetic acid for ten hours did however convert the nitrate groups into acetate groups, as indicated in Figure 2.1 above. The corresponding ^{1}H NMR spectrum (Figure 2.1(C)) shows complete conversion of nitrate into acetate, without evidence for any crosslinking.

2.4.2.2 Parameters Influencing the Oxidation Yield of Poly(4-methylstyrene)

2.4.2.2a Effect of Cosolvent

The selective oxidation of poly(4-methylstyrene) in different mixed solvents was explored. Generally the criteria for choosing a solvent system were that it should be a good solvent for poly(4-methylstyrene) and it should dissolve ceric ammonium nitrate completely or partially. Based on the above considerations, several binary solvent mixtures were chosen as reaction medium.

Glacial acetic acid was chosen because it dissolves ceric ammonium nitrate and is miscible with many organic solvents. Benzene, heptane, methyl ethylketone, and dimethyldigol were used as cosolvents to acetic acid, since they are all good solvents for poly(4-methylstyrene). All experiments in this series were carried out with 50 vol % of acetic acid and 50 vol % of organic solvent, 1:1 mol ratio of oxidant to poly(4-methylstyrene), and at 80°C under nitrogen.

We investigated the effect of cosolvents on oxidation first, with the results shown in Table 2.1.

Table 2.1 Effect of Cosolvent on Oxidation

Run#	Cosolvent	Mn	Mw/Mn	%Acet.	%Nitrate	%Total
a-19	benzene	8,100	1.82	12.3	21.7	34
a-23	MEK#	18,200	1.85	-	-	-
a-24	dimethl-digol	14,500	2.24	1.2	5.7	6.9
a-29	n-heptane	9,500	1.94	9.4	15.1	24.5

Reaction conditions: P4MS 2.5 mmol; CAN 2.5 mmol; HOAc 30 mL; Cosolvent 30 mL; 80°C; 1 hour; N_2. MEK#: methyl ethylketone.

From Table 2.1, it can be seen that the benzene/acetic acid and the *n*-heptane/acetic acid mixture are the least polar solvent system, but gave the highest yield. Dimethyldigol resulted in a much smaller degree of oxidation, and no oxidation of the polymer was observed in the methylethylketone/acetic acid system. It seems plausible that these two polar solvents were oxidized faster than the polymer under our conditions.

2.4.2.2b Effect of Molar Ratio of CAN to P4MS

Table 2.2 Effect of Molar Ratio of CAN on Oxidation

Run#	P4MS (mmol)	CAN (mmol)	Mn	Mw/Mn	%Acet.	%Nitrate	%Total
a-21	2.5	5.0	8,400	1.79	14.2	23.9	38.1
a-19	2.5	2.5	8,100	1.82	12.3	21.7	34
a-13	2.5	1.25	11,800	1.84	6.6	10.2	16.8
a-22	2.5	1.0	13,200	1.80	5.3	9.0	14.3

Reaction conditions: P4MS 2.5 mmol; HOAc 30 mL; Benzene 30 mL; 80°C; 1 hour; N_2.

The oxidation of alkyl aromatic compounds by CAN in the absence of oxygen requires two moles of CAN per mole of 4-methylstyrene unit oxidized, according the mechanism outlined in Figure 2.3. Since our reaction comprises polymeric substrate, mixed solvents, and partial oxidation, we decided to test the effect of the CAN/P4MS ratio on oxidation rate, performing experiments at constant polymer concentration (0.0417 M), but decreasing oxidant concentration (0.0832 M - 0.0167 M). Table 2.2 shows the effect of the molar ratio of CAN/P4MS on the oxidation. The oxidation yield increased with an increase in the molar ratio of CAN/P4MS. When the CAN/ P4MS ratio was equal 1.0, the total oxidation yield obtained was 34%, so most of our subsequent reactions were therefore performed at 1:1 CAN/P4MS ratio. In entry a-19 34% of the methyl groups on the polymer have been oxidized. Considering each oxidation requires two CAN per methyl group, this value corresponds to a 68% yield based on CAN used.

2.4.2.2c Effect of Reaction Time

Table 2.3 Effect of Reaction Time on Oxidation

Run#	Reaction Time (hours)	Mn	Mw/Mn	%Acet.	%Nitrate	%Total
a-16	3.0	7,400	1.78	12.9	23.8	36.7
a-17	2.0	7,600	1.75	14.6	23.9	38.5
a-18	1.5	7,600	1.80	13.6	25.8	39.4
a-19	1.0	8,100	1.82	12.3	21.7	34.0
a-20	0.5	10,600	1.85	10.1	14.1	24.2

Reaction conditions: P4MS 2.5 mmol; CAN 2.5 mmol; HOAc 30 mL; Benzene 30 mL; 80°C; N_2.

The effect of reaction time on oxidation is shown in Table 2.3. The oxidation yield increases with reaction time up to approximately 1.5 hours, to give a 39.4% degree of oxidation.[25] This corresponds to a 78.8% chemical yield based on CAN. Visually, the undissolved CAN turned from orange to colourless around this time. It also shows that the reaction is almost completed after 1.5 hours.

2.4.2.2d Effect of Reaction Temperature on Oxidation

Table 2.4 shows the effect of reaction temperature on oxidation in benzene/acetic acid mixtures. There is a significant effect of reaction temperature: no reaction occurred at 30°C, but the higher the temperature, the higher the oxidation yield. This may in part be due to the higher solubility of the CAN at higher temperature. The reaction at 80°C proceeded about eight times faster than those at 50°C. So, most subsequent reactions were therefore carried out at 80°C.

Table 2.4 Effect of Reaction Temperature on Oxidation

Run#	Reaction Temp. (°C)	Mn	Mw/Mn	%Acet.	%Nitrate	%Total
a-19	80	8,100	1.82	12.3	21.7	34.0
a-25	70	11,300	1.77	9.3	14.7	23.6
a-26	60	14,900	1.81	5.3	7.4	12.7
a-27	50	17,000	1.84	1.5	2.5	4.0
a-28	30	17,300	1.76	-	-	-

Reaction conditions: P4MS 2.5 mmol; CAN 2.5 mmol; HOAc 30 mL; Benzene 30 mL; 1 hour; nitrogen.

2.4.2.2e Effect of Sodium Acetate Addition on Oxidation

The oxidized polymers resulting from our process contain acetoxy and nitrate groups randomly distributed along the chain. The ratio of nitrate to acetoxy groups observed in all reaction is 1.7 (+/- 0.15) under our conditions, with no significant variation. It appears likely that the product ratio reflects the relative rates of acetoxy and nitrate anions to transfer from the ceric(III) complex to the benzyl cation.[26] For our purposes, the nitrate group reflects the result of an undesired side reaction. Increasing the acetate/CAN ratio (Table 2.2) has no effect of the resulting acetoxymethyl/nitrate ratio, presumably because the limiting ligand shell distribution of acetate and nitrate anions does not vary over the range covered. Similarly, addition of moderate amounts of sodium acetate did not shift the acetoxymethyl/nitrate ratio noticeably (Table 2.5). This is analogous to Baciocchi's observation that the addition of ammonium nitrate did not affect the acetate/nitrate ratio in the CAN oxidation of tri and tetramethylbenzene.[24] Fortunately the nitrate groups could be easily displaced by refluxing the oxidized mixed polymer in glacial acetic acid for 10 hours. No crosslinking was observed during this process, and the acetoxymethylated polymer (see Figure 2.1(C)) was obtained in quantitative yield.

Table 2.5 Effect of Sodium Acetate Addition on Oxidation

Run#	Cat. System	Mn	Mw/Mn	%Acet.	%Nitrate	%Total
a-21	CAN 5mmol	8,400	1.79	14.2	23.9	38.1
a-11	CAN 5mmol NaOAc 5mmol	6,500	1.65	16.9	28.3	45.2

Reaction conditions: (a-11): HOAc 60 mL; Benzene 60 mL; P4MS 2.5 mmol; (a-21): HOAc 30 mL; Benzene 30 mL; P4MS 2.5 mmol.

2.4.3 Introduction of Formyl Groups into Poly(4-methylstyrene) by CAN-Trichloroacetic Acid/Acetic Acid-Benzene/Oxygen System

In this section, we describe materials prepared by selective functionalization of poly(4-methylstyrene) to produce novel poly(4-methylstyrene) polyals with the pendant-aldehyde group distributed along the polymer backbone. With the method that we employ, we can readily control the amount of formyl functionality on poly(4-methylstyrene).

The following shows the basic oxidation scheme, with aldehyde groups introduced randomly along the polymer chain.

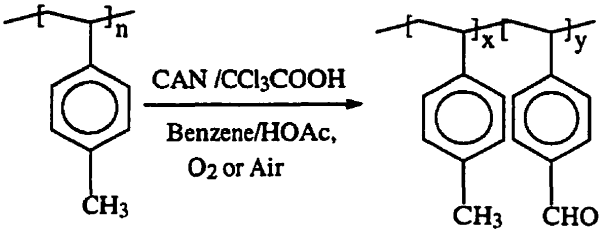


Figure 2.2(A) shows the ¹H NMR spectrum for poly(4-methylstyrene) oxidized in acetic acid/benzene solution for 1 hour at 50°C, and incorporating 9.2% of aldehyde. The single aldehyde proton appears at 9.90 ppm, while the aromatic protons *ortho* to the aldehyde appear at 7.49 ppm. Figure 2.2(B) is the ¹H NMR spectrum for oxidized polymers containing 8.8% of aldehyde and 18.7% of carboxylic acid (the aromatic protons *ortho* to carboxylic acid appear at 7.80 ppm).

2.4.3.1 Oxidation Mechanism

The first step of the mechanism is the electron transfer from the aromatic ring of poly(4-methylstyrene) to CAN to form the radical cation, subsequently, loss of a proton leads to the formation of a benzyl radical. Due to the presence of oxygen, these benzyl radicals react with molecular oxygen to generate benzyl peroxy radicals. These are decomposed by reaction with Ce(IV) or Ce(III) to form aldehyde (in the case of the primary benzyl peroxy radicals) or lead to backbone cleavage (in the case of the tertiary methine peroxy radicals). If the reaction is carried out at high temperatures or for extended periods, the aldehyde can then be oxidized by a second pass through this cycle to form carboxylic acid. The latter process is just similar to the one discussed earlier.[2,3]

Because of the steric congestion of the long polymer chain, the initial hydrogen abstraction occurs preferentially from the primary benzyl groups rather than the tertiary methine groups. This initial abstraction reactivity ultimately permits the selective oxidation of poly(4-methylstyrene).

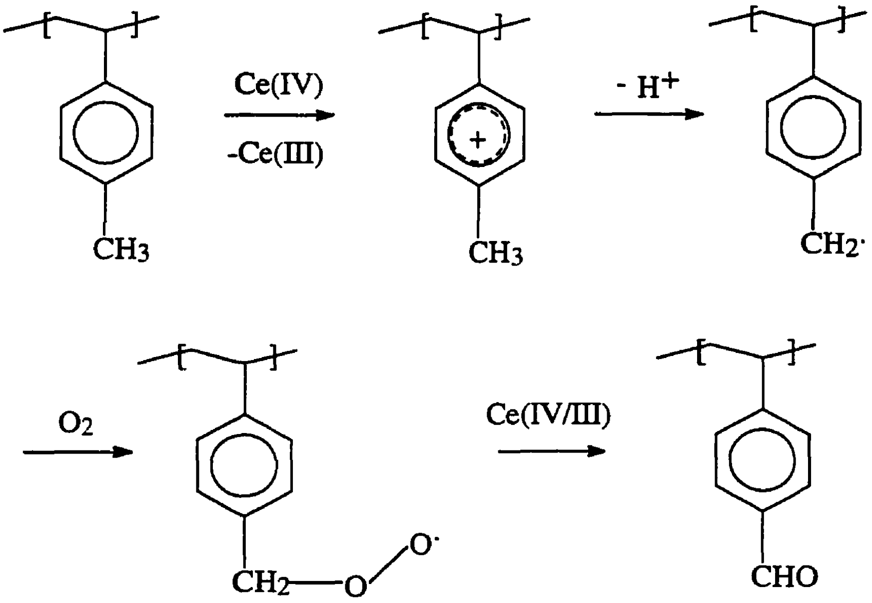


Figure 2.4 Oxidation mechanism of poly(4-methylstyrene) by CAN-trichloroacetic acid/oxygen

2.4.3.2 Parameter Influencing the Oxidation Yield of Poly(4-methylstyrene)

In this work, we also will explore several factors which affect the oxidation of poly(4-methylstyrene) homopolymers.

The following parameters were changed systematically.

1. The ratio of CAN to P4MS
2. The ratio of trichloroacetic acid to P4MS.

3. Reaction time

4. Reaction temperature

5. Oxygen partial pressure

2.4.3.2a Effect of Molar Ratio of CAN to P4MS on Oxidation

The effect of the molar ratio of CAN/P4MS was studied (Table 2.6). It was found that oxidation occurred when the ratio of CAN/P4MS was 0.4 : 1, or 0.5 : 1 with very low yield (4 ~ 5 % of aldehyde). When this ratio was increased to 1 or 2, a higher yield was obtained (10% of aldehyde). When CAN/P4MS reached 4, the yield only increased somewhat to 11%. Most subsequent reactions, therefore, were carried out with a 1 : 1 CAN/P4MS ratio. For most applications, polymers containing 10% of aldehyde would be sufficient.

Table 2.6 Effect of Molar Ratio of CAN/P4MS on Oxidation

Run#	CAN (mmol)	P4MS (mmol)	CAN/P4MS	Mn	Mw/Mn	%-CHO	%-COOH
c-2	10.0	2.5	4.0	9,700	2.16	11.3	<0.5
c-3	5.0	2.5	2.0	10,200	2.07	9.34	<0.5
c-1	2.5	2.5	1.0	11,400	1.96	9.48	-
c-4	1.25	2.5	0.5	10,900	1.99	4.53	-
c-5	1.0	2.5	0.4	11,200	2.04	4.46	-

Reaction conditions: Trichloroacetic acid 37.5 mmol; Acetic acid 30 mL; Benzene 30 mL; 50°C; 1 hour; Oxygen 15.1 mL/min.

2.4.3.2b Effect of Molar Ratio of Trichloroacetic Acid to P4MS

In our selective oxidation of poly(4-methylstyrene), the effect of trichloroacetic acid (TCA) was remarkable (Table 2.7). Below a 10 : 1 molar ratio of TCA/P4MS (monomer equivalent), a very low yield (~3-4% of aldehyde) was obtained. With 37.5 mmol of TCA (molar ratio of TCA/P4MS was 15:1), around 10% aldehyde was introduced into poly(4-methylstyrene). The molecular weight decreased a little.

Table 2.7 Effect of Trichloroacetic Acid on Oxidation

Run#	TCA (mmol)	P4MS (mmol)	Mn	Mw/Mn	%-CHO	%-COOH
c-1	37.5	2.5	11,400	1.96	9.48	-
c-6	25.0	2.5	11,800	2.05	4.11	-
c-7	15.0	2.5	13,200	2.03	4.92	-
c-8	10.0	2.5	14,600	1.93	3.31	-
c-9	5.0	2.5	16,000	2.03	3.10	-

Reaction conditions: CAN 2.5 mmol; Acetic acid 30 mL; Benzene 30 mL; 50°C; 1 hour; Oxygen 15.1 mL/min.

2.4.3.2c Effect of Reaction Time on Oxidation

Table 2.8 shows that the degree of oxidation increases with reaction time. After 2 hours, a mixture of aldehyde and carboxylic acid was obtained. If only aldehyde groups are required, short reaction time is necessary. Hence most reactions were run for one hour.

Table 2.8 Effect of Reaction Time on Oxidation

Run#	Reaction Time (hours)	Mn	Mw/Mn	%-CHO	%-COOH
c-11	0.5	10,400	2.63	5.65	-
c-1	1.0	11,400	1.96	9.48	-
c-10	2.0	8,100	2.21	7.01	2.49

Reaction conditions: P4MS 2.5 mmol; CAN 2.5 mmol; Trichloroacetic acid 37.5 mmol; Acetic acid 30 mL; Benzene 30 mL; 50°C; Oxygen 15.1 mL/min.

2.4.3.2d Effect of Reaction Temperature on Oxidation

Table 2.9 shows the effect of reaction temperature on oxidation in benzene/acetic acid mixture. The degree of oxidation increased with temperature. When the temperature was 60° C, a mixture of aldehyde and carboxylic acid was obtained. When the temperature was raised from 60°C to 80°C, the content of carboxylic acid increased and the backbone cleavage increased as well. For our purpose, low temperature is required (50°C).

Table 2.9 Effect of Reaction Temperature on Oxidation

Run#	Reaction Temp. (°C)	Mn	Mw/Mn	%-CHO	%-COOH
c-12	35	14,600	1.80	2.42	-
c-6	50	11,800	2.05	4.11	-
c-13	60	10,200	2.18	6.48	6.42
c-14	70	7,500	2.36	6.08	25.78
c-15	80	7,400	2.43	7.98	25.10

Reaction conditions: P4MS 2.5 mmol; CAN 2.5 mmol; Trichloroacetic acid 25.0 mmol; Acetic acid 30 mL; Benzene 30 mL; 1 hour; Oxygen 15.1 mL/min.

2.4.3.2e Effect of Oxygen Partial Pressure on Oxidation

The effect of oxygen flow rate on oxidation was studied. Table 2.10 indicates that with flow rate of 84.3 ml/min. and 204 ml/min, a mixture of aldehyde and carboxylic acid was obtained. It means that by increasing the flow rate of oxygen, the content of carboxylic acid increased. The aldehyde was oxidized again to form carboxylic acid.

Table 2.10 Effect of Flow Rate of Oxygen on Oxidation

Run#	Flow Rate of O_2 (mL/minute)	Mn	Mw/Mn	%-CHO	%-COOH
c-6	15.1	11,800	2.05	4.11	-
c-18	84.3	13,800	1.99	5.66	3.32
c-19	204	12,600	2.16	6.74	7.18

Reaction conditions: P4MS 2.5 mmol; CAN 2.5 mmol; Trichloroacetic acid 25.0 mmol; Acetic acid 30 mL; Benzene 30 mL; 1 hour; 50°C.

A couple of reactions were run using air instead of oxygen to test the effect of oxygen partial pressure on the reaction in benzene/acetic acid (Table 2.11). In a comparison of 15.1 mL/min. of oxygen with 84.3 mL/min. and 204 mL/min. of air, almost the same results were obtained. 10% of methyl groups of poly(4-methylstyrene) was selectively oxidized to aldehyde with same molecular weight (Mn ~ 14,000). It indicated that the use of air instead of oxygen is feasible, and clearly reduces hazards during the scale up of this process.

Table 2.11 Comparison of Oxygen and Air on Oxidation

Run#	Flow Rate of O_2 or Air (mL/minute)	Mn	Mw/Mn	%-CHO	%-COOH
c-1	15.1 (O_2)	14,600	1.80	9.48	-
c-25	84.3 (air)	14,100	2.07	9.94	-
c-26	204 (air)	14,000	2.09	9.97	-

Reaction conditions: P4MS 2.5 mmol; CAN 2.5 mmol; Trichloroacetic acid 37.5 mmol; Acetic acid 30 mL; Benzene 30 mL; 1 hour; 50°C.

2.5 CONCLUSION

The selective oxidation of poly(4-methylstyrene) with ceric ammonium nitrate salts in glacial acetic acid in the absence and presence of molecular oxygen leads to functional polymers.

In the absence of oxygen, ceric ammonium nitrate/glacial acetic acid-benzene was chosen as an oxidant system. The oxidation reaction proceeds through initial electron transfer followed by proton loss to form transient polymeric benzyl radicals. Because of the absence of oxygen, these radicals transfer a second electron to the oxidant to form polymeric benzyl cations. These in turn react with any nucleophiles present in the reaction mixture. Because of the presence of glacial acetic acid, up to 45% of acetoxymethyl groups can be introduced into poly(4-methylstyrene). This procedure is simple and practical. The reactions can be run in a short time (1.5 hours), and at high temperature (80°C). The oxidized polymer suffers some backbone cleavage and leaving of average molecular weight from 17,800 to 7,000. We can control the degree of introduction of acetoxymethyl groups units into the polymers by changing experimental conditions.

In the presence of oxygen, ceric ammonium nitrate-trichloroacetic acid /glacial acetic acid-benzene were used as the oxidation system. Regarding the oxidation mechanism, the first step is the same as in the CAN/nitrogen system. After benzyl radicals form, they react with molecular oxygen to generate peroxide radicals, followed by reaction with Ce(IV) or Ce(III) to form aldehyde (in the case of primary benzyl peroxide radicals) or lead to backbone cleavage (in the case of the tertiary methine peroxide radicals). Up to 10% of aldehyde groups was easily introduced. If the reaction was performed at high temperature, or longer time, or high oxygen pressure, then aldehyde can be reoxidized by a second pass through this cycle to form carboxylic acid. Based on an experiment using air instead of oxygen is available.

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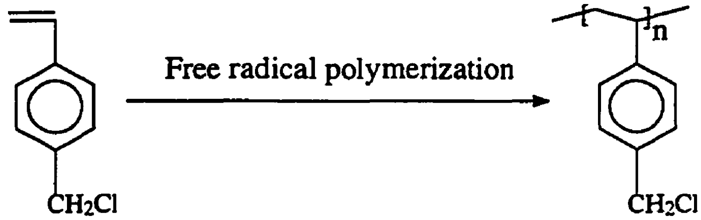
CHAPTER 3

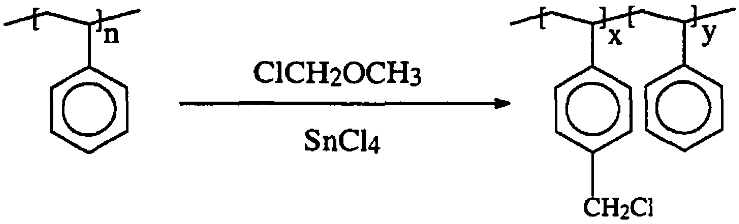
SELECTIVE OXIDATION OF POLY(4-METHYLSTYRENE) BY COBALT(III) ACETATE

3.1 INTRODUCTION

As discussed above, functional polymers have been involved in many of the most important trends in polymer science in the last two decades. Functional polymers are produced either by chemical modification[1,2,3] of preformed nonfunctional polymers, or by direct (co)polymerization[4,5] of the desired functional monomers with suitably chosen structural and optionally crosslinking monomers. Polystyrenes incorporating functional groups are widely used in many industries.[6] Among these, chloromethylstyrene-based resins are the most important ones.[7,8] Chloromethylated polystyrenes play an important role in Merrifield's synthesis of peptides.[9,10] They are used as a high sensitivity and high contrast electron beam negative image resist,[11,12,13] and are key intermediates in the preparation of anion-exchange resins.[14] Chloromethyl groups were easily converted to a host of other functional groups.[15]

There are two methods available for the preparation of polystyrene containing the chloromethyl group: chloromethylation of polystyrene[14] and polymerization of vinylbenzyl chloride.[16,17]

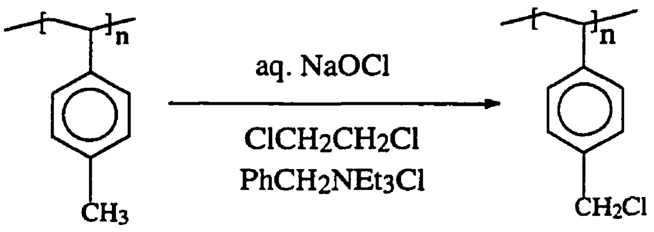




Two drawbacks of the Lewis acid catalyzed chloromethylation are that the degree of chloromethylation is difficult to control, and that many chloromethylating agents such as chloromethylmethylether are carcinogenic. On the other hand, copolymerization of vinylbenzylchloride is costly, and limited to radical polymerization processes.

4-Methylstyrene is industrially produced by *para*-selective alkylation of toluene in the presence of a shape-selective zeolite catalyst, followed by dehydrogenation.[18] It can be polymerized by free radical, anionic, or cationic processes and used to prepare homopolymers and copolymers. Functionalizing the 4-methyl groups of poly(4-methylstyrene) to chloromethyl groups, is therefore potentially very useful.

Mohanraj and Ford[19] reported a phase transfer catalyzed chlorination of poly(4-methylstyrene). They employed aqueous sodium hypochlorite as a chloromethylation reagent and benzyltriethylamine chloride as a phase transfer reagent. The mechanism was a free radical process. Jones and Matsubayashi recently took this process further.[20,21] The concern with this process is that free chlorine radicals carry a chain-reaction consisting of benzyl hydrogen abstraction and addition. Chlorine radicals are known to be reactive enough to also abstract aliphatic hydrogens from the backbone, leading to non-specific chlorination.



Sheng and Stöver[22] have reported the selective functionalization of poly(4-methylstyrene) by cobalt acetate or cerium ammonium nitrate systems, introducing acetoxy or trichloroacetoxy groups into poly(4-methylstyrene). This chapter describe the selective oxidative chlorination of poly(4-methylstyrene) using cobalt(III) acetate/lithium chloride. The resulting polymers contain up to 20% of chloromethyl moieties.

As well, this chapter will report on the cobalt(III) acetate mediated introduction of acetoxy and trichloroacetoxy groups into poly(4-methylstyrene) under nitrogen. This reaction is related to the introduction of acetoxy and nitrooxy groups into poly(4-methylstyrene) using cerium (IV) as discussed in chapter 2. The results of cerium (IV) and cobalt (III) oxidation of methyl to acetoxymethyl groups will be compared with respect to reactivity and selectivity.

3.2 AIM OF THE RESEARCH

The purpose of this research is to explore two novel oxidation processes using cobalt(III) acetate as an oxidant to introduce different functional groups.

One process uses a cobalt (III) acetate-trichloroacetic acid/benzene-glacial acetic acid system to introduce acetoxy groups into poly(4-methylstyrene). Another process uses a cobalt(III) acetate/lithium chloride/benzene-glacial acetic acid system to selectively introduce chlorine groups into poly(4-methylstyrene). Both processes were carried out under a nitrogen atmosphere. To optimize the reaction conditions the experimental parameters that affect the degree of oxidation of poly(4-methylstyrene) were varied. Their effect on oxidation yields were studied, and oxidation mechanisms are proposed for both processes.

The two processes (cerium(IV) ammonium nitrate and cobalt(III) acetate systems) which were employed to introduce the same functionality (acetoxy groups) are compared with respect to reactivity and selectivity.

3.3 EXPERIMENTAL METHODS

3.3.1 Materials and Their Purification

Reagent grade 4-methylstyrene monomer (4MS) was purchased from Deltech Corp, Baton Rouge. It was purified by passage through an alumina column to remove inhibitors prior to polymerization. 2,2'-Azobisisobutyronitrile (AIBN) was purchased from Kodak and used as received. Cobalt (II) acetate, glacial acetic acid, trichloroacetic acid, benzene, *n*-

heptane, methylethylketone, and dimethyldigol were purchased from Aldrich and used as received. Lithium chloride was purchased from Fisher Scientific and used as received. Poly(4-methylstyrene) was prepared as described earlier (Chapter 2).

3.3.2 Preparation of Cobalt (III) Acetate

Cobalt (III) acetate was prepared by ozonation of cobalt (II) acetate in a mixture of glacial acetic acid and acetic anhydride using the procedure reported by Lande et *al.*[23]

3.3.2.1 Preparation of Anhydrous Cobalt (II) Acetate

Cobalt (II) acetate hydrate ($Co(OAc)_2•4H_2O$) 190 g, acetic anhydride 290 mL, and glacial acetic acid 400 mL were placed in a 1000 mL three-neck round bottom flask fitted with a condenser, and a nitrogen inlet. The pink mixture was heated for 5 hours, during which time, $Co(OAc)_2$ precipitated as a pink solid. The solution was filtered to isolate the pink solid and the pink solid was dried by rotary evaporator under reduced pressure. The yield was 100% (139 g).

3.3.2.2 Preparation of Cobalt(III) Acetate

Anhydrous cobalt(II) acetate (139 g) was dispersed in 980 mL of glacial acetic acid in a 2000 mL of three-neck round bottom flask equipped with a glass inlet tube, a condenser (vented into a potassium iodide solution), and a magnetic stirring bar. Acetic anhydride (70 mL) was added slowly to the mixture and then ozone, generated from oxygen using a Welsbach T-40B ozonator, was carried to the reaction vessel through tygon tubing equipped with a three way stopcock. Gas flow was measured by a wet test meter (Precision Scientific). The ozone was passed through the solution at 370 mL/min flow rate for seven hours. During oxidation, the colour of the solution changed from pink to deep black. Finally, the solution was heated on a water bath at 70°C. Acetic acid was removed on a vacuum rotary evaporator until a solid material formed on the walls of the flask. The near black material was broken up and dried further in a vacuum desiccator over sodium hydroxide pellets. The yield of cobalt(III) acetate was 144 g (69%).

3.3.3 Selective Functionalization of Poly(4-methylstyrene) by Cobalt(III) Acetate/ Trichloroacetic Acid/Acetic Acid-Benzene/Nitrogen System

Poly(4-methylstyrene) 0.296 g (2.5 mmol) and trichloroacetic acid 6.13 g (37.5 mmol) were dissolved in a mixture of 30 mL glacial acetic acid and 30 mL benzene (or other organic cosolvent) in a 100 mL three-neck round bottom flask fitted with a condenser, nitrogen inlet and a thermometer reaching below the liquid level. The temperature was raised to 50°C, and cobalt (III) acetate (dried and stored in a desiccator) 1.18 g (5.0 mmol) was added to the flask all at once. During the reaction, the color of the system changed from black to red-black. After three hours the reaction mixture was cooled and filtered, and the benzene component of the filtrate was removed on a rotary evaporator. The remaining solution of oxidized polymer and cobalt salts (little) in acetic acid was precipitated into 200 mL of a mixture of methanol and water (4:1 v/v). After standing overnight, the white precipitate was filtered, washed with a 4:1 methanol/water mixture, and dried under vacuum at 60°C overnight. Yields were typically around 90%.

One 30g batch of poly(4-methylstyrene) having a number average molecular weight (Mn) of 19,800 and a polydispersity (Mw/Mn) of 1.74, was used for all the above experiments in this project.

3.3.4 Displacement of Trichloroacetoxy Groups with Acetoxy Groups

The oxidized polymer was dissolved in the mixture of 30 mL glacial acetic acid and 10 mL xylene, then 2 drops sulfuric acid were added, and the mixture heated to reflux for twenty hours under nitrogen. The resulting acetoxymethylated polymer showed no signs of crosslinking, and was isolated quantitatively by precipitation into methanol. ^{1}H-NMR confirmed that all trichloroacetoxy groups had been converted to acetoxy groups.

3.3.5 Displacement of Acetoxy Groups with Trichloroacetoxy Groups

The oxidized polymer was melted with an excess of trichloroacetic acid, and heated under vacuum (10^{-2} torr) at 60°C for 10 minutes. The resulting trichloroacetoxymethylated polymer was isolated quantitatively by dilution with benzene, and precipitation into methanol. ^{1}H-NMR showed that all acetoxy groups had been converted to trichloroacetoxy groups.

3.3.6 Selective Functionalization of Poly(4-methylstyrene) by Cobalt(III) Acetate/ Lithium Chloride/Acetic Acid-Benzene/Nitrogen System

Poly(4-methylstyrene) 0.296 g (2.5 mmol) and lithium chloride 0.85 g (20 mmol) were dissolved in a mixture of 15 mL glacial acetic acid and 15 mL benzene (or other co-solvent) in a 100 mL three-neck round bottom flask with a condenser, a nitrogen inlet, and a thermometer reaching below the liquid level. The temperature was raised to 50°C, and cobalt acetate 1.18 g (5.0 mmol) solid was added to the flask all at once. During the reaction, the color of the solution was dark green. After two hours the reaction mixture was cooled and filtered, and the benzene component of the filtrate was removed on a rotary evaporator. The remaining solution of oxidized polymer and cobalt salt in acetic acid was precipitated into 200 mL of a mixture of methanol and water (4:1 v/v). After standing overnight, the white precipitate was collected by filtration, washed with a 4:1 methanol/water mixture, and dried under vacuum at 60°C overnight. Yields were typically around 90%.

One 30 g batch of poly(4-methylstyrene) having a number average molecular weight (Mn) of 18,900 and a polydispersity (Mw/Mn) of 1.73, was used for all the above experiments of this project.

3.3.7 Oxidation Reaction of Oxidized Polymer (Containing 20% Chloromethyl Group)

Oxidized polymer 0.20 g and sodium hydrogen carbonate 0.30 g were stirred in 18 mL dimethylsulfoxide at 155°C for five hours. The product was filtered, washed with dimethylsulfoxide and hot water, and dried at 60°C under vacuum overnight.[24,25,26]

3.3.8 Characterization of Functional Polymer by NMR, FT-IR, SEC, Elemental Analysis (EA), and Neutron Activation Analysis (NAA)

The characterization of functional poly(4-methylstyrene) was carried out by ^{1}H and ^{13}C nuclear magnetic resonance (NMR), infrared (IR) and size exclusion chromatography (SEC), elemental analysis (EA), and neutron activation analysis (NAA).

Most NMR spectra were measured in deuteriochloroform solution on a Bruker AC200 or AC300 NMR instrument. Chemical shifts are in ppm relative to tetramethylsilane at zero ppm for proton chemical shift, and carbon (deuteriochloroform) signals at 77.0 ppm.

Molecular weights were determined on a Waters size exclusion chromatography (SEC) system using three Waters Ultramicrostyragel columns in series. It was calibrated using narrow-disperse polystyrene standards.

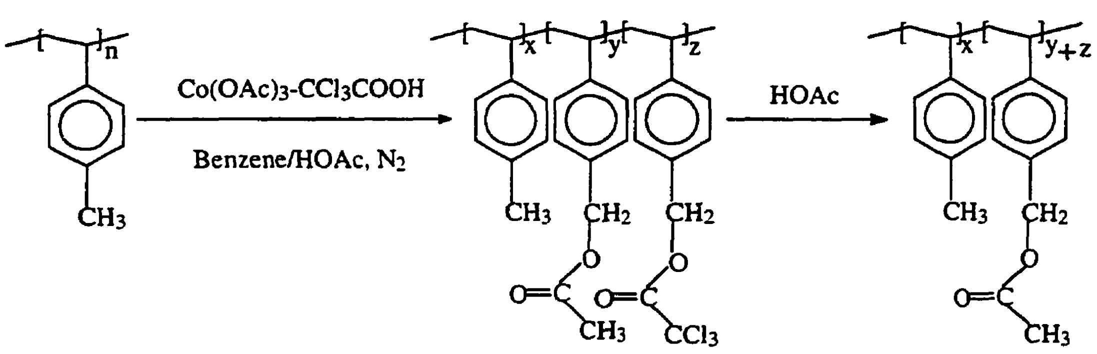
The infrared spectra were obtained using a BIO-RAD FTS-40 instrument. The IR sample was prepared by dissolving the polymer in methylene chloride and then forming a thin film on a sodium chloride plate.

The elemental analysis was carried out by Guelph Chemical Laboratories Ltd. The sodium fusion experiment was carried out to confirm the presence of chlorine. Neutron activation analysis was performed by Al Guest and John Valliant at the McMaster Nuclear Reactor.

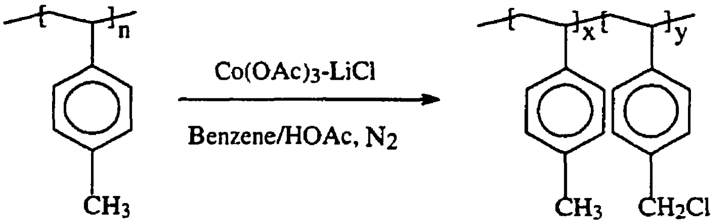
3.4 RESULTS AND DISCUSSION

In this chapter, cobalt (III) acetate was used as an oxidant for the oxidation of poly(4-methylstyrene). A mixture of 50% : 50% v/v glacial acetic acid and benzene was used as a solvent under a nitrogen atmosphere, and different nucleophiles were employed to introduce different functional groups.

In the presence of trichloroacetic acid, terpolymers of acetoxymethylstyrene, trichloroacetoxymethylstyrene, and 4-methylstyrene were obtained. However, trichloroacetoxymethyl groups can be easily displaced by acetoxymethyl groups by refluxing the polymers in the mixture of acetic acid and xylene overnight.



In the presence of lithium chloride, a portion of the methyl groups was selectively chlorinated, forming chloromethyl groups.



3.4.1 Characterization of the Functional Polymers

3.4.1.1 Confirmation of Structure of the Functional Polymers by ^{1}H and ^{13}C NMR

Figure 3.1 shows the ^{1}H NMR spectrum of poly(4-methylstyrene) before and after cobalt (III) acetate-trichloroacetic acid/nitrogen oxidation. The proton NMR spectrum of poly(4-methylstyrene)is shown in Figure 3.1(A). The peak at 2.3 ppm corresponds to the 4-methyl hydrogens, the peaks at 6.6 ppm and 6.9 ppm correspond to the disubstituted aromatic groups. The methylene hydrogens in the backbone appear at 1.4 ppm, the methine hydrogens in the backbone appear at 1.9 ppm.

During oxidation, some of the 4-methyl groups were selectively oxidized to acetoxymethyl and trichloroacetoxymethyl groups. The 4-methyl peaks should decrease in either intensity or area, and new signals (benzylic) should appear in the 5- 6 ppm region of the spectrum, which is characteristic of benzylic methylene groups. After oxidation, there are two additional signals in this region. The peak at 5.00 ppm is characteristic of a benzyl acetate methylene and the peak at 5.25 ppm corresponds to the benzyl trichloroacetate methylene group (Figure 3.1(B)). The peak at 2.03 ppm corresponds to the methyl hydrogens of the acetoxy group. These NMR results indicate the selective functionalization of poly(4-methylstyrene) by the cobalt (III) acetate-trichloroacetic acid/nitrogen system.

In the oxidation of poly(4-methylstyrene) with cobalt(III) acetate/lithium chloride /nitrogen, the methyl groups of 4-methylstyrene were selectively oxidized to chloromethyl groups. In the proton NMR spectrum (Figure 3.2(B)), this results in a new peak at 4.48 ppm, corresponding to the benzyl chloride methylene group.

The ^{13}C NMR spectrum of poly(4-methylstyrene) is shown in Figure 3.3(A). The 4-methyl carbon appears at 21.03 ppm, the four secondary carbons of the aromatic ring at 127.60 ppm and 128.50 ppm, and the two quaternary carbons of the aromatic ring appear at 134.6 and 142.5 ppm respectively. The backbone carbons appear at 39.9 ppm (methine), and in the region of 40 - 48 ppm (methylene). Figure 3.3(B) shows the ^{13}C NMR spectrum of the chloromethyl polymers. Compared to the spectrum of poly(4-methylstyrene) (Figure 3.3(A)), there are two additional peaks for the oxidized polymer. The peak at 46.29 ppm represents the carbon of the chloromethyl group; while the peak at 145.78 ppm represents the aromatic carbon bearing the chloromethyl group.[20] The degree of oxidation of poly(4-methylstyrene) by cobalt(III) acetate-trichloroacetic acid/nitrogen can be determined by comparing the benzylic methylene signals with the aromatic signals.

Similarly, the degree of oxidation of poly(4-methylstyrene) by cobalt (III) acetate/lithium chloride/nitrogen can be calculated by the ratio of integration of protons signals between chloromethyl and aromatic ring. The calculation methods were the same as those described in Chapter 2. The total degree of oxidation represents the percentage of methyl groups in poly(4-methylstyrene) that were oxidized to the functional groups.

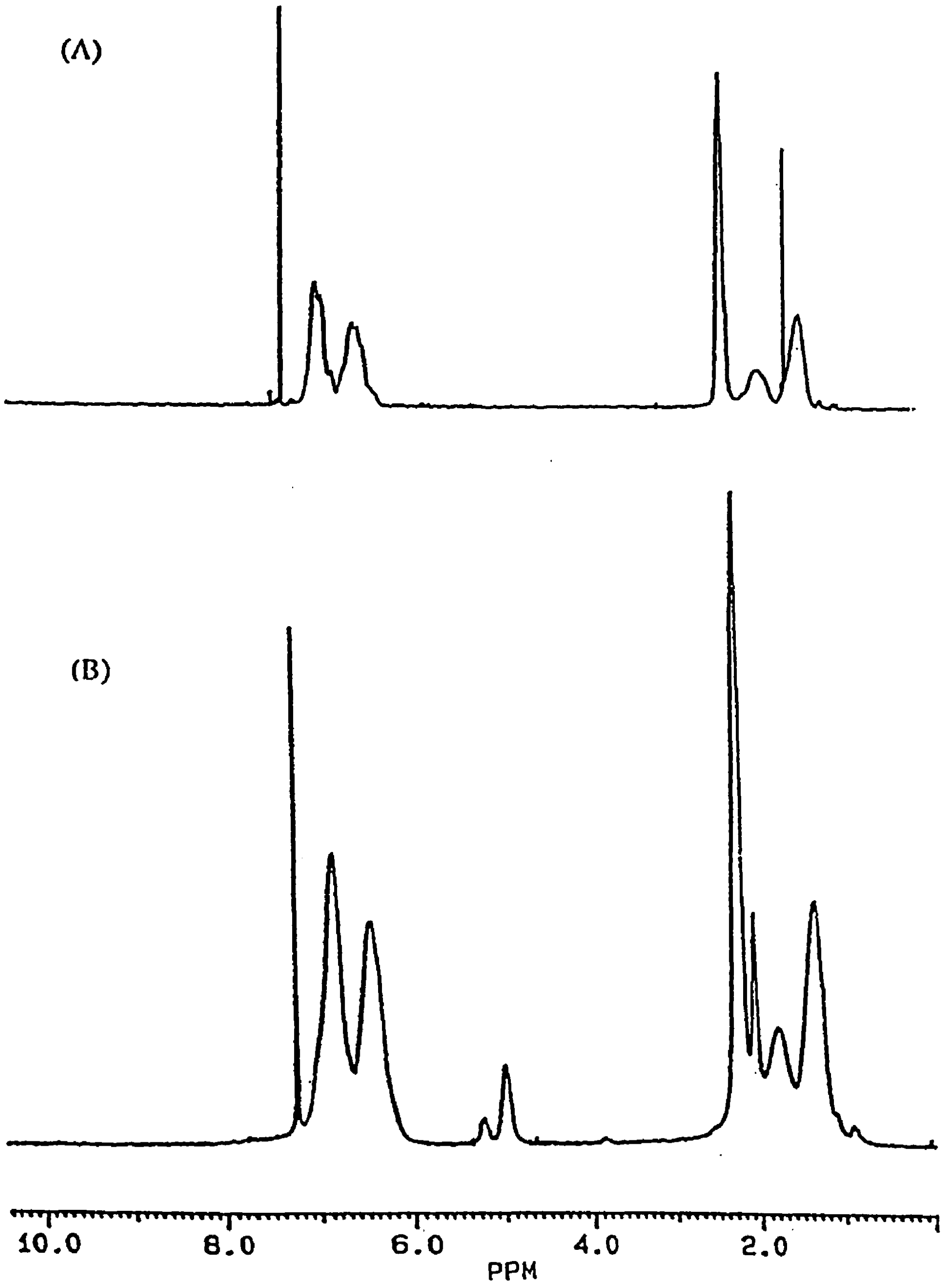


Figure 3.1 ^{1}H NMR spectrum. (A): Poly(4-methylstyrene), (B): after oxidation of poly(4-methylstyrene) by cobalt(III) acetate/trichloroacetic acid.

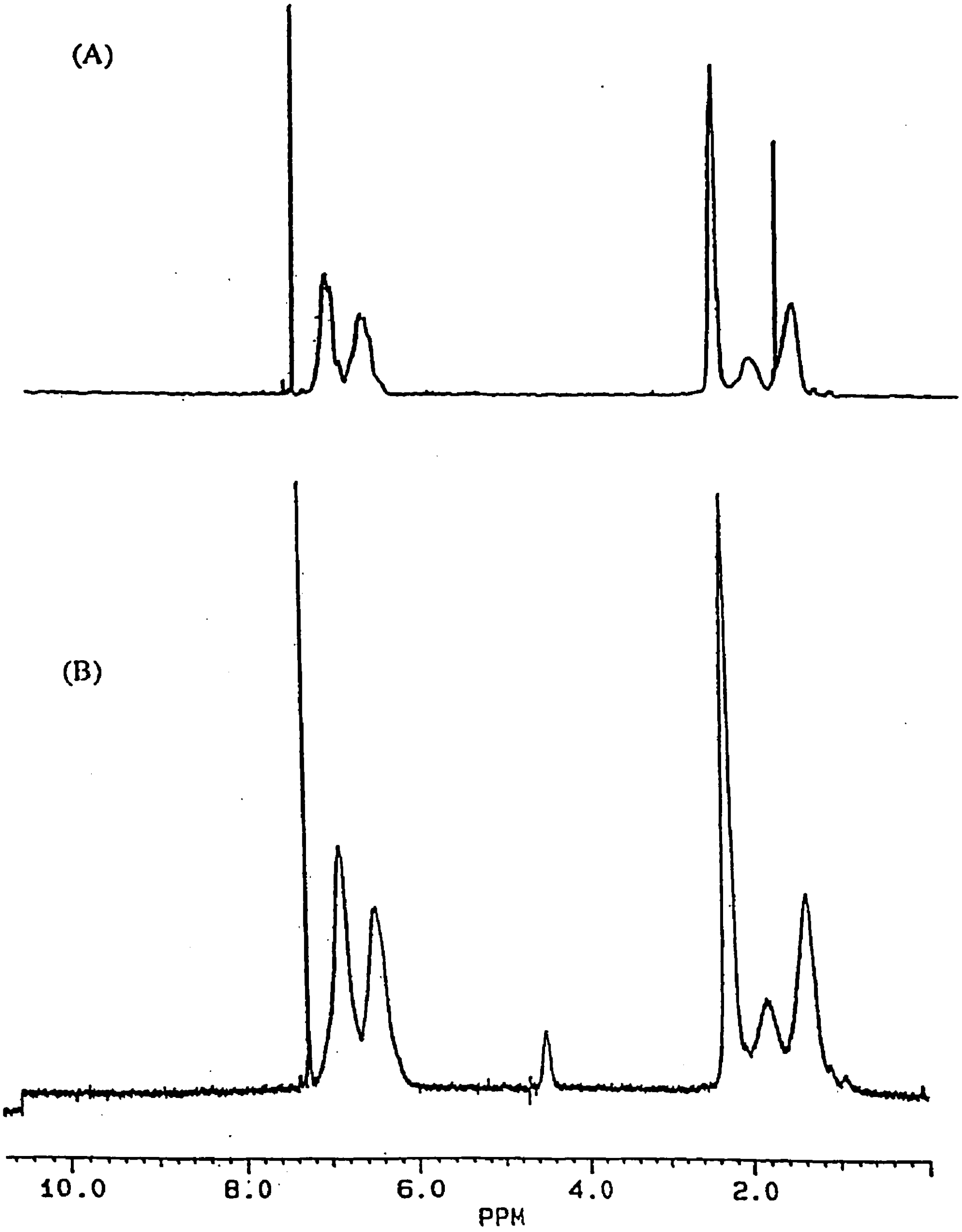


Figure 3.2 ^{1}H NMR spectrum. (A): Poly(4-methylstyrene), (B): after oxidation of poly(4-methylstyrene) by cobalt(III) acetate/lithium chloride.

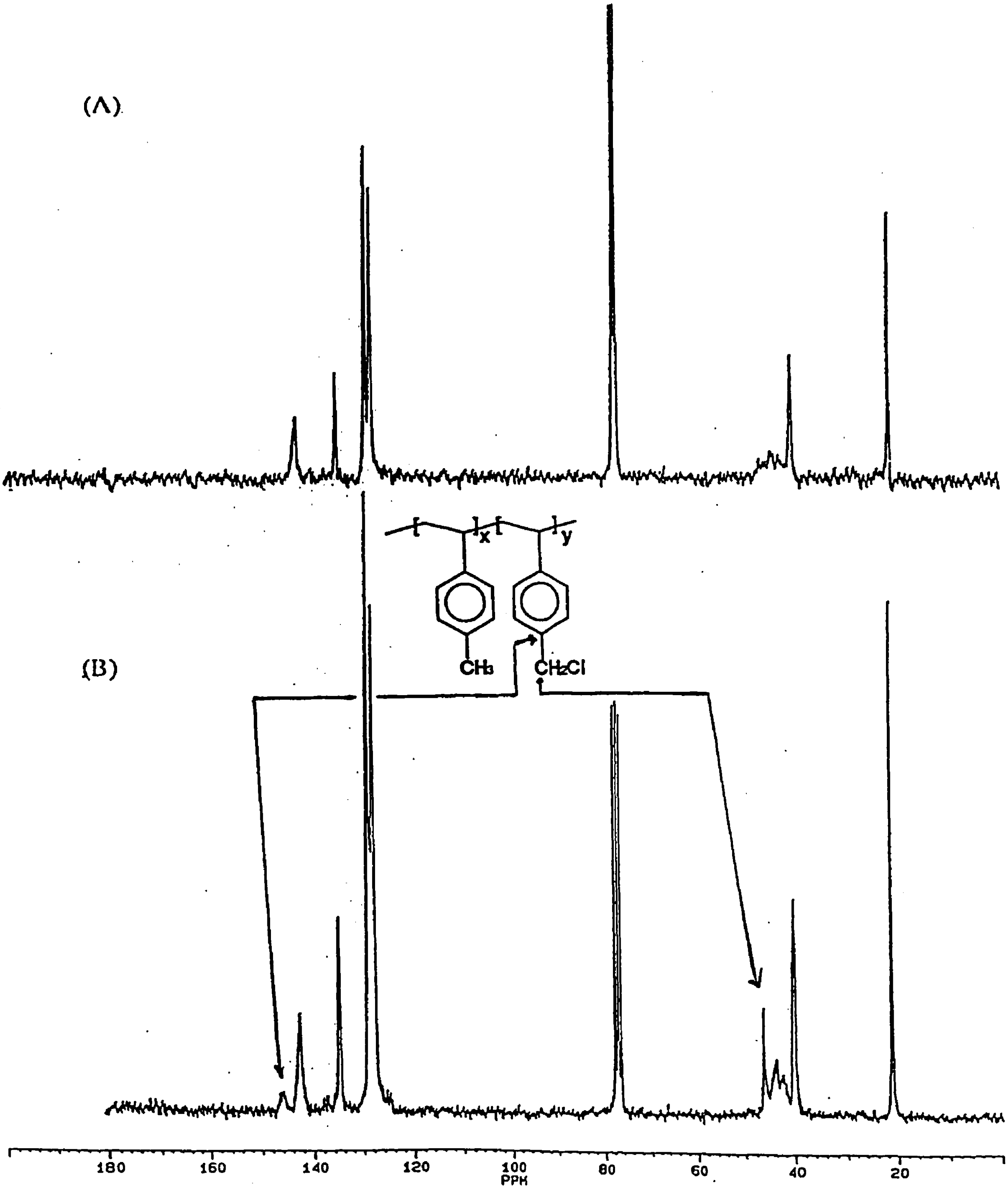


Figure 3.3 ^{13}C NMR spectrum. (A): Poly(4-methylstyrene), (B): after oxidation of poly(4-methylstyrene) by cobalt(III) acetate/lithium chloride.

4.1.2 Confirmation of Oxidation by FT-IR

FT-IR spectra show the infrared absorption frequencies 1266 cm^{-1}, 725 cm^{-1}, 816 cm^{-1}, and 676 cm^{-1}, which are characteristic of the chloromethylstyrene units.[24] Following are the assignments of each peak: 1266 cm^{-1}, $-CH_2Cl$ wagging; 725 cm^{-1}, and 816 cm^{-1}, aromatic C-H out of plane bending; 676 cm^{-1}, C-Cl stretching vibration.

3.4.1.2 Confirmation of Oxidation by Elemental Analysis

The combination of elemental analysis and neutron activation analysis were used to confirm the introduction of chlorine during the $Co(OAc)_3$ - LiCl oxidation. The following are the results for the polymer (18) shown in Figure 3.2(B).

Experimental Methods	Carbon (wt%) (found)	Hydrogen (wt%) (found)	Chlorine (wt%) (found)	$-CH_2Cl$ (mol%)
EA[1]:	85.59	7.90	6.07	21.5
NAA:	-	-	6.0	20.6
^{1}H NMR:	-	-	6.04[2]	21.0

---

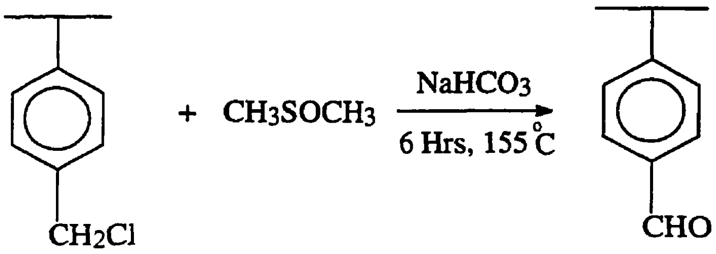
[1] sum to 99.56%.

[2] :Calculated from the ratio of the benzylic methylene/aromatic region areas in the ^{1}H NMR (Figure 3.2(B)).

Sodium fusion experiments also indicated qualitatively the presence of chlorine in our oxidized polymer.

3.4.1.3 Confirmation of The Structure of Chlorinated Poly(4-methylstyrene) by Further Oxidation to Aldehyde

Poly(*p*-chloromethylstyrene) is known to be oxidized to the polyaldehyde in the presence of dimethyl sulfoxide as shown below.[24,25,26]



To test the presence of chlorine in the oxidized polymer, the same oxidation with DMSO was carried out. The ^1H NMR spectrum (Figure 3.4) of the reaction product showed the presence of the benzaldehyde proton (9.9 ppm), and orthor protons of the aldehyde group of the benzene ring (7.48 ppm), but no chloromethyl protons. There was also no spectral or chemical evidence of functional groups other than aldehyde. In addition, some crosslinked polymer was obtained.[27]

3.4.2 Introduction of Acetoxy Groups into Poly(4-methylstyrene) by Cobalt(III) Acetate- Trichloroacetic Acid/Acetic Acid-Benzene/Nitrogen System.

3.4.2.1 Study of Oxidation Mechanism

In 1969, Sakota and his co-workers[28] reported the detailed kinetic study of oxidation of toluene, ethylbenzene, cumene and other aromatics by cobalt(III) acetate in acetic acid

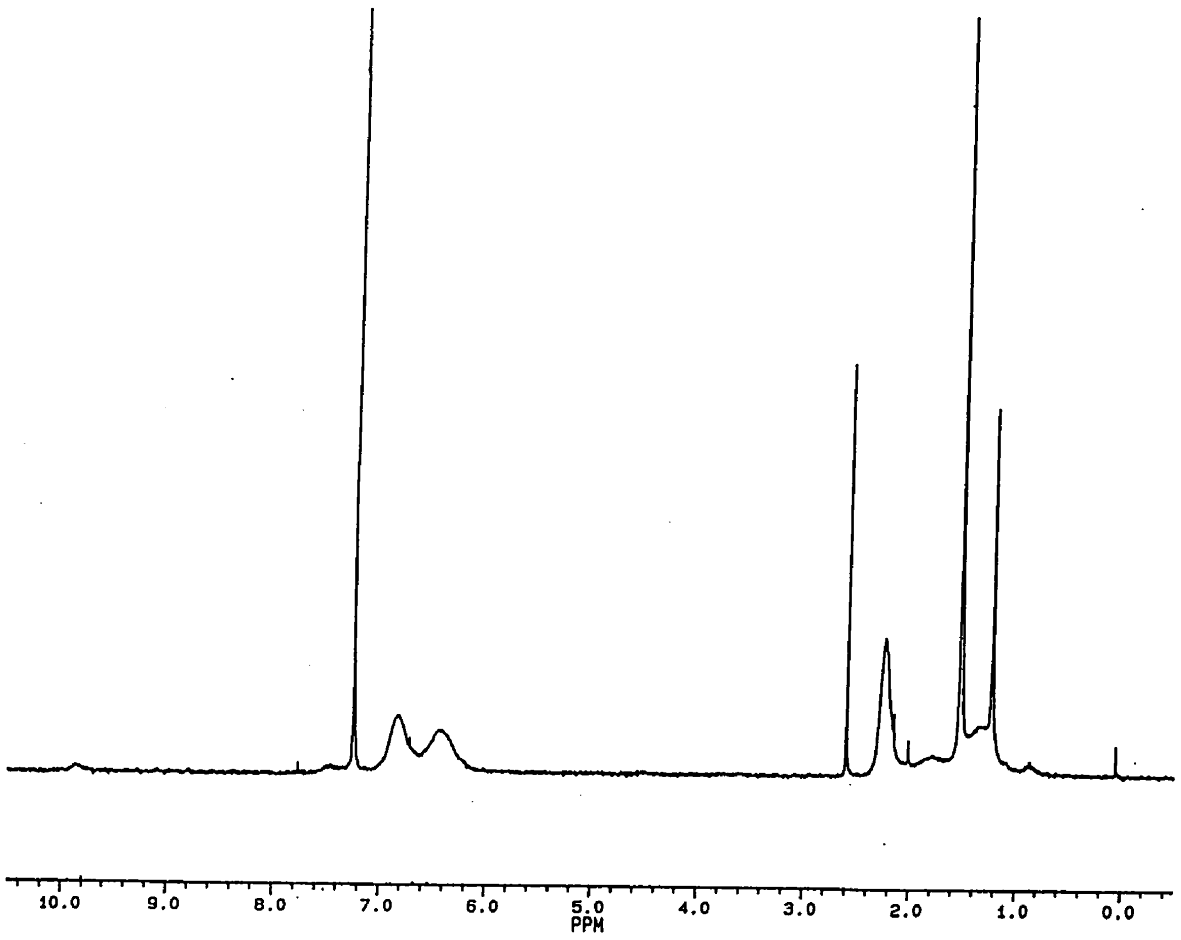


Figure 3.4 ^{1}H NMR spectrum of reaction product of chlorinated poly(4-methylstyrene) with dimethyl sulfoxide.

under argon. They noted that the order of reactivity (1:1.2:0.2 (per active hydrogen) for toluene : ethylbenzene : cumene) differed from that usually observed during radical oxidation (i.e. with cumylperoxide), and also from the order expected on the basis of the benzylic C-H bond strengths involved. Based on these reactivities and on kinetic arguments, Sakota et *al.* suggested a mechanism involving an initial, reversible and rate-determining electron transfer from the aromatic substrate to Co(III). This would be followed by the loss of a proton to give the benzylic radicals. In the absence of oxygen, this radical would be oxidized further to the benzyl cation, which would capture an acetate to finally yield the corresponding benzylacetate. This mechanism is similar to that described above for cerium ammonium nitrate. In the same year, Heiba et *al.* reported an excellent study with similar results.[29]

Onopchenko and Schulz[30] also found higher methyl over isopropyl reactivities in Co(III) oxidation of *p*-cymene, leading to predominantly *p*-isopropylbenzoic acid under oxygen and *p*-isopropylbenzyl acetate under nitrogen.[31] However, with manganese(III) acetate, a mixture of cymene dimers was formed predominantly. Because of the two different products, two different mechanisms were suggested: electron transfer with cobalt and a free-radical pathway with manganese.

The reaction products and kinetics of oxidation (anaerobic and aerobic) of several substituted toluenes by Co(III) acetate in an acetic acid solution were determined by Hendriks.[32] It was found that for anaerobic oxidation, one mole of substituted toluene was oxidized by two moles of Co(III) acetate to the corresponding benzylacetate, which was subsequently oxidized by another two moles of Co(III) acetate to the corresponding benzaldehyde.

Recently, Trivedi and Bhawan[33] reported the efficient electrochemical preparation and regeneration of Co(III) acetate *in situ*, and the successful application of this indirect electrochemical oxidation to convert toluene to benzyl acetate. They also proposed an electron transfer for the initial step.

In the meantime, doubt has been cast on the importance of this initial radical cation formation.[34] Baciocchi and Ruzziconi compared the CAN versus Co(III) oxidation of diphenylethane and tetramethyldiphenylethane, producing good evidence for the presence of a radical cation intermediate in the case of CAN, but not in the case of Co(III). For diphenylethane the expected side chain acetoxylation products were obtained. For tetramethyldiphenylethane. on the other hand, no reaction was observed, presumably due to the absence of benzylic hydrogens. Instead they suggest an initial hydrogen abstraction leading directly to the benzylic radical.[30]

$$\mathrm{ArCH_3 + Co(III) \rightarrow \quad ArCH_2\cdot + H^+ + Co(II)}$$

This reaction involves a direct attack of the Co(III) on the benzylic carbon-hydrogen bond. In this mechanism, side chain acetoxylation takes place only when benzylic hydrogens are available; otherwise there is no reaction.

The above discussion indicates that reaction of Co(III) with alkyltoluene under anaerobic conditions leads to intermediate alkyl benzyl radicals, or an initial radical cation. This oxidation shows a pronounced selectivity for the methyl group over higher alkyl substituents, because the rate-determining loss of the proton (or hydrogen atom, according to Baciocchi) is controlled by stereo-electronic considerations (i.e. resonance stabilization of the forming benzylic radical), and not by the thermodynamic stability of the products alone.[30] Based on this information, the use of Co(III) acetate in the anearobic oxidation of poly(4-methylstyrene) was explored. In this system, the bulky backbone strongly hinders radical (or radical cation) stabilization through the aromatic system, and hence prevents backbone oxidation.[35,36]

The oxidation of poly(4-methylstyrene) is expected to follow the same mechanism as described above: first an electron transfer from the aromatic ring to the oxidant, then loss of a proton to form the benzyl radical. This transfers a second electron to oxidant, and becomes a benzyl cation. This benzyl cation finally reacts with nucleophiles present in the system to form the side chain acetoxylated polymers.

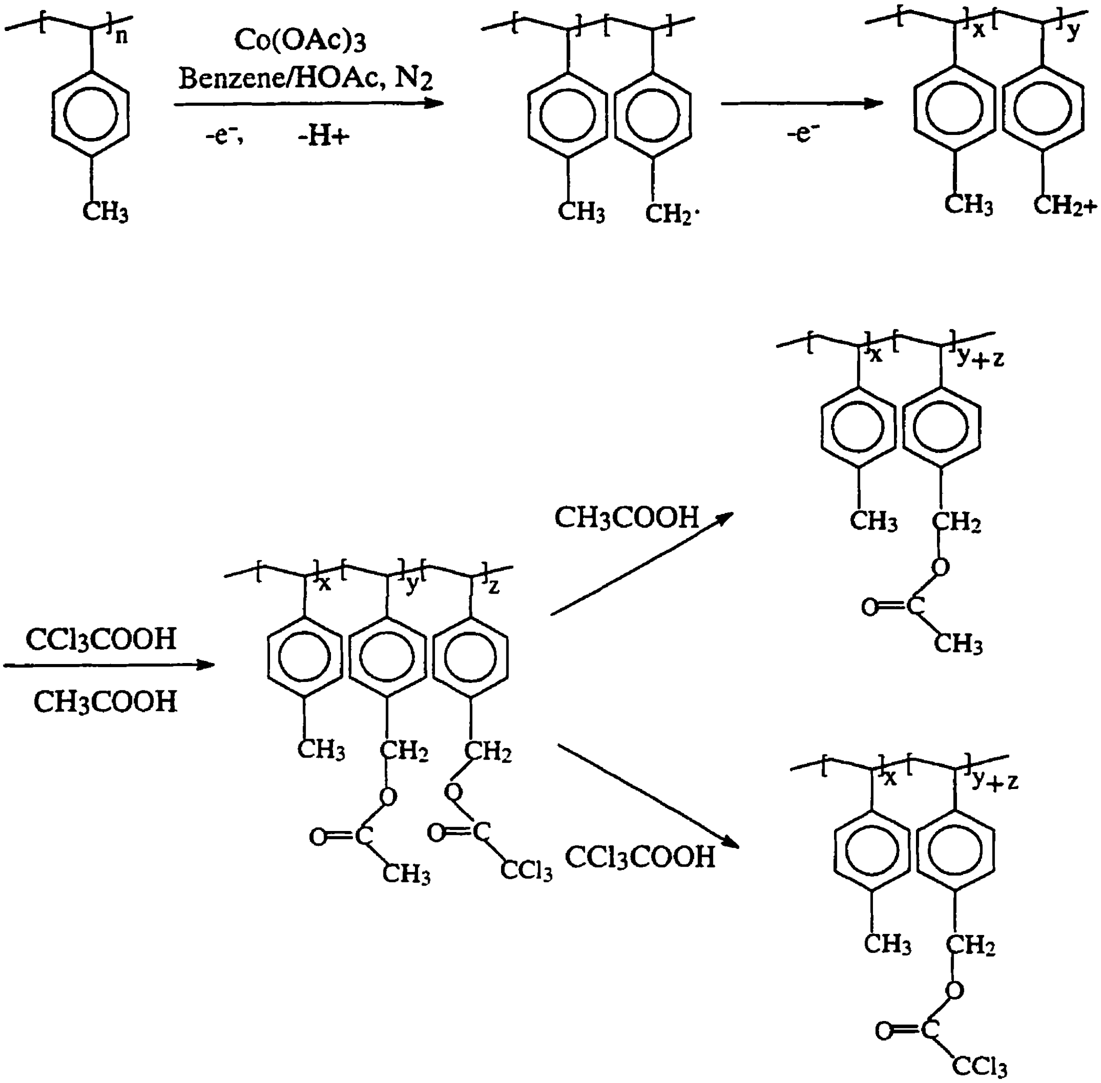


Figure 3.5 Oxidation of poly(4-methylstyrene) by cobalt (III) acetate

3.4.2.2 Factors Affecting the Oxidation Yield of Poly(4-methylstyrene)

3.4.2.2a Effect of Trichloroacetic Acid on Oxidation

Initially, no oxidation of the polymer was observed using cobalt acetate as an oxidant, and benzene and acetic acid as a mixed solvent. Indeed, Hanotier *et al.* [37] had suggested that in concentrated solution in acetic acid, Co(III) and Co(II) are apparently associated into inactive dimeric structures, and that strong acids needed to be added in order to dissociate such dimers and to liberate more reactive cobaltic species. Trichloroacetic acid is a strong acid that is used in the oxidation of low molecular weight alkylarenes by cobaltic acetate in acetic acid.[37]

In the present selective oxidations of poly(4-methylstyrene), the addition of trichloroacetic acid proved equally essential (Table 3.1). When the molar ratio of trichloroacetic acid to P4MS was less than 1:1, no oxidation occurred, but with an increase in this ratio, the oxidation yield increased. A maximum degree of oxidation of 25% was obtained for a 15:1 molar excess of trichloroacetic acid (37.5 mmol) over poly(4-methylstyrene) (2.5 mmol). Accordingly, subsequent reactions were usually carried out using 37.5 mmole of trichloroacetic acid. The ratio of trichloroacetoxymethyl to acetoxymethyl groups on the final polymers also increases with the fraction of trichloroacetic acid (Table 3.1, 3.6).

Table 3.1 Effect of Trichloroacetic Acid on Oxidation

Run#	TricA. (mmol)	Mn	Mw/Mn	%Acet.	%Tric.	%Tot.
b-6	37.5	18,500	1.89	19.1	6.0	25.1
b-11	25.0	20,800	1.87	7.4	1.0	8.4
b-12	12.5	18,200	2.22	3.5	-	3.5
b-13	0.0	19,900	1.80	-	-	-

Reaction conditions: P4MS 2.5 mmol; $Co(OAc)_3$ 5.0 mmol; HOAc 30 mL; Benzene 30 mL; 50°C; 3 hours; N_2. (TricA.: Trichloroacetic acid; Acet.: acetoxy; Tric.: Trichloroacetoxy; Tot.: total oxidation degree)

3.4.2.2b Effect of Cobalt(III) Acetate on Oxidation

When varying the molar ratio of cobalt(III) acetate/P4MS, oxidation was observed only above a threshold Co(III)/P4MS ratio of 1 (Table 3.2). At higher ratios the degree of oxidation rapidly increased to 25%, corresponding to a chemical yield based on cobalt(III) acetate of 50%, much lower than the approximately 70-80% chemical yield observed in the CAN oxidations above at similar reaction times (Ref. to Table 2.1, 2.2, 2.3, and 2.4, page 52, 53, 54, and 55 respectively, Chapter 2).

Table 3.2 Effect of Molar Ratio of Cobaltic Acetate on Oxidation

Run#	Co(III) (mmol)	Mn	Mw/Mn	%Acet.	%Tric.	%Tot.
b-6	5.0	18,500	1.89	19.1	6.0	25.1
b-7	2.5	17,400	1.96	9.8	2.5	12.3
b-8	1.25	19,000	1.82	2.7	<0.3	<3.0
b-9	1.00	18,000	1.87	2.3	<0.3	<2.6
b-10	0.5	18,900	1.89	<0.5	-	<0.5

Reaction conditions: P4MS 2.5 mmol; CCl_3COOH 37.5 mmol; HOAc 30 mL; Benzene 30 mL; 50°C; 3 hours; N_2.

3.4.2.2c Effect of Reaction Time on Oxidation

Table 3.3 Effect of Reaction Time on Oxidation

Run#	Reaction Time (hours)	Mn	Mw/Mn	%Acet.	%Tric.	%Tot.
b-6	3.0	18,500	1.89	19.1	6.0	25.1
b-14	2.5	18,600	1.82	15.6	4.8	20.4
b-15	2.0	18,500	1.83	14.8	4.0	18.8
b-16	1.0	19,000	2.03	12.6	3.4	16.0
b-17	0.5	18,700	1.98	10.7	3.4	14.1

Reaction conditions: P4MS 2.5 mmol; $Co(OAc)_3$ 5.0 mmol; CCl_3COOH 37.5 mmol; HOAc 30 mL; Benzene 30 mL; 50°C; N_2.

Table 3.3 shows that the degree of oxidation increases with increasing reaction time. It is possible that longer reaction times could further increase conversion and yield to some extent.

Table 3.3 further indicates that the ratio of trichloroacetoxymethyl to acetoxymethyl does not change noticeably during the reaction.

3.4.2.2d Effect of Cosolvent on Oxidation

The effect of cosolvents on oxidation of poly(4-methylstyrene) is similar to the cerium ammonium nitrate system. No reaction was observed when using methylethylketone or dimethyldigol as cosolvents. Benzene and *n*-heptane were good cosolvents.

Table 3.4 Effect of Cosolvent on Oxidation

Run#	Cosolvent	Mn	Mw/Mn	%Acet.	%Tric.	%Tot.
b-6	benzene	18,500	1.89	19.1	6.0	25.1
b-18	*n*-heptane	18,900	1.79	15.8	4.5	20.3
b-19	dimethyldigol	20,200	1.84	-	-	-
b-20	MEK	19,800	1.76	-	-	-

Reaction Conditions: P4MS 2.5 mmol; $Co(OAc)_3$ 5.0 mmol; CCl_3COOH 37.5 mmol; HOAc 30 mL; Cosolvent 30 mL; 50°C; 3 hours; N_2. MEK methylethylketone.

3.4.2.2e Effect of Reaction Temperature on Oxidation

Reaction temperature has only a remarkably small influence on the oxidation yield (Table 3.5); in fact, the oxidation reaction can be carried out at room temperature. At temperatures above 50°C, the reaction yield is almost unchanged, but backbone cleavage becomes more pronounced.

Table 3.5 Effect of Reaction Temperature on Oxidation[a]

Run#	Reaction Temp.(°)	Mn	Mw/Mn	%Acet.	%Tric.	%Tot.
b-1[b]	r.t.	14,500	1,96	11.2	3.4	14.6
b-26	35	13,400	1.90	19.0	4.5	23.5
b-6	50	18,500	1.89	19.1	6.0	25.1
b-23	60	14,500	1.96	20.9	5.2	26.1
b-24	70	14,500	1.86	21.5	6.8	28.3
b-25	80	12,400	1.97	18.3	6.6	24.9

[a] Reaction Conditions: P4MS 2.5 mmol; $Co(OAc)_3$ 5.0 mmol; CCl_3COOH 37.5 mmol; HOAc 30 mL; Benzene 30 mL; 3 hours; N_2.

[b] Reaction Conditions: P4MS (Mn 16,100, Mw/Mn 2.13)10 mmol; $Co(OAc)_3$ 20 mmol; CCl_3COOH 150 mmol; HOAc 50 mL; Benzene 50 mL; 3 hours; N_2.

3.4.2.2f Effect of Acetic Acid Volume Fraction on Oxidation

Table 3.6 summarizes the attempts to increase the trichloroacetoxymethyl/acetoxymethyl ratio during the reaction.

Table 3.6 Effect of Acetic Acid on Oxidation

Run#	*n*-heptane (mL)	C_6H_6 (mL)	HOAc (mmol)	Mn	Mw/Mn	%Ace.	%Tri.	%Tot.
b-6	-	30	30mL	18,500	1.89	19.1	6.0	25.1
b-34	-	30	37.5	8,000	2.3	11.0	11.2	22.2
b-35	-	30	0.0	8,100	1.62	5.4	16.2	21.6
b-18	30	-	30mL	18,900	1.79	15.8	4.5	20.3
b-38	30	-	0.0	7,900	8.60	-	13.3	13.3

Reaction conditions: P4MS 2.5 mmol; $Co(OAc)_3$ 5.0 mmol; CCl_3COOH 37.5 mmol; 50 °C; 3 hours (except b-38 2 hours); N_2.

Typically, reactions were carried out in equal volumes of benzene (or heptane) and glacial acetic acid. When the acetic acid fraction was reduced to a 1:1 molar ratio relative to trichloroacetic acid (b-34), the resulting oxidized polymer contained a 1:1 molar ratio of acetoxy to trichloroacetoxy units, but with significantly reduced molecular weight (enhanced backbone cleavage). In the complete absence of acetic acid (b-35), trichloroacetoxy groups (16.2%) were predominantly introduced into the polymer side chain, with only a few percent of acetoxymethylstyrene (5.4%) derived from the cobalt(III) acetate. Again, backbone cleavage was significant. In both experiments involving small amounts of acetic acid (b-34 and b-35), a small peak appeared at 3.7-3.8 ppm in the ^1H NMR spectra. This peak is attributed to the methylene protons of *p*-benzylstyrene units formed by an the electrophilic aromatic substitution side reaction between benzyl cation and benzene cosolvent.

Using *n*-heptane as a cosolvent, similar results were obtained. In the presence of acetic acid, acetoxymethylstyrene units were introduced predominantly, and with only little backbone cleavage (b-18). In the absence of acetic acid, trichloroacetoxymethyl units were introduced predominantly, with significant backbone cleavage (b-38). No NMR signal appears at 3.7-3.8 ppm in the oxidations carried out with benzene replaced by *n*-heptane (b-18, b-38).

Table 3.6 again indicates that the acetoxymethyl/trichloroacetoxymethyl ratio varies with solvent composition. Perhaps more importantly, the presence of acetic acid can largely prevent the undesired backbone cleavage which was always observed in the CAN oxidations described in Chapter 2. If a functional polymer containing only trichloroacetoxymethyl groups is desired, the residual acetoxymethyl groups can be displaced by heating the polymer in the presence of trichloroacetic acid under vacuum at 60°C for 10 minutes. The resulting trichloroacetoxymethylated polymer shows only one benzylic proton signal at 5.25 ppm (^{1}H NMR spectrum not shown).

Conversely, if a polymer containing only acetoxymethyl groups is desired, the residual trichloroacetoxymethyl groups can be replaced by refluxing the oxidized polymer in a 3:1 mixture of acetic acid and *p*-xylene in the presence of two drops of concentrated sulfuric acid for 12 hours under nitrogen. The resulting acetoxymethylated polymer is obtained in quantitative yield, with no evidence of crosslinking. The ^{1}H NMR shows only one benzylic signal, corresponding to acetoxymethylstyrene groups.

3.4.2.3 Comparison Between CAN and Co(III) Systems

We have described two oxidation processes which can be used to introduce the same functional groups (acetoxymethyl and trichloroacetoxymethyl group). One oxidation system was cerium ammonium nitrate/glacial acetic acid- benzene/nitrogen. Another system was cobalt (III) acetate-trichloroacetic acid/glacial acetic acid-benzene/nitrogen.

For the CAN-based oxidation system, a higher reaction temperature (80°C), and a shorter reaction time (1.5-2.0 hours) were needed. This process had higher chemical yield (70- 80% based on CAN), but suffered substantial backbone cleavage (molecular weight reduced from 17,800 to about 10,000). For the Co(III)-based oxidation system, lower reaction temperatures (25 - 50°C), and a longer reaction time (3 hours) were used. This process had lower chemical yield (50% based on Co(III)), but caused on the whole little backbone cleavage. Figure 3.6 shows molecular weight decrease as function of total oxidation for both CAN and Co(III) - based oxidations. All data from Table 3.3 for Co(III) and from Table 2.3 and Table 2.4 for CAN are plotted.

For Co(III) oxidation (in presence of acetic acid), increasing the degree of oxidation causes only a small reduction in molecular weight. For Ce(IV) oxidation, increasing the degree of oxidation leads to large reduction in the molecular weight of the final product. This may be caused by the higher reaction temperatures required for CAN oxidation.

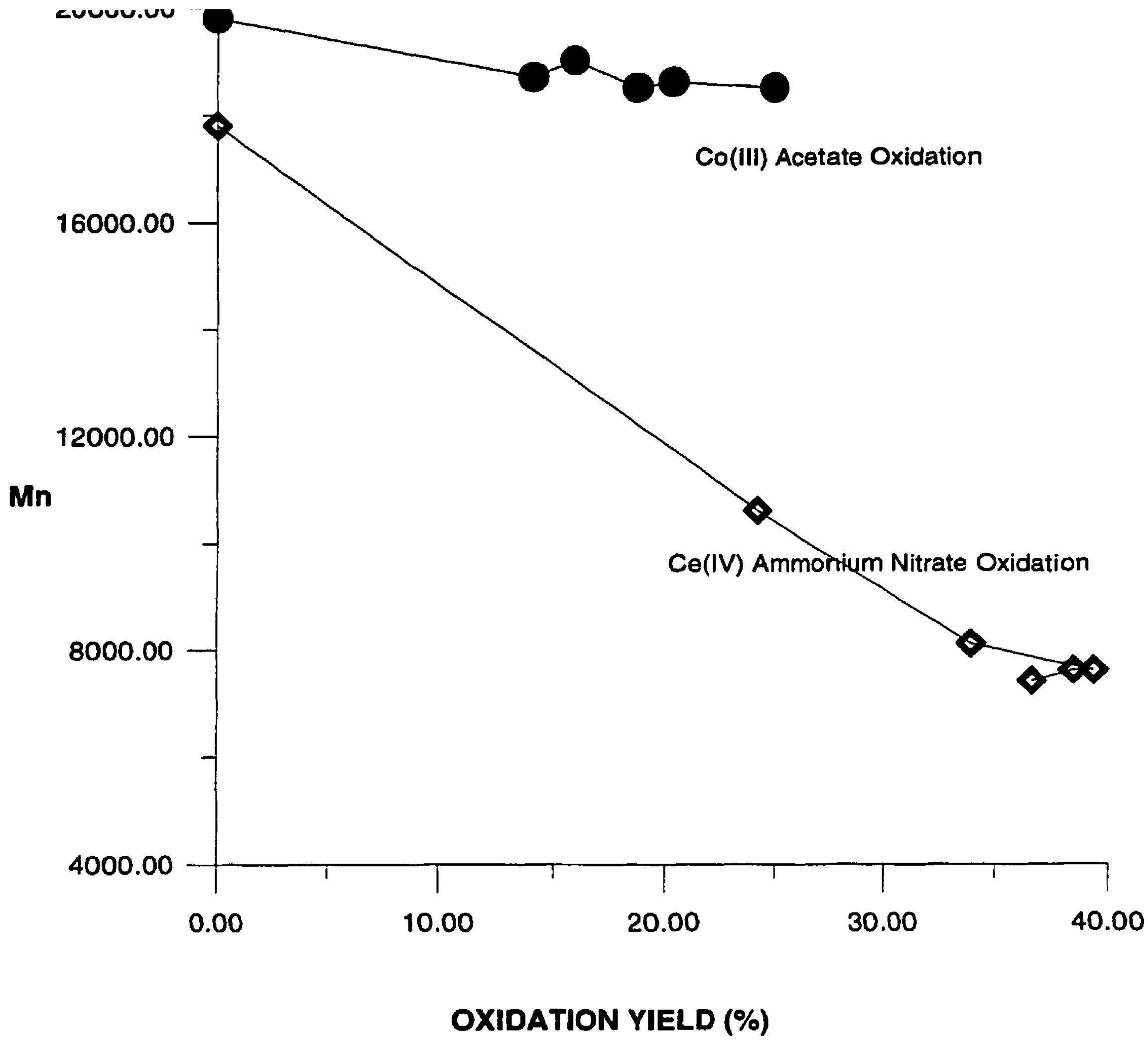


Figure 3.6 Comparison between Co(III) and Ce(IV) system

Experimental Conditions:	Co(III) acatate oxidation:	Ce(IV) oxidation:
	P4MS 2.5 mmol;	P4MS 2.5 mmol;
	$Co(OAc)_3$ 5.0 mmol;	CAN 2.5 mmol;
	CCl_3COOH 37.5 mmol;	HOAc30mL;
	HOAc 30 mL; Benzene 30 mL;	Benzene 30 mL;
	50°C; N_2.	80°C; N_2.

3.4.3 Introduction of Chloromethyl Groups into Poly(4-methylstyrene) by Cobalt)III) Acetate/Lithium Chloride/Acetic Acid-Benzene/Nitrogen

3.4.3.1 Study of Oxidation Mechanism

The selective oxidation of poly(4-methylstyrene) in the presence of a) cerium ammonium nitrate under nitrogen , and b) cobalt(III) acetate/trichloroacetic acid under nitrogen has been discussed above.[22] The oxidized polymer contain a) acetoxymethylstyrene and nitrooxymethylstyrene or b) acetoxymethylstyrene and trichloroacetoxymethylstyrene units respectively. In both cases polymeric radical cations were formed first by the transfer of an electron from the benzene ring of poly(4-methylstyrene) to Ce(IV) or Co(III), then the loss of a proton to form polymeric benzyl radicals (because the initial hydrogen abstraction favored the methyl group over the backbone methine group by about 25:1). As the oxygen was carefully excluded from the reaction system, the benzyl radicals lost an electron again to a second oxidant [Ce(IV) or Co(III)] to form benzyl cations. These polymeric benzyl cations finally reacted with any nucleophiles present in the system (acetate, trichloroacetate, and nitrate).

Now this process is extended by adding lithium chloride into the reaction system.[38] The polymeric benzyl cations should react with chloride anions (as nucleophiles) to form chloromethyl groups. The mechanism is shown in Fig 3.7:

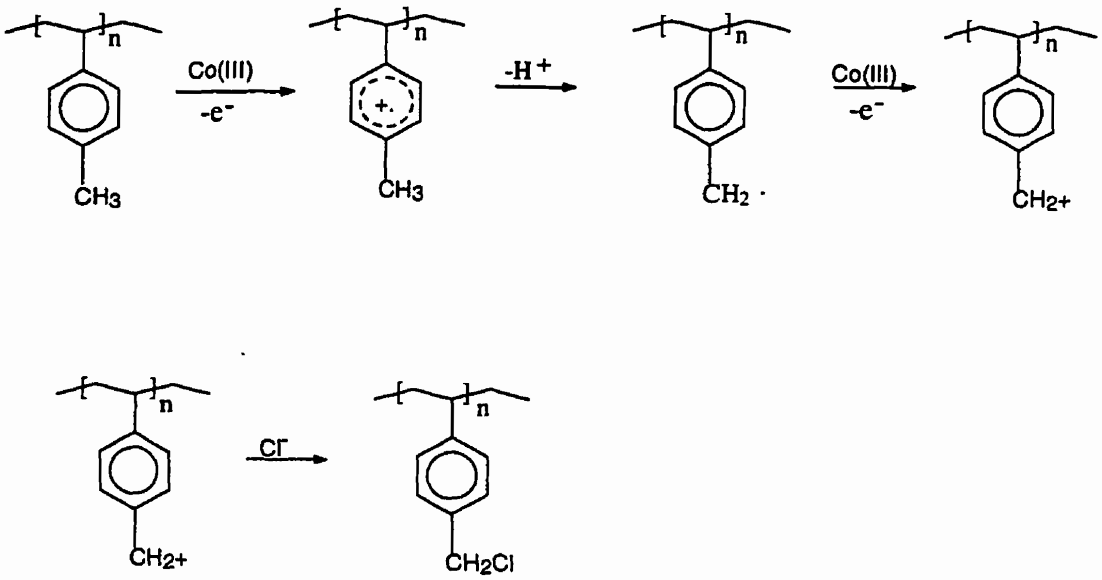


Figure 3.7 Mechanism of oxidation of poly(4-methylstyrene) by Cobalt(III) acetate/lithium chloride system

3.4.3.2 Factors Affecting the Oxidation Yield of Poly(4-methylstyrene)

3.4.3.2a Effect of Number of Moles of Lithium Chloride on Oxidation

First the effect of lithium chloride concentration on oxidation was investigated. Table 3.7 shows that with increasing lithium chloride, the oxidation yield increased. We used acetic acid/benzene cosolvents in order to increase the solubility of the lithium chloride. The solution became turbid at 30 mmol of lithium chloride due to solubility limits, and hence most of the subsequent reaction were carried out using 20 mmol of lithium chloride.

It is remarkable that while in the Co(III) oxidation described above, no oxidation reaction took place (page 91, Table 3.1) in the absence of trichloroacetic acid, the chlorination reaction described here does proceed in absence of trichloroacetic acid. These results (Table 3.7) suggest that lithium chloride, in addition to providing the nucleophile, also acts as reaction catalyst or promoter. Plausibly, like trichloroacetic acid, it converts the inactive Co(III) dimer species into a more active species. This activation may either involve lithium cations acting as Lewis acid, or chloride anions acting as cobalt ligands. In either case, this activating function of lithium chloride can explain the increasing chlorination yield with increasing salt concentration. No oxidation product other than chloromethyl groups were observed, in particular no aldehyde nor carboxylic acid.

Table 3.7 Effect of Lithium Chloride Concentration on Oxidation

Run#	LiCl (mmol)	Mn	Mw/Mn	%-$ClCH_2$
7	7.0	16,500	2.05	1.3
10	15	16,900	1.79	12.5
8	20	17,000	1.92	12.4
9	30	14,200	1.93	21.2

Reaction Conditions: P4MS 2.5 mmol; $Co(OAc)_3$ 5 mmol; HOAc 15 mL; Benzene 15 mL; N_2; 50°C; 2 hrs.

3.4.3.2b Effect of Cobalt (III) Acetate on Oxidation

The effect of the molar ratio of cobalt acetate/poly(4-methylstyrene) on oxidation was investigated below. Table 3.8 shows that the oxidation yield increased with cobalt acetate concentration.

Table 3.8 Effect of Cobalt (III) Acetate Moles on Oxidation

Run#	$Co(OAc)_3$ (mmol)	P4MS	LiCl (mmol)	Mn	Mw/Mn	%-$ClCH_2$
13	0.5	2.5	20	17,400	1.85	0.7
12	1.0	2.5	20	16,200	1.89	1.9
11	2.5	2.5	20	15,600	1.89	8.0
8	5.0	2.5	20	17,000	1.92	12.4
14	10	2.5	20	17,000	1.89	13.8

Reaction Conditions: HOAc: 15 mL; Benzene: 15 mL; N_2; 50°C; 2 hours.

3.4.3.2c Effect of Reaction Time on Oxidation

The effect of reaction time on oxidation was also investigated. From the results shown in Table 3.9, the oxidation was found to continue more slowly after the reaction had proceeded for two hours, and with enhanced backbone cleavage. The oxidation should therefore be limited to two hours duration.

Table 3.9 Effect of Reaction Time on Oxidation

Run#	Reaction Time(Hrs)	P4MS	LiCl (mmol)	$Co(OAc)_3$	Mn	Mw/Mn	%-$ClCH_2$
15	1.0	2.5	20	5.0	16,400	1.81	6.4
8	2.0	2.5	20	5.0	17,000	1.92	12.4
16	3.0	2.5	20	5.0	13,600	1.94	14.7
17	5.0	2.5	20	5.0	11,900	2.12	16.5

Reaction Conditions: HOAc: 15 mL; Benzene: 15 mL; N_2; 50°C;

3.4.3.2d Effect of Reaction Temperature on Oxidation

Table 3.10 indicates the effect of reaction temperature on oxidation. When the reaction temperature was changed from 35°C to 60°C, the oxidation yield remained almost the same. When the reaction temperature was raised from 60°C to 70°C or 80°C, the oxidation yield increased. At these higher temperatures, significant backbone cleavage was found to occur.

Table 3.10 Effect of Reaction Temperature on Oxidation

Run#	Reaction Temp.(°C)	P4MS	$Co(OAc)_3$ (mmol)	LiCl	Mn	Mw/Mn	%-$ClCH_2$
19	35	2.5	5.0	20	16,700	1.91	15.8
8	50	2.5	5.0	20	17,000	1.92	12.4
20	60	2.5	5.0	20	12,400	2.06	14.7
21	70	2.5	5.0	20	9,600	2.45	20.1
22	80	2.5	5.0	20	9,600	2.26	18.5

Reaction Conditions: HOAc: 15 mL; Benzene: 15 mL; N_2; 2 hours.

3.4.3.2e Effect of Cosolvent on Oxidation

Finally, the effect of co-solvents on oxidation was studied. It was found that benzene was a good solvent, but with methylethylketone or *n*-heptane as cosolvents, oxidation of the polymers did not occur.

Table 3.11 Effect of Cosolvent on Oxidation

Run#	Cosolvent	Mn	Mw/Mn	%-$ClCH_2$
8	benzene	17,000	1.92	12.4
23	MEK	19,000	1.80	-
24	n-heptane	18,000	1.77	-

Reaction Conditions: P4MS 2.5 mmol; $Co(OAc)_3$ 5.0 mmol; LiCl 20 mmol; HOAc 15 mL; Cosolvent 15 mL; N_2; 50°C; 2 hours.

3.5 CONCLUSIONS

The selective oxidation of poly(4-methylstyrene) with cobalt(III) acetate in glacial acetic acid under nitrogen in presence of different nucleophiles leads to different functional polymers.

In the presence of nitrogen, cobalt (III) acetate in glacial acetic acid/benzene was used as the oxidizing system. The oxidation reaction proceeds through initial electron transfer followed by proton loss to form transient polymeric benzyl radicals. Because of the absence of oxygen, these radicals transfer a second electron to the oxidant to form polymeric benzyl cations. These can react with any nucleophiles present in the reaction system. Additionally, either trichloroacetic acid or lithium chloride were required to activate the Co(III) complex, and give acceptable oxidative yields..

If acetic acid and trichloroacetic acid present in the reaction system, up to 25% of total oxidation yield (acetoxymethyl group and trichloroacetoxymethyl group) was obtained. These oxidation reactions were run for three hours, and at low temperature (50°C). The two resulting functional groups could be converted into each other.

In the presence of lithium chloride, up to 21% of chloromethyl group could be introduced into poly(4-methylstyrene). These oxidation reactions were run for two hours, and also at low temperature (50°C). For both oxidation processes, the oxidized polymers suffer little molecular weight reduction (backbone cleavage). Both processes were clean oxidations, allowing controlled introduction of functional groups into the polymers.

The oxidation mechanism for both methods shares the first overall step, electron loss plus proton loss, or hydrogen loss, with the CAN/nitrogen system described in chapter 2. After benzyl radicals form, a second electron is transferred to oxidant to form polymeric benzylic cations. These cations immediately react with nucleophiles present in the system. In this way the acetoxymethyl, trichloroacetoxymethyl, and chloromethyl functional groups could be introduced into poly(4-methylstyrene) in a practical manner.

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CHAPTER 4

MECHANISM OF POLY(4-METHYLSTYRENE) BACKBONE DEGRADATION BY CERIC AMMONIUM NITRATE (CAN)

4.1 GENERAL INTRODUCTION OF POLYMER DEGRADATION

Polymer degradation reactions may be broadly classified according to the form in which energy is transmitted to the polymer to cause bond breaking in the backbone. The most important forms of energy in this regard are thermal, oxidative, chemical, and mechanical energy.[1,2]

4.1.1 Thermal Degradation

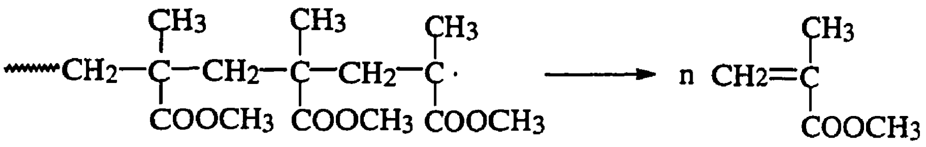
Thermal degradation of polymer can be divided into three types: random degradation, depolymerization (chain degradation), and a combination of both.[3]

(1). In random depolymerization, rupture takes place at random points along the chain, leaving fragments which can be considered large by comparison to monomer units.

(2). Depolymerization proceeds by successive release of monomer units from the chain ends. This reaction is the opposite of propagation in addition polymerization, and is hence also referred to as depropagation.

(3). Both reactions may occur simultaneously, with the random backbone cleavage, serving as initiation sites for depolymerization.

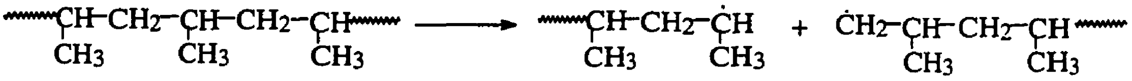
In an example for the second case, poly(methyl methacrylate) can be degraded almost quantitatively back to the monomer by heat, with depolymerization occurring from the terminal sites, with the result that molecular weight decreases slowly in proportion to volatilization. [4,5,6,7,8]



$$\sim CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}\cdot \longrightarrow n\ CH_2=\underset{COOCH_3}{\overset{CH_3}{C}}$$

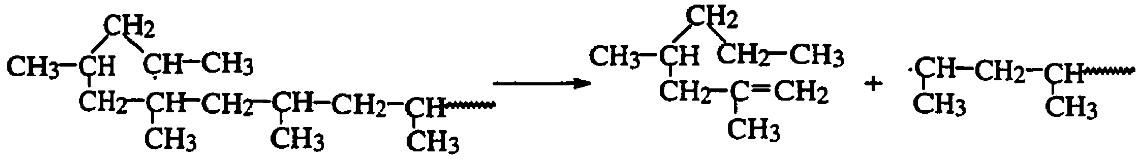
On the other hand, polyethylene and polypropylene decompose randomly into longer olefinic fragments, while actually yielding little monomer. At the same time, the molecular weight decreases rapidly, with only a small amount of volatilization taking place.[9,10,11,12]

The thermal degradation of polypropylene in the absence of oxygen proceeds as follows:

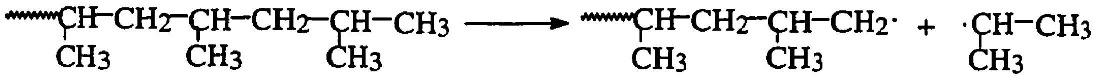


$$\sim\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}\sim \longrightarrow \sim\underset{CH_3}{CH}-CH_2-\underset{CH_3}{\dot{C}H} + \dot{C}H_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}\sim$$

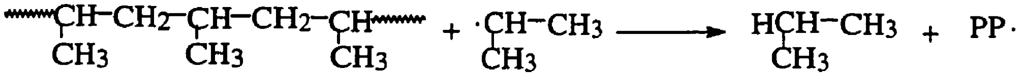
Here, weaker links such as secondary - tertiary C-C bonds, are believed to be the major sites for degradation initiation. The secondary radicals which are formed then undergo intramolecular chain transfer reactions as follows:



Saturated hydrocarbons can also be formed by scission at the chain end which is then followed by hydrogen abstraction to form propane and another propylene radical.

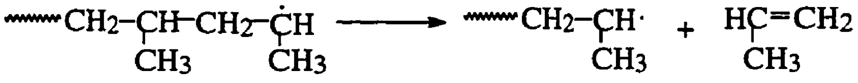


$$\sim\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_3 \longrightarrow \sim\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2\cdot + \cdot\underset{CH_3}{CH}-CH_3$$



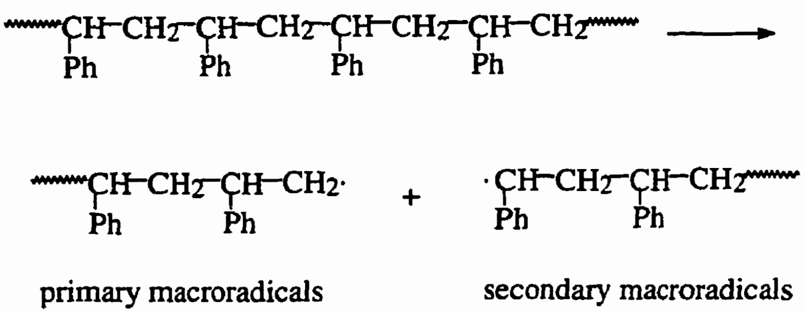
$$\sim\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}\sim + \cdot\underset{CH_3}{CH}-CH_3 \longrightarrow H\underset{CH_3}{C}H-CH_3 + PP\cdot$$

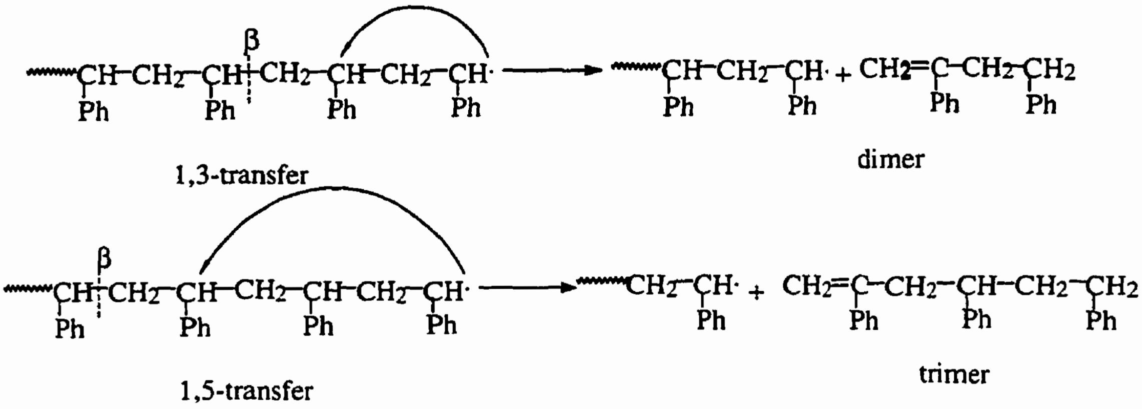
Other longer chain saturated products are presumed to be formed by a similar mechanism. Depolymerization can also occur by β-fragmentation of a C-C bond from a secondary radical.



$$\sim CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{\dot{C}H} \longrightarrow \sim CH_2-\underset{CH_3}{CH}\cdot + H\underset{CH_3}{C}=CH_2$$

For polystyrene, both random scission and depolymerization take place. The thermal degradation of polystyrene, probably starts out as a random fragmentation process, but soon involves depolymerization, hydrogen transfer and β-scission. The main observed products of thermal degradation of polystyrene are monomer, dimer, trimer, and other volatile materials,[13,14,15,16,17,18] as illustrated below.





The initially formed macroradicals mainly depolymerize to form monomer. In addition, the macroradicals can engage in hydrogen abstraction. However, the dimer and trimer cannot be formed through any transfer reaction of the primary radicals. Thus the primary macroradical undergoes almost quantitatively depolymerization. The formation of the dimer and trimer has been interpreted by intermolecular 1,3- and 1,5- transfer from the terminal group of the secondary macroradical to the reactive tertiary carbon, followed by β-scission.

4.1.2 Autoxidation Degradation

The oxidation of organic compounds with atmospheric oxygen is often termed autoxidation, because the rate of the reaction almost always shows an autoacceleration. The rate and course of an autoxidation reaction are both strongly affected by light, heat, oxygen concentration, moisture and the presence of trace impurities which can be act as either catalysts or inhibitors (antioxidants). Oxidation reactions are free radical in mechanism, and as such, each oxidation reaction has separate initiation, propagation, and termination steps.

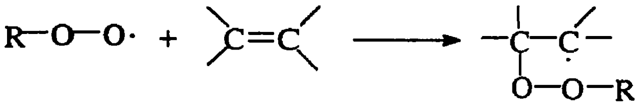
Oxygen is a diradical in the ground state, and in the presence of free radicals, its reaction with polymer RH is the following:[19,20,21,22]

Initiation: The formation of polymer radicals may be induced by UV radiation, ionizing radiation, temperature, ultrasonic energy, residual initiator, and oxygen.

Propagation: a polymer radical R• reacts with O_2, to start chain propagation.

$$R\cdot + O2 \xrightarrow{kp1} R{-}O{-}O\cdot \xrightarrow[kp2]{RH} R\cdot + R{-}O{-}OH$$

or a radical may react with compounds containing a double bond

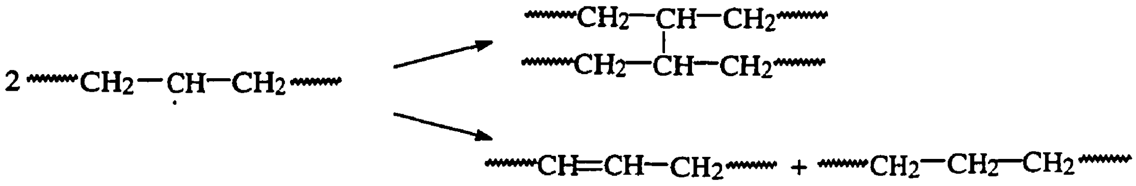


Termination:

$$R\cdot + R\cdot \xrightarrow{kt_1} R\text{-}R$$

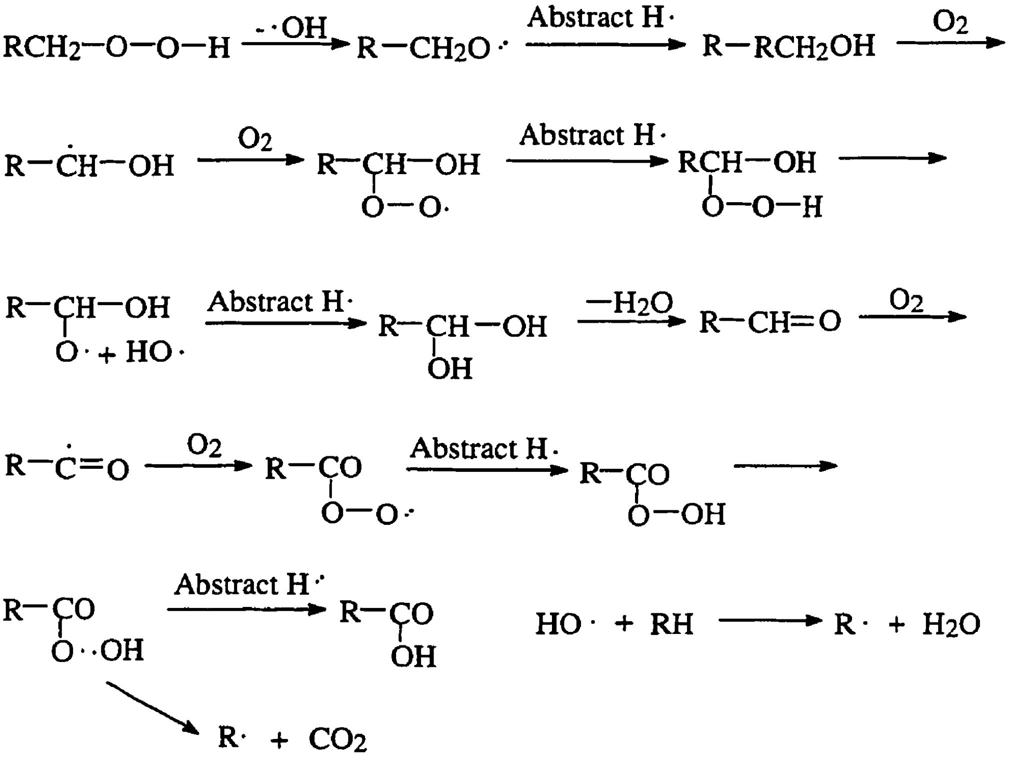
$$R\cdot + R{-}O{-}O\cdot \xrightarrow{kt_2} R\text{-}O\text{-}O\text{-}R$$

For example, two carbon radicals can terminate in two ways: coupling and disproportionation.



$$2\ \sim CH_2{-}\dot{C}H{-}CH_2\sim \;\rightarrow\; \sim CH_2{-}CH{-}CH_2\sim \,/\, \sim CH_2{-}CH{-}CH_2\sim \quad ; \quad \rightarrow\; \sim CH{=}CH{-}CH_2\sim + \sim CH_2{-}CH_2{-}CH_2\sim$$

R-O-O-H produced in these reactions is not stable: it undergoes a series of reactions to become an aldehyde, or a carboxylic acid, CO_2, and H_2O.[23]



$$RCH_2{-}O{-}O{-}H \xrightarrow{-\cdot OH} R{-}CH_2O\cdot \xrightarrow{\text{Abstract H}\cdot} R{-}RCH_2OH \xrightarrow{O_2}$$

$$R{-}\dot{C}H{-}OH \xrightarrow{O_2} R{-}CH(O{-}O\cdot){-}OH \xrightarrow{\text{Abstract H}\cdot} RCH(O{-}O{-}H){-}OH \longrightarrow$$

$$R{-}CH(O\cdot){-}OH + HO\cdot \xrightarrow{\text{Abstract H}\cdot} R{-}CH(OH){-}OH \xrightarrow{-H_2O} R{-}CH{=}O \xrightarrow{O_2}$$

$$R{-}\dot{C}{=}O \xrightarrow{O_2} R{-}CO(O{-}O\cdot) \xrightarrow{\text{Abstract H}\cdot} R{-}CO(O{-}OH) \longrightarrow$$

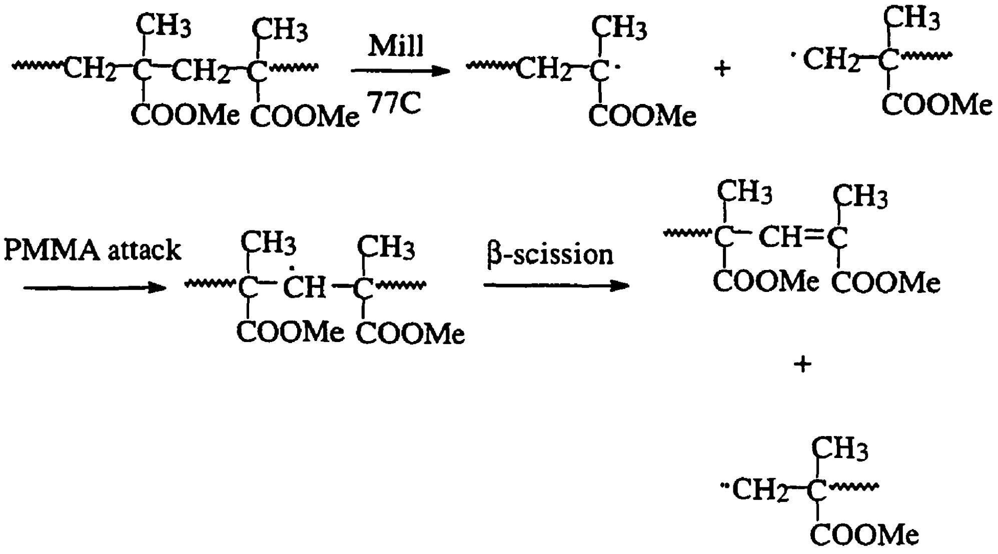
$$R{-}CO(O\cdot\cdot OH) \xrightarrow{\text{Abstract H}\cdot} R{-}CO(OH) \qquad HO\cdot + RH \longrightarrow R\cdot + H_2O$$

$$R{-}CO(O\cdot\cdot OH) \rightarrow R\cdot + CO_2$$

The autoxidation degradation of polymers occurs by reaction with atmospheric oxygen, usually at elevated temperature. This oxidation can occur at all stages from synthesis, through use, to recycling, causing undesirable changes in mechanical, aesthetic, and electrical properties. Commercial polymer products contain a certain amount of antioxidants, which are used to protect the polymer against autoxidative degradation. For example, hindered phenols, aromatic amines, hindered amines, and divalent sulfur derivatives are commonly used and efficient antioxidants.[24]

4.1.3 Mechanical Degradation

Mechanical degradation of polymers has been studied extensively.[25,26,27,28,29] Electron-spin resonance spectroscopy has graphically demonstrated that stretching, grinding, milling, and any type of polymer shearing process, produces free radicals as a result of main chain fracture.[30] In the absence of oxygen, various carbon radicals are generated from polyolefins or poly(methyl methacrylate).[31] These attack other polymer chains and lead to further scission reactions through radical rearrangements. Shearing force could lead to the degradation of the polymer.



During mechanical degradation, the molecular weight of a polymer decreases with time as illustrated in Figure 4.1:[32]

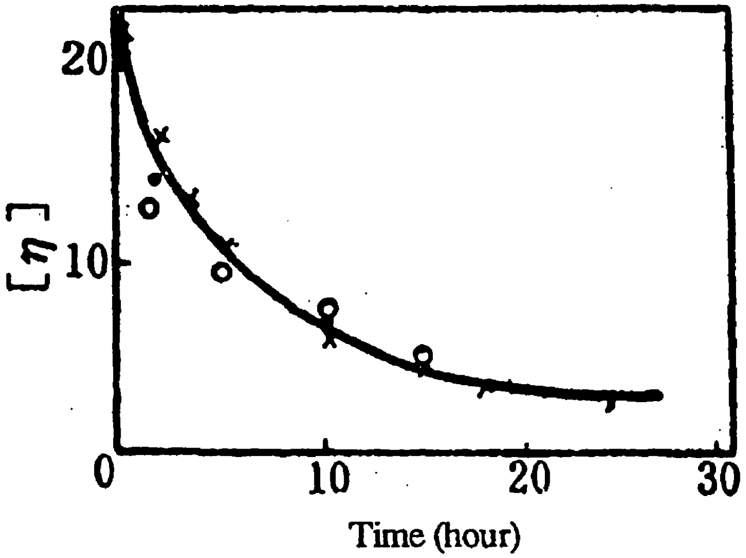


Figure 4.1 The relationship of intrinsic viscosity of polystyrene and grinding time at different temperature.

× - 20°C; º - 40°C; • - 60°C;

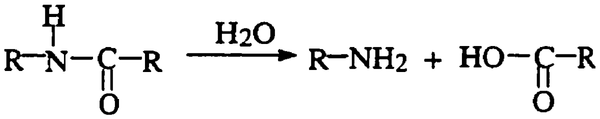
Figure 4.1 shows the relationship of the intrinsic viscosity of polymer with grinding time. It indicates that there is more effect on polymers with higher molecular weight during mechanical degradation. At the beginning, the rate of degradation is very fast. However, when the molecular weight of the polymer goes down to a certain lower limit, there is no further reaction. This limiting molecular weight is 7000 for polystyrene, 4000 for poly(vinyl chloride), 9000 for poly(methyl methacrylate), and 11000 for poly(vinyl acetate). In addition, the degradation rate is independent of temperature (in the experimental temperature range -20 - 60°C), and indicates the activation energy of mechanical degradation in this temperature range is zero. In the presence of oxygen or air, the oxygen accelerates the degradation of polymers during mechanical degradation.

Mechanical degradation has been utilized for processing natural rubber since the middle of the 19th century, with mastication usually being carried out on roll molls. In the presence of air, it leads to a marked decrease in the average molecular weight, thus increasing the natural rubber's plasticity.[33]

Mixing two polymers under high shear can lead to block copolymers.[34,35] A typical example is the graft synthesis caused by vibromilling poly(methyl methacrylate) in the presence of gaseous vinyl chloride at 25°C for 12 hours.

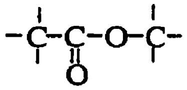
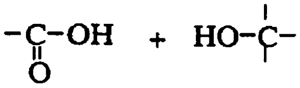
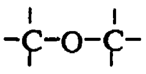
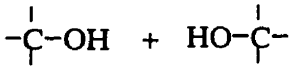
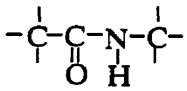
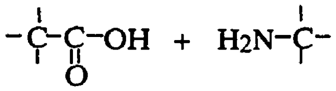
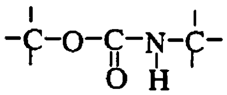
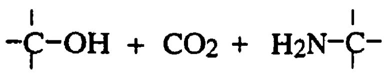
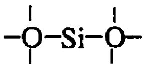
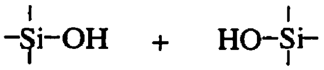
4.1.4 Chemical Degradation

Chemical degradation is the process in which polymers degrade by chemical reagents besides oxygen. In general, polyethylene, polypropylene, and other saturated hydrocarbon polyolefins are stable to chemical reagents except under thermal, autoxidation, and mechanical degradation. However, polymers containing heteroatoms are sensitive to chemical reagents. Degradation reactions involving water (hydrolysis) are the most important and those polymers that are synthesized by condensation reactions are particularly susceptible to hydrolysis. Random scission of bonds along the backbone chain can occur, as in:



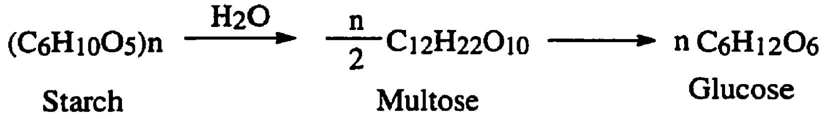
$$R-\overset{H}{\overset{|}{N}}-\underset{\underset{O}{\|}}{C}-R \xrightarrow{H_2O} R-NH_2 + HO-\underset{\underset{O}{\|}}{C}-R$$

Table 4.1 Hydrolysis of linear polymers (typical examples)[36]

Main Chain Linkage under Attack	Products of Hydrolysis	Examples
 $-\overset{\vert}{\underset{\vert}{C}}-\underset{\underset{O}{\Vert}}{C}-O-\overset{\vert}{\underset{\vert}{C}}-$ carboxylic acid ester	 $-\underset{\underset{O}{\Vert}}{C}-OH + HO-\overset{\vert}{\underset{\vert}{C}}-$	polyester
 $-\overset{\vert}{\underset{\vert}{C}}-O-\overset{\vert}{\underset{\vert}{C}}-$ ether, glycoside	 $-\overset{\vert}{\underset{\vert}{C}}-OH + HO-\overset{\vert}{\underset{\vert}{C}}-$	polyether, polysaccharides (cellulose, amylose, atc.)
 $-\overset{\vert}{\underset{\vert}{C}}-\underset{\underset{O}{\Vert}}{C}-\underset{\underset{H}{\vert}}{N}-\overset{\vert}{\underset{\vert}{C}}-$ amides (peptides)	 $-\overset{\vert}{\underset{\vert}{C}}-\underset{\underset{O}{\Vert}}{C}-OH + H_2N-\overset{\vert}{\underset{\vert}{C}}-$	polyamides, proteins, polypeptides
 $-\overset{\vert}{\underset{\vert}{C}}-O-\underset{\underset{O}{\Vert}}{C}-\underset{\underset{H}{\vert}}{N}-\overset{\vert}{\underset{\vert}{C}}-$ urethane	 $-\overset{\vert}{\underset{\vert}{C}}-OH + CO_2 + H_2N-\overset{\vert}{\underset{\vert}{C}}-$	polyurethanes
 $-\overset{\vert}{\underset{\vert}{O}}-Si-\overset{\vert}{\underset{\vert}{O}}-$ siloxane	 $-\overset{\vert}{\underset{\vert}{Si}}-OH + HO-\overset{\vert}{\underset{\vert}{Si}}-$	polydialkylsiloxanes

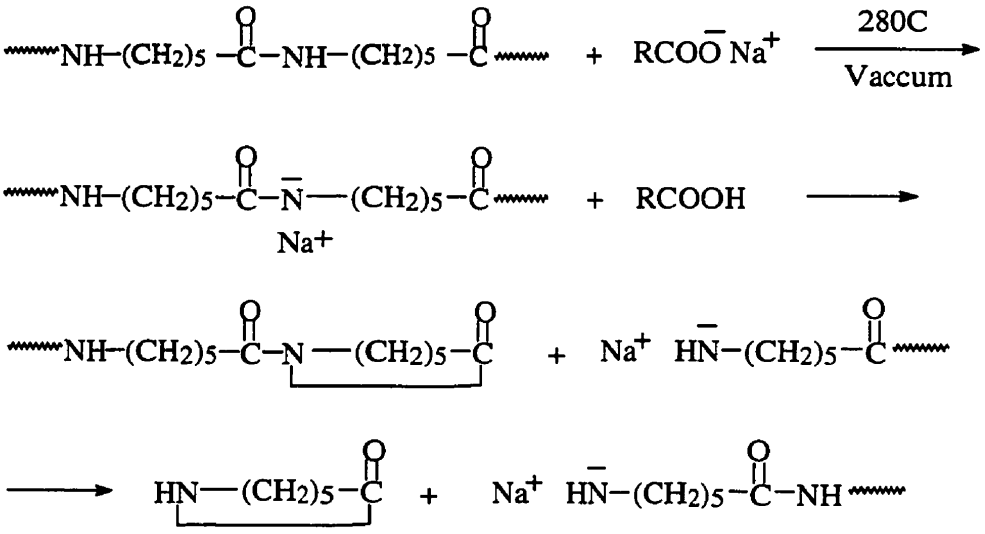
Poly(methyl methacrylate) on the other hand, is an additional-type polymer which undergoes hydrolytic degradation without chain scission, the reaction taking place at the ester bond on substituent groups.[37] Hydrolysis may be catalyzed by either acids or bases, and additional catalysis may come from with the polymer as a result of accompanying thermal oxidation.

For example, acid hydrolysis of natural polyacetal (starch) provides glucose.



$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} \xrightarrow{H_2O} \underset{\text{Multose}}{\frac{n}{2}C_{12}H_{22}O_{10}} \longrightarrow \underset{\text{Glucose}}{n\,C_6H_{12}O_6}$$

Heterochain polymers containing amide, ester, carbonate, urethane, and urea linkage undergo a catalyzed thermal decomposition in the presence of alkali metal salts. For example, the depolymerization of nylon-6 is strongly catalyzed by 1-2 wt% sodium and potassium salts to give a high yield of caprolactam.



In addition to the above types of degradation, other effects also can cause a polymer to degrade, such as radiation.

4.2 AIM OF THE RESEARCH

In above chapters[38,39] the selective functionalization of poly(4-methylstyrene) by three different oxidation systems is described, namely: ceric ammonium nitrate, cobalt(III) acetate/trichloroacetic acid, and cobalt(III) acetate/lithium chloride. For all of these systems, a mixture of organic solvent/glacial acetic acid was used as a cosolvent, and oxygen was excluded. Poly(4-methylstyrene) was selectively oxidized and up to 40% of the 4-methyl groups were converted into acetoxymethyl/nitrooxymethyl, acetoxymethyl/trichloroacetoxymethyl, and chloromethyl groups respectively. It was found that during oxidation, competitive backbone cleavage occurred through the oxidation of the benzylic backbone carbon. This key problem reduced the molecular weight of oxidized polymers, severely limiting the use of this procedure with block copolymers of 4-methylstyrene. There is therefore a need to investigate both what is happening to the polymer chain during oxidation by i.e. ceric ammonium nitrate, and how to minimize this undesired side reaction.

The purpose of this research is to study the degradation of poly(4-methylstyrene) during ceric ammonium nitrate oxidation in presence of nitrogen and oxygen, and to propose mechanisms of poly(4-methylstyrene) backbone degradation in both systems.

First, poly(4-methylstyrene) of different molecular weights was synthesized by anionic living polymerization using *sec*-butyl lithium as initiator, and heptane as solvent.

The relationship between degradation, oxidation time, and selective functionalization of poly(4-methylstyrene) of low molecular weight by a cobalt (III) acetate-lithium chloride oxidation system was studied, to provide evidence for the lack of detected backbone cleavage of these low molecular weight polymers. Next, the main chain's susceptibility to ceric ammonium nitrate oxidation for poly(4-methylstyrene) and polystyrene was compared. Finally, degradation mechanisms for poly(4-methylstyrene) with ceric ammonium nitrate oxidation under oxygen and nitrogen atmospheres were proposed.

4.3 EXPERIMENTAL METHODS

4.3.1 Materials and Their Purification

Ceric ammonium nitrate (CAN), *sec*-butyl lithium (1.3M solution in cyclohexane), benzene, and glacial acetic acid were purchased from Aldrich and used as received. 4-Methylstyrene was purchased from Aldrich and passed neat through a column of alumina to remove inhibitors prior to polymerization. 2,2'-Azobis-isobutyronitrile (AIBN) was purchased from Kodak and used as received. Polystyrene was prepared by anionic polymerization by Rhonda Whittaker in our group as described below. *n*-Heptane was purchased from Aldrich, and dried as described as in the procedure below.

Heptane (600 mL) and 500 mL of concentrated sulfuric acid were placed in a 1000 mL round bottomed flask with magnetic stirring. The mixture was stirred for two days, and then poured into a separating funnel. The top layer (heptane layer) was washed ten times with 400 mL of distilled water, and tested to a have neutral pH. It was then washed with concentrated aqueous sodium hydroxide solution, and separated. The heptane was transferred into a round bottomed flask. Calcium hydride was added to the flask and the heptane was distilled twice under nitrogen. The collected heptane was poured into another 1000 mL flask fitted with a condenser and nitrogen inlet and containing Na-K alloy. The heptane was refluxing overnight.

4.3.2 Anionic Polymerization of 4-Methylstyrene

Dried heptane 50 mL was injected into a 250 mL polymerization bottle (clean, dry, sealed with a rubber cap, and filled with dry nitrogen). *sec*-Butyl lithium (3.70 mL) was added to the polymerization bottle by syringe, and the bottle was shaken vigorously. Then 10 mL of 4-methylstyrene was injected and the bottle was shaken again. The reaction bottle was then placed in a water bath at 50°C for two hours during whole time, the colour of the solution became deep red. Methanol (5 mL) was added to terminate the polymerization reaction, and the viscous liquid was dropped into methanol in a dry-ice bath. The precipitate was dissolved in tetrahydrofuran and reprecipitated into methanol to give a white powder solid (8.8 g, 95%).

All of the poly(4-methylstyrene) used in this project was made by this anionic polymerization procedure, and had narrow molecular weight distributions (1.09 ± 0.02).

4.3.3 Determination of Relationship between Molecular Weight and Reaction Time in the CAN System

Poly(4-methylstyrene) (0.296 g, 2.5 mmol) was dissolved in a mixture of 30 mL benzene and 30 mL glacial acetic acid in a 100 mL three-neck round-bottom flask fitted with a condenser, a nitrogen inlet, and a thermometer reaching below the liquid level. After nitrogen was passed through the system for 10 minutes and the temperature was raised to 80° C, 1.37 g (2.5 mmol) of ceric ammonium nitrate (dried at 85°C for 1 hour and stored in a desiccator) was added to the flask all at once. During the reaction, after 0.5, 1.0, 1.5, 2.0, and 4.0 hours, 7 mL aliquots of solution (containing dispersed solid) were withdrawn by syringe. Benzene was removed by a rotary evaporator at reduced pressure, and the remaining solution of oxidized polymer and ceric salts in acetic acid was precipitated into a mixture of methanol and water (4:1 v/v). The white precipitate was filtered, washed with a 4:1 mixture of methanol and water, and dried under vacuum at 60°C overnight. The molecular weight of the oxidation products were determined by size exclusion chromatography.

4.3.4 CAN Oxidation of the Mixture of Poly(4-methylstyrene) and Polystyrene

Poly(4-methylstyrene) 0.148 g (1.25 mmol) and polystyrene 0.130 g (1.25 mmol) were dissolved in a mixture of 30 mL glacial acetic acid and 30 mL benzene (or other organic cosolvent as noted) in a 100 mL three-neck flask fitted with a condenser, a nitrogen inlet, magnetic stirring, and a thermometer reaching below the liquid level. The temperature was raised to 80°C, and 1.37 g (2.5 mmol) of ceric ammonium nitrate (dried at 85°C for 1 hour and stored in a dessicator) was added to the flask all at once. During the reaction, the color of the solid changed from orange to light yellow or colourless, and the color of the solution changed from yellow to pale yellow. After three hours the reaction mixture was cooled and filtered, and the benzene component was removed on a rotary evaporator at reduced pressure. The remaining solution of oxidized polymer and ceric salts in acetic acid was precipitated into 200 mL of a mixture of methanol and water (4:1 v/v). After standing overnight, the white precipitate was filtered, washed with a 4:1 methanol/water mixture, and dried under vacuum at 60°C overnight.

4.3.5 Chlorination of Low Molecular Weight Poly(4-methylstyrene) by Cobalt(III) Acetate-Lithium Chloride Oxidation

Poly(4-methylstyrene) 0.296 g (2.5 mmol) and lithium chloride 0.848 g (20 mmol) were dissolved in a mixture of 15 mL glacial acetic acid and 15 mL benzene in a 100 mL three-neck round bottom flask fitted with a condenser, a nitrogen inlet and a thermometer reaching below the liquid level. The temperature was raised to 50°C, and cobalt acetate 1.18 g (5.0 mmol) solid was added to the flask all at once. During the reaction, the color of the solution was dark green. After two hours the reaction mixture was cooled, filtered, and the benzene component was removed on a rotary evaporator at reduced pressure. The remaining solution of oxidized polymer and cobalt salt in acetic acid was precipitated into 200 mL of a mixture of methanol and water (4 : 1 v/v). After standing overnight, the white precipitate was collected by filtration, washed with 4:1 methanol/water, and dried under vacuum at 60°C overnight.

4.3.6 Characterization of Functional Polymers

The characterization of functional poly(4-methylstyrene) was carried out by nuclear magnetic resonance (NMR), infrared (IR) and size exclusion chromatography (SEC), and elemental analysis (EA) as described in Chapter 2.2.

4.4 RESULTS AND DISCUSSION

4.4.1 Anionic Polymerization of 4-Methylstyrene

There are several polymerization procedures to synthesize macromolecules, such as anionic, cationic, radical, and condensation polymerizations. Throughout this thesis, all polymers were made by radical polymerization processes except those made in this chapter. Living anionic polymerization was the method used to prepare the polymers described in this chapter. The most outstanding feature of homogeneous living anionic polymerization is the absence of significant chain termination. This enables the following control in the synthesis of polymers:

(i) predictable molecular weight through control of initiator/monomer ratio;

(ii) narrow molecular weight distributions through proper adjustment of initiation versus propagation kinetics;

(iii) synthesis of true block copolymers by sequential addition of different monomers to the living polymer chains; and

(iv) formation of polymers with functional end groups by selective termination with appropriate reagents.

It is generally accepted that the anionic mechanism applies to those chain addition polymerizations in which the growing chain has a negative charge (real or formal), and these are initiated by bases of varying base strength. Organolithium bases are currently most widely used. One advantage is that organolithium species are soluble in both polar and nonpolar solvents, while higher organoalkali compounds generally require ethers as a solvent. *Sec*-butyl lithium was used as initiator in the present work, because of its higher reactivity compared with *n*-butyl lithium. Heptane was a good solvent for *sec*-butyllithium, 4-methylstyrene, and poly(4-methylstyrene).

The number-average degree of polymerization for a living anionic polymer is given simply by the ratio of the concentration of monomer and living ends

$$Xn = [M]/[M^-] \tag{1}$$

For the usual situation where all of the catalyst is converted into propagating anionic ends,

$$Xn = 2[M]/[C] \tag{2}$$

or

$$Xn = [M]/[C] \tag{3}$$

depending on the mode of initiation. Our initiation process involved one polymer molecule per catalyst molecule and Eq. 3 is applicable. Polymers with a desired molecular weight can be synthesized by controlling both concentration of monomer and initiator. For example:

Table 4.2 Anionic Polymerization of 4-Methylstyrene by *s*-Butyl Lithium

Run#	*s*-Butyl Li (mL)	4MS (mL)	Mn (Des.)	Mn (Expt.)	Mw/Mn
75	0.69	10	10,000	9,300	1.10
79	1.38	10	5,000	5,400	1.07
84	3.45	10	2,000	2,100	1.10
81	6.90	10	1,000	1,000	1.11

Experimental Conditions: Heptane 50 mL; 50°C, water bath.

Table 4.2 indicates that poly(4-methylstyrene) was successfully prepared by anionic polymerization. The number-average molecular weight of the polymers made matched reasonably the desired value, and the molecular weight distribution of the polymers was narrow. These poly(4-methylstyrene)s were used to study the mechanism of backbone cleavage of polymers by ceric ammonium nitrate.

4.4.2 Degradation of Poly(4-methylstyrene) in the Presence of Oxygen (CAN-Trichloroacetic Acid/Oxygen System)

In chapter 2, aldehyde groups were selectively introduced into poly(4-methylstyrene) by a ceric ammonium nitrate-trichloroacetic acid/oxygen system. The degree of oxidation to aldehyde could be controlled, and polymers containing up to 9.5% aldehyde were easily obtained. However, during the oxidation, polymer backbone cleavage occurred as well.

For the ceric ammonium nitrate/oxygen system, the effect of reaction time on oxidation in Chapter 2, Table 2.8 shows that the molecular weight decreased with increasing reaction times. The molecular weight of the starting polymer was 16,800, but after two hours of oxidation, the molecular weight reduced to 8,100, just half of the molecular weight of the starting polymer. Also, the effect of reaction temperature on oxidation (Chapter 2 Table 2.9) shows that the higher the reaction temperature, the larger the reduction in molecular weight.

When poly(4-methylstyrene) was functionalized by ceric ammonium nitrate-trichloroacetic acid/oxygen, degradation of the polymer chain always took place. It is proposed that the mechanism of the degradation of the polymer followed the steps:

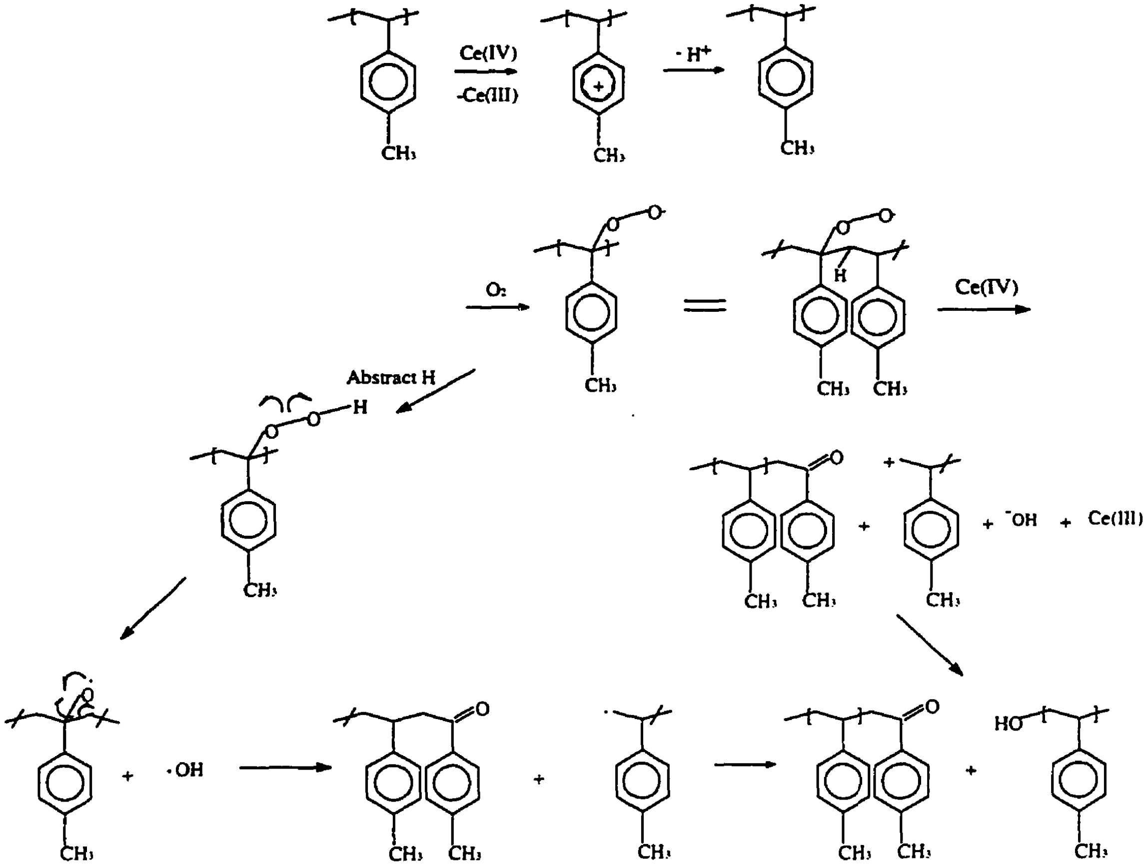


Figure 4.2. Degradation mechanism of poly(4-methylstyrene) by CAN/oxygen

The first step of this process involves electron transfer from the benzene ring to CAN(IV), and leads to the formation of a polymeric radical cation. This rapidly loses a proton from either the primary methyl group or the tertiary methine group (backbone) and forms the corresponding benzylic radical. The former leads to functionalization of poly(4-methylstyrene), the latter leads to the degradation of the backbone. Once the tertiary benzylic radical forms, it will be quenched immediately with dissolved oxygen to form the corresponding tertiary peroxy radical, which can cause the backbone cleave in two ways. One way is for these peroxy radicals to abstract hydrogen from the main chain of another polymer molecule to form hydroperoxide, which decomposes to a polymeric oxy radical and a hydroxy radical, followed by electron transfer and β-scission to generate finally polymers with a ketone end group and a primary radical. The latter reacts with a hydroxy radical to form a polymer with an OH-end group. The alternative pathway is for the peroxy radicals to decompose by further reaction with cerium(IV) to lead to backbone cleavage and eventually polymers with ketone and OH-end groups.

4.4.3 Degradation of Poly(4-methylstyrene) in the Absence of Oxygen (CAN/Nitrogen System)

4.4.3.1 Relationship of Molecular Weight of Oxidized Polymer and Reaction Time

To study the effect of reaction time on the molecular weight of polymers, poly(4-methylstyrene) was prepared by anionic polymerization. The molecular weight of the poly(4-methylstyrene) obtained ranged from 2000 to 90000, and the molecular weight distribution was about 1.10.

Experimental conditions for the oxidations were the same as those described above, namely poly(4-methylstyrene) 2.5 mmol, ceric ammonium nitrate 2.5 mmol, in glacial acetic acid and benzene 30 mL, at 80°C, and with nitrogen passing through the reaction mixture.

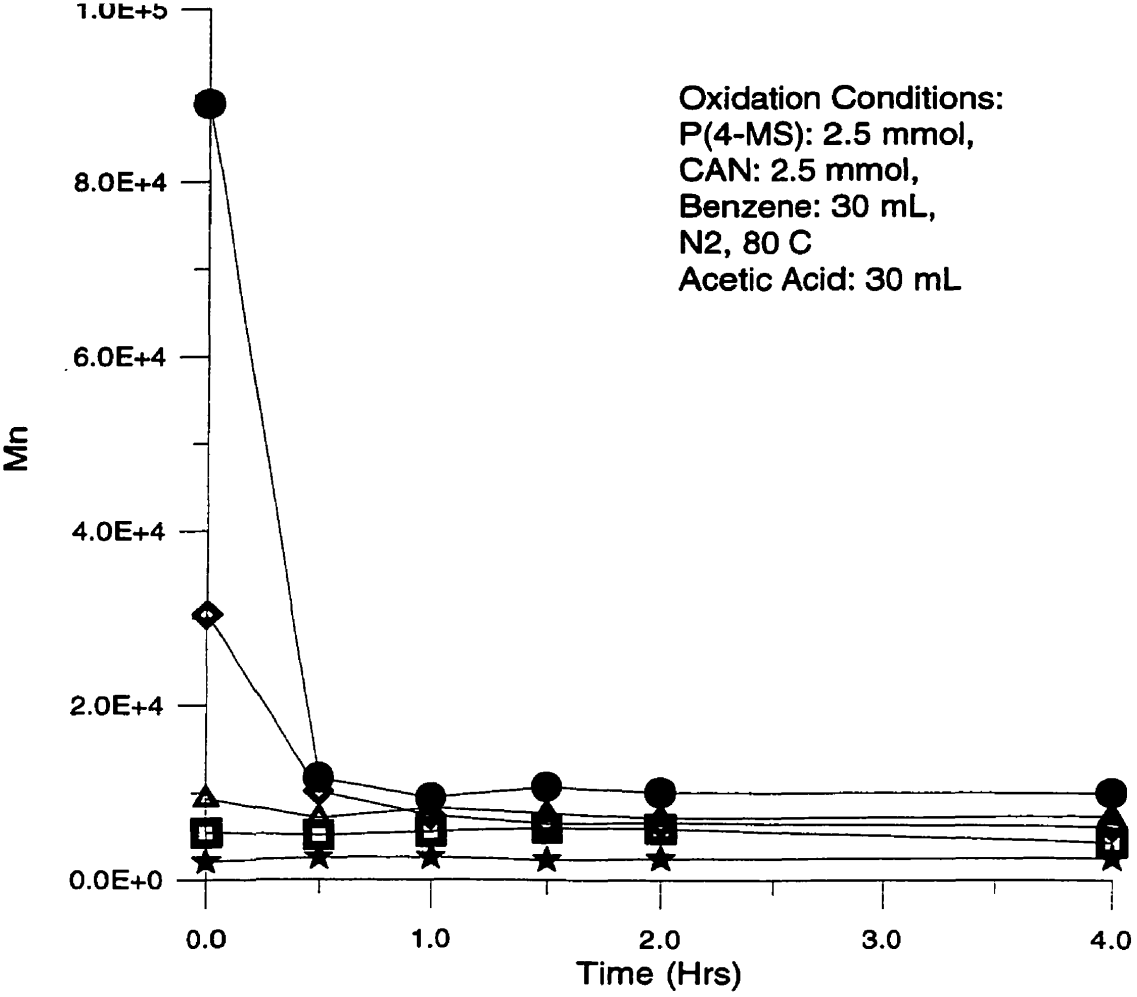


Figure 4.3 The changes in Mn with time during the oxidation of P4MS

Fig. 4.3 shows the relationship between reaction time and the number average molecular weight during CAN/nitrogen oxidation. In the first half hour of the reaction, the molecular weight decreased very rapidly for polymers with initial molecular weights of 89,000, 30,400, and 9,300, then quickly leveled off indicating that most of the backbone cleavage was completed in the first half hour. The results coincided with the fact that after 1 hour's oxidation the oxidation yield was up to 85-90% of the oxidation yield obtained after 4 hours.

Fig. 4.3 also shows that almost no molecular weight decrease was observed during oxidation of poly(4-methylstyrene) with molecular weights of 5,400 and 2,100. The oxidation of poly(4-methylstyrene) with a molecular weight of 1,000, was also checked, and the same results obtained, indicating that there is a critical value of molecular weight of about 5,000, below which no backbone cleavage can be detected after ceric ammonium nitrate/nitrogen oxidation.

Figure 4.3 also indicates that different functional groups could be introduced into low molecular weight poly(4-methylstyrene) under ceric ammonium nitrate/nitrogen system without significant molecular weight decrease. The reason for this phenomenon is likely a statistical one. Stöver et *al.*[40,41,42] reported the selective oxidation of poly(4-methylstyrene) by cobalt (II) acetate/sodium bromide/oxygen system. They observed that the preference of oxidation at the primary methyl was 25-30 times greater than the tertiary methine in the polymer backbone. The present experimental conditions were different to Stöver's, but it can still be assumed that the oxidation reactivity of the primary methyl is about 30 times that of the tertiary methine on the backbone. Then the theoretical molecular weight of the oxidized polymer can be calculated, and compared to the molecular weight of the starting polymer. The calculated results are shown in Table 4.3.

Table 4.3 Comparison of the Molecular Weights of Starting Polymer and Oxidized Polymer After Backbone Cleavage

No. of 4MS units	Mn	Oxidation Yield(%)	No. of Oxid. 4MS	No. of B.B.C.[a]	Mn after B.B.C. (calcd.[b])
1,000	120,000	30	300	10	10,900
100	12,000	30	30	1	6,000
50	6,000	30	15	0.5	4,000
40	4,800	30	12	0.4	3,400
20	2,400	30	6	0.2	2,000

[a] backbone cleavage; [b] calculated according to the number of backbone cleavage events.

Note: assuming the reactivity ratio of methyl to methine to be 30:1.

The molecular weight of 4-methylstyrene is about 120 (actual M. W. is 118.18). If the starting poly(4-methylstyrene) has a molecular weight of 120,000 (containing 1,000 4-methylstyrene units) and the oxidation yield is 30% (that is 300 of the 4-methyl groups are oxidized), the backbone of the polymer should have experienced 10 cleavage reactions, and hence, the molecular weight (Mn) of the final product should be about 10,900 (120,000/11 = 10,900). According to this method, the number average molecular weights of final products can be calculated for starting molecular weights of 12000, 6000, 4800, and 2,400. Table 4.3 shows that the higher the molecular weight of starting polymer, the more severe the degradation that takes place during CAN oxidation. If the molecular weight is below a certain range, the reduction in molecular weight cannot be detected any more.

4.4.3.2 Chlorination of Low Molecular Weight Poly(4-methylstyrene)

The above discussion indicates that during ceric ammonium nitrate/nitrogen oxidation, no molecular weight decrease can be observed if a polymer is of starting MW 5,000 or less. Another example of the same phenomenon was obtained using cobalt(III) acetate/lithium chloride/nitrogen system which also follows the electron transfer mechanism. The results are shown in Table 4.4.

Table 4.4 $Co(OAc)_3$/LiCl Oxidation of Low MW Poly(4-methylstyrene)

Run#	Oxidation Yield	P4MS		Oxidized Polymer	
	($-ClCH_2$%)	Mn	Mw/Mn	Mn	Mw/Mn
100	17.6	2,100	1.10	1,900	1.17
101	17.4	5,400	1.07	5,800	1.11

Reaction Conditions: P4MS 2.5 mmol; $Co(OAc)_3$ 5.0 mmol; LiCl 20 mmol; Benzene 15 mL; Glacial acetic acid 15 mL; N_2; 50°C; 2 hours.

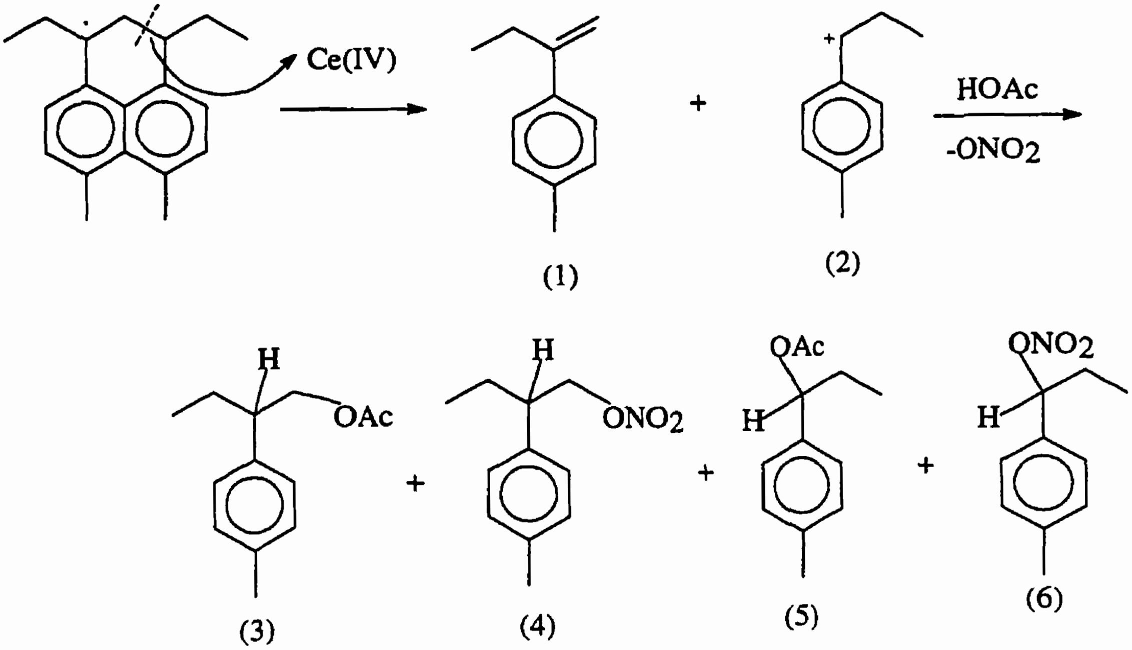
The results in Table 4.4 indicates that (i) using a different oxidation system (cobalt(III) acetate/ lithium chloride, not ceric ammonium nitrate), if the molecular weight of starting polymer is equal to or less than 5,000, no MW decrease of the polymer was detected by GPC.

(ii) The reproducibility of the chlorination experiment for poly(4-methylstyrene) is very good.

4.4.3.3 Proposed Mechanism of Degradation of Poly(4-methylstyrene) by CAN/ Nitrogen

The selective functionalization of poly(4-methylstyrene) has been explored by ceric ammonium nitrate/nitrogen, cobalt(III) acetate/trichloroacetic acid/nitrogen and cobalt(III) acetate/lithium chloride systems. Different functional groups were introduced into the 4-position of the benzene ring of poly(4-methylstyrene) according to the nucleophiles present. The mechanism for CAN oxidation is clearly an electron transfer mechanism. In the cerium(IV) and cobalt (III) cases, polymeric radical cations are formed first by transfer an electron from the benzene ring of poly(4-methylstyrene) to the oxidant, then loss of a proton to form the polymeric benzyl radical. These may be of two kinds: one is from the 4-methyl groups, and the other is from the methine groups of the polymer backbone. Because hydrogen abstraction favours the methyl group over the methine group by about 25 : 1,[40,41,42] and oxygen is carefully excluded from our reaction system, the benzyl radical loses an electron again to the oxidant to form a cation which reacts with any nucleophile present to give the final functional polymer.

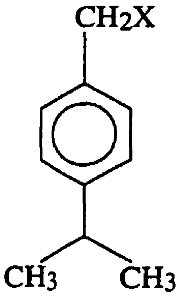
For the apparently slower tertiary radical formation, which results in the backbone cleavage of the polymer, a suggested mechanism is shown in Scheme 1.[43]



Scheme 1

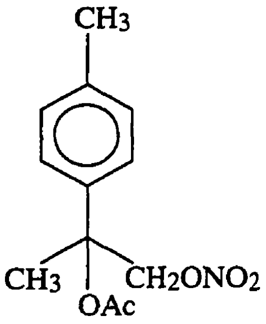
The initially formed methine radical can transfer another electron to Ce(IV), with simultaneous β-scission, leading to polymer chain cleavage. One possibility is the formation of polymer with end groups containing alkene (1) and a tertiary carbon cation (2) from Ce(IV) oxidation of the benzyl radical, as intermediates, which can then be converted by ceric ammonium nitrate and acetic acid into the addition products (3), (4), (5), and (6). The end groups of backbone cleavage products are $-CH_2OAc$, $-CH_2ONO_2$, $-CH(C_7H_7)OAc$, and $-CH(C_7H_7)ONO_2$ respectively. The chemical shifts of these methylene or methine protons are about 4.32 ppm, 4.67 ppm, ≥5.35 ppm, and ≥5.07 ppm. As the concentration of these protons in the polymer is low, they cannot be detected directly underneath the signals from functionalized 4-methyl groups.

However, Enrico Baciocchi and his co-worker have reported the oxidation of *p*-cymene by ceric ammonium nitrate in acetic acid.[43] The experimental conditions were the same as in the procedure used here (CAN in acetic acid, under nitrogen at 80°C for 2 hours) and they found the final product was a mixture of (7), (8), (9), and (10).

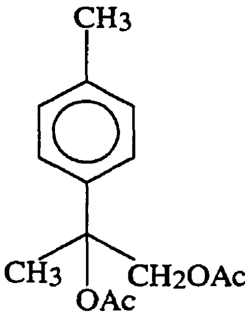


(7) X=ONO2

(8) X=OAc

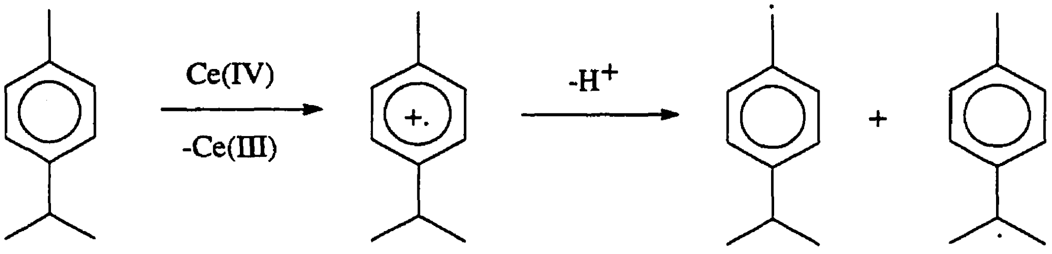


(9)



(10)

Compounds (7), (8), and (9) were the major products (29, 21 and 46% respectively) whereas (10) was the minor product (4%). Products (7) and (8) can be rationalized on the basis of the mechanism (scheme 2) where an electron transfer process occurs first to lead to the radical cation (11), which can then lose a proton from either methyl or isopropyl, giving (12, and (13) respectively.



(11) (12) (13)

Oxidation of compound (12) by ceric ammonium nitrate in acetic acid was expected to lead to the formation of compounds (7) and (8). The formation of compounds (9) and (10) was thought to proceed through the intermediate 2-(*p*-methylphenyl)-propene, which could react with ceric ammonium nitrate and acetic acid to give oxidation products (9) and (10). This suggested mechanism was confirmed by oxidation of model compound 2-phenylpropene by ceric ammonium nitrate in acetic acid to give mainly (9) and (10).

Baciocchi's work provides a basis for the proposed mechanism of backbone cleavage of poly(4-methylstyrene) by ceric ammonium nitrate/nitrogen.

4.4.3.4 Comparison of Susceptibility of the Polymer Backbone to CAN Oxidation for Poly(4-methylstyrene) and Polystyrene

4-Methylstyrene is a styrenic type of monomer, and the properties of the poly(4-methylstyrene) and polystyrene are similar. However, as there is no 4-methyl group in polystyrene, selective oxidation cannot take place for polystyrene. As a consequence, the effect of ceric ammonium nitrate oxidation on the main chain of polystyrene was examined.

Polystyrene with a number average molecular weight of 172,000 and a molecular weight distribution of 1.17 was used. The oxidation reaction conditions were the same as for poly(4-methylstyrene) oxidations discussed above. After oxidation, the Mn was almost the same (168,000) and the Mw/Mn was 1.22. This result suggested that the main chain of polystyrene is inert to CAN oxidation; that is inert to an electron transfer mechanism.

To confirm this result, a mixture of poly(4-methylstyrene) and polystyrene was used in the same run. The experimental conditions were as follows:

Poly(4-methylstyrene) (Mn 23,500, Mw/Mn 1.08) 1.25 mmol; polystyrene (Mn 163,000, Mw/Mn 1.10) 1.25 mmol; CAN 2.5 mmol; benzene 30 mL; acetic acid 30 mL; 80°C; 3 hours, N_2. Figure 4.4 shows the overlap of GPC graphs of the starting mixture and final mixture after CAN oxidation. It clearly shows that during CAN oxidation, poly(4-methylstyrene) suffered backbone cleavage but polystyrene did not, and confirms that the main chain of polystyrene is not susceptible to ceric ammonium nitrate oxidation.

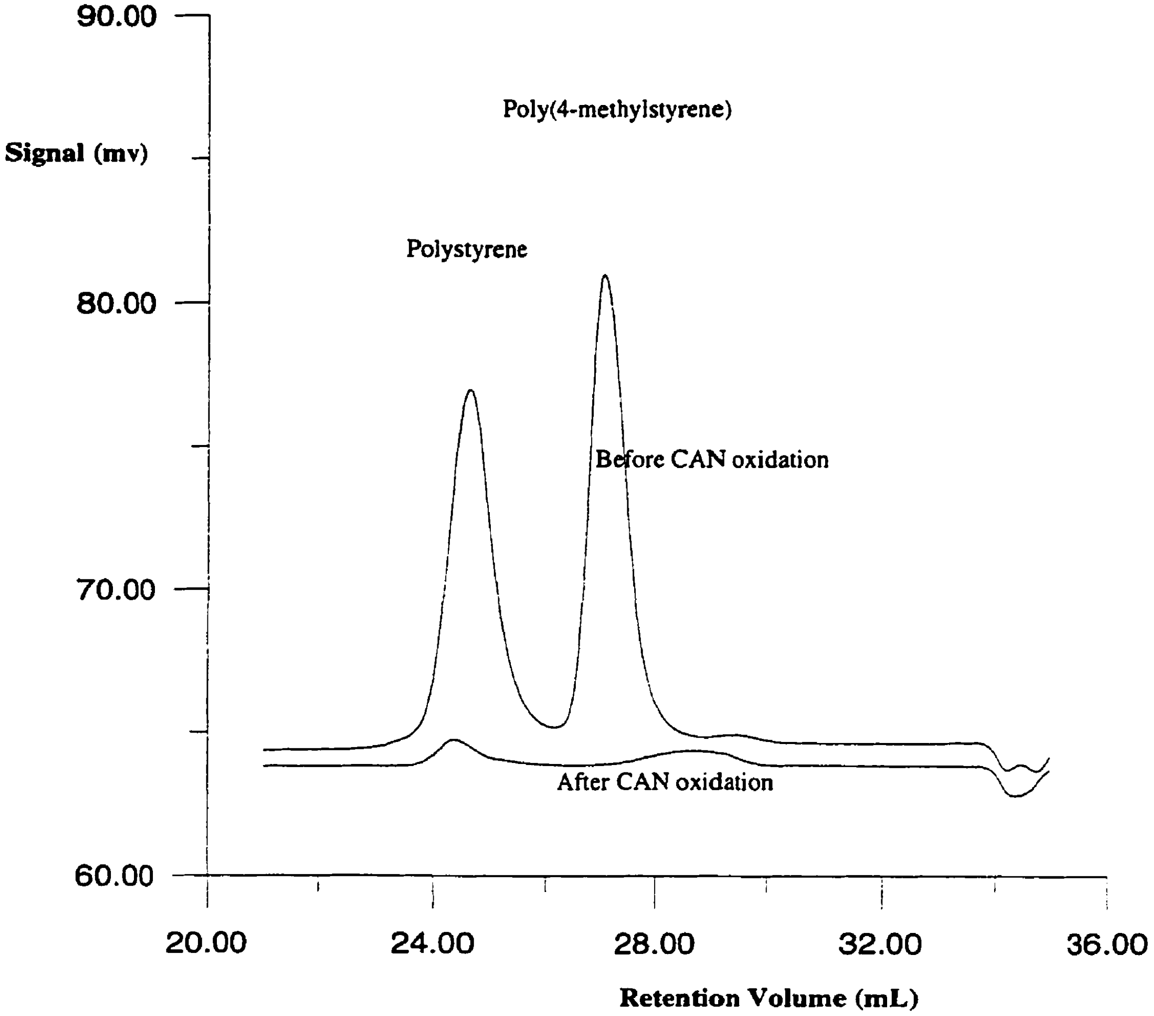


Figure 4.4 GPC Overlays of the mixture of poly(4-methylstyrene) and polystyrene before and after oxidation

4.5 CONCLUSION

This chapter describes the effect of reaction time on the molecular weight of poly(4-methylstyrene) during its oxidation by ceric ammonium nitrate/nitrogen. Most of the backbone cleavage take place in the first half hour. If the molecular weight is equal to or less than 5000, the oxidation was carried out without a decrease in molecular weight, and it is facile to introduce different functional groups to low molecular weight poly(4-methylstyrene). This conclusion was confirmed by cobalt (III) acetate/lithium chloride oxidation, where the chloromethyl group was introduced into low molecular weight poly(4-methylstyrene) without reduction in molecular weight. This effect was explained with the low statistical probability of backbone cleavage on a low molecular weight polymer.

For ceric ammonium nitrate oxidation under oxygen or nitrogen, backbone cleavage mechanisms were suggested. In the presence of oxygen, the tertiary methine radicals react with oxygen immediately to form peroxy radicals. This is followed by hydrogen abstraction; then the peroxide radicals decompose, leading to degradation of the polymer chain.

In the presence of nitrogen, it is suggested backbone cleavage proceeds by methine radical transfer and ß-scission, and the formation of an intermediate alkene terminated polymer and tertiary carbocation-terminated polymer.

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CHAPTER 5

SYNTHESIS AND OXIDATIVE FUNCTIONALIZATION OF 4-METHYLSTYRENE COPOLYMERS

5.1 INTRODUCTION

In the last two decades, functional polymers have shown increasing importance in both industrial applications and scientific research. For example, chloromethylated crosslinked polystyrene resin can be used as polymer support beads for Merrifield peptide synthesis,[1,2] and as a precursor for ion-exchange beads.[3,4]

Styrenic copolymers also are very useful materials. The copolymer of 4-methylstyrene and α-methylstyrene has applications in adhesives, sealants, and molding compounds.[5] Styrene, butadiene and unsaturated carboxylic acids are terpolymerized to produce a self-curing, coating latex called carboxylated SBR. These latexes, which have reactive sites for cross-linking, have excellent colloidal properties, which allow high filler loading. They also have excellent adhesion to textile fibers and are used extensively in the carpet industry.[6]

The copolymers of styrene and alkyl methacrylates also have found many applications. The styrene/methyl methacrylate copolymer is used in the medical field as a bone cement.[7] The styrene/butyl methacrylate copolymer is used in the xerographic industry as a common toner for roll and flash fusing.[8] The styrene/dodecyl methacrylate copolymer is added to engine oil as a viscosity improver.[9]

Functional copolymers can be prepared by direct copolymerization of the functional monomers with, if necessary, other monomers.[10] The reactivity ratios of styrene/methylmethacrylate, styrene/butyl methacrylate, and styrene/dodecyl methacrylate in copolymerization have been reported as 0.52/0.45, 0.54/0.64, and 0.528/0.30 respectively.[11,12,13]

Bataille and Granger have studied in detail the formation of alternating copolymers of styrene/methyl methacrylate. This alternating copolymer was obtained by the reaction of the two monomers in the aqueous phase and in the presence of zinc chloride acting as a complexing agent. When the monomer concentrations were equal, they obtained the optimum conditions, and the polymer obtained had a very narrow molecular weight distribution.[14]

Brar and Kapur reported the sequence determination of styrene-methyl methacrylate copolymers by use of ^{13}C NMR spectroscopy on copolymers prepared in bulk by radical polymerization using AIBN as initiator. Reactivity ratios were determined from ^{1}H NMR spectra and the triad sequences were determined by using the α-methyl and phenyl (C-1) signals in their ^{13}C NMR spectra.[15]

Emulsion copolymerization and mini-emulsion copolymerization of styrene and methyl methacrylate has received considerable attention.[16,17,18,19] In 1992, Bhatnagar and Srivastava reported the metal-ylide complex initiated radical copolymerization of styrene and methyl methacrylate.[20] They used a phenacyl dimethylsulfonium ylide complex of mercuric chloride (PDSY-$HgCl_2$) to initiate radical copolymerization of styrene and methyl methacrylate at 85°C using dioxane as an inert solvent. This yielded random copolymers. They proposed a mechanism for the reaction for this system, and studied the properties of the copolymers in the form of films.

More recently, Hawker and Elce[21] reported well-defined, random copolymerization by a "living" free-radical polymerization process for styrene/methyl methacrylate. They used unimolecular initiator, based on 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) as a mediating counterradical,[22,23,24,25] to synthesize a wide variety of random styrene/methyl methacrylate copolymers with well-defined end groups, controlled molecular weights, and low polydispersity. They found that these copolymers have the sequence distributions essentially identical to that found in a classical free radical system.

In addition to the copolymer of styrene/methyl methacrylate, the copolymerization of styrene/butyl methacrylate has been studied as well. In 1954, the reactivity ratio of styrene and butyl methacrylate were measured at 0.54 and 0.64 by J. W. Vanderhoff.[12] Joshi and Mukesh[26] reported the free-radical induced suspension copolymerization of styrene and butyl methacrylate with poly(vinyl alcohol) (PVA) as a co-surfactant. The effects of the initiator (benzoyl peroxide) (BPO) concentration, reaction temperature, and PVA amount on reaction rate and final product quality was studied. Increase in concentration of BPO decreased molecular weight. Kinetics of the reaction revealed an autoacceleration type of behavior at 93°C, which could be eliminated by reducing reaction temperature. ^{1}H NMR spectra of the samples revealed the monomer sequence.

The photopolymerization of styrene, methyl methacrylate, and butyl methacrylate with poly(methylphenylsilane) (PMPS) as a photoinitiator was reported by Ho and Chen.[27]

They found that the initiator PMPS gives a greater rate of initiation, a smaller k_p and k_t, and higher molecular weight polymer products. They observed a good correlation ($\text{Log } P = \alpha + \beta\mu$) between the resonance stabilization (P) of the chain radicals and the dipole moment (μ) of the monomers.

However, the copolymerization of 4-methylstyrene/alkyl methacrylate has been paid less attention. Walling[28] measured the reactivity ratio of copolymerization of 4-methylstyrene/methyl methacrylate to be 0.44 and 0.40 at 60°C. An experimental study of the kinetics of the free radical bulk copolymerization of 4-methylstyrene/methyl methacrylate was conducted by Hamielec et al.[29,30] The copolymerization was conducted at 60°C and 80°C with AIBN as an initiator and conversion was measured gravimetrically and by gas chromatography, and weight average molecular weight by low-angle laser light scattering photometry. A kinetic model was proposed using free-volume theory which seemed adequate to account for diffusion-controlled termination and propagation. Model predictions were in reasonable agreement with published data on homopolymerization of methyl methacrylate as well as data on copolymerization of these monomers reported here. This model should find use in the design, simulation, optimization, and control of polymer reactor systems for the production of 4-methylstyrene/methyl methacrylate copolymers.

Copolymerization of tetrahydrofurfuryl methacrylate with styrene and 4-methylstyrene was studied by Lee.[31] They measured the monomer reactivity ratio and evaluated the thermal stability of the copolymer.

A heat-resistant methacrylic polymer based on methyl methacrylate, maleic anhydride and 4-methylstyrene was prepared using lauroyl peroxide as an initiator at 60 - 85°C for 18 hours by Asahi Chemical Industry Co. Ltd. The thermal distortion temperature of the copolymer was 128°C.[32]

4-Methylstyrene is an inexpensive, commercially available, styrenic monomer with properties similar to those of styrene. It can be polymerized by free radical, living cationic, and living anionic processes, and can be made into copolymers, which can be either block, random, or alternating copolymers. Previous research work[33,34,35,36,37] showed that poly(4-methylstyrene) can be selectively functionalized by novel oxidation processes. Up to 97% of carboxylic acid, 10% of aldehyde, 45% of acetoxy, and 20% of chloromethyl groups were introduced into the side chain of poly(4-methylstyrene) using different oxidant systems. These oxidation processes were extended in this thesis to copolymers of 4-methylstyrene (including the copolymer of 4-methylstyrene/α-methylstyrene, and copolymers of 4-methylstyrene/methyl methacrylate, /butyl methacrylate, and /dodecyl methacrylate), while at the same time minimizing the backbone cleavage of the polymers.

5.2 AIM OF THE RESEARCH

In this chapter, our aim of research is to try to reduce backbone cleavage during oxidation and to extend our novel oxidation processes to the copolymers of 4-methylstyrene with methyl methacrylate (P4MS/MMA), *n*-butyl methacrylate (P4MS/BMA), and dodecyl methacrylate (P4MS/DMA).

First, we describe how to prepare copolymers of 4MS/MMA, 4MS/BMA, and 4MS/DMA with different monomer feed ratios by free radical polymerization and to characterize them using ^1H and ^{13}C NMR spectroscopy.

We try to oxidize these three types of copolymers using a cobalt (II) acetate tetrahydrate/sodium bromide/air reaction system, and study their functionality and resistance of the copolymer backbones to oxidation.

Further, we describe the chlorination of the 4-methylstyrene/methyl methacrylate copolymer and introduction of different functional groups into the 4-methylstyrene/α-methylstyrene copolymer.

5.3 EXPERIMENTAL METHODS

5.3.1 Materials and Their Purification

In this study, reagent grade 4-methylstyrene (4MS) was purchased from Deltech Corp. *n*-Butylmethacrylate and dodecyl methacrylate were purchased from Aldrich, and used as monomers. They were passed through an alumina column to remove inhibitors prior to polymerization.

2,2'-Azobisisobutyronitrile (AIBN) was purchased from Kodak and used as received. Cobalt (II) acetate tetrahydrate, glacial acetic acid, sodium bromide, benzene, and cyclohexane were purchased from Aldrich and used as received. Lithium chloride was purchased from Fisher Scientific and used as received. Ceric ammonium nitrate was purchased from SIGMA. It was dried at 85°C for one hour and stored in a desiccator before use. The copolymer of 4-methylstyrene and α-methylstyrene was obtained from Hercules Chemical Inc. and used as received. The molar ratio of 4-methylstyrene : α-methylstyrene was 2:1. It had molecular weight of 2,400, and a molecular weight distribution of 3.1. Cobalt (III) acetate was prepared as described in Chapter 3.

5.3.2 Solution Polymerization of Methyl methacrylate

2,2-Azobis(2-methyl-propionitrile) (AIBN) (0.411 g, 0.00244 mol) was dissolved in a mixture of methyl methacrylate (30 mL, 28.0 g, 0.280 mol) and cyclohexane (90 mL) in a 250 mL three-neck round bottom flask fitted with a condenser, a nitrogen inlet, and magnetic stirring. The polymerization reaction was carried out under a nitrogen atmosphere at 75°C for 23 hours.

The resulting polymer was then diluted with 50 mL of methylene chloride, and slowly precipitated into 1200 mL of methanol that was cooled in a dry ice/acetone bath. The polymer was then filtered, washed with cold methanol and reprecipitated once from methylene chloride into a 6-fold excess of methanol. After filtering and washing, it was dried at 60°C in a vacuum oven. The product was a white solid. Yield: 23.70 g, 85%, M_n: 36,500 M_w/M_n: 1.37.

5.3.3 Oxidation of Poly(methyl methacrylate) (PMMA)

In a 100 mL three-neck round bottom flask, fitted with an oxygen inlet, condenser, and thermometer, cobalt diacetate tetrahydrate ($Co(OAc)_2{\cdot}4H_2O$) (0.325 g, 1.30 mmol) and sodium bromide (NaBr) (0.134 g, 1.30 mmol) were mixed in 30 mL acetic acid/methylethylketone (1:1.5) solution. Poly(methyl methacrylate) (1.30 g, 13.0 mmol) was dissolved in 30 mL of a 1:1.5 glacial acetic acid, methylethylketone mixture, and added to the flask over 10 minutes. Oxygen was bubbled through the mixture at 80°C for three hours.

The reaction mixture was cooled, and precipitated into 250 mL of methanol at 0°C. The solid polymers were filtered, washed with methanol, and air-dried. They were dissolved in 40 mL of dichloromethane and precipitated once more into a 7-fold excess of methanol at 0°C. After filtering and washing, the product was dried at 60°C in a vacuum oven. A white precipitate was obtained. Yield: 70% - 80% (1.03 g).

5.3.4 Preparation of Poly(4-methylstyrene-co-methyl methacrylate)

4-Methylstyrene 23.64 g (0.20 mol), methyl methacrylate (MMA) 20.02 g (0.20 mol) were mixed in a 100 mL cylinder. Cyclohexane was added to make up the volume to 100 mL. 0.82 g (0.005 mol) of AIBN was added. The mixture was stirred until all of the AIBN was dissolved.

The mixture was transferred into a 250 mL three-neck round bottom flask equipped with a condenser, a nitrogen inlet, and a thermometer which reached below the liquid level. The flask was heated to 80°C for 23 hours under stirring, during which time, the copolymer solution became viscous. The reaction mixture was cooled, 50 mL of dichloromethane was added, and the diluted solution was poured into 1000 mL of methanol cooled to -78°C. The white solid copolymer which precipitated was filtered and washed with cold methanol several times. The copolymer was purified by dissolution into dichloromethane and precipitation in cold methanol again. Finally, the collected copolymer was dried under vacuum at 60°C overnight. The yield was 90% (39.30 g). Copolymers with different feed molar ratios (4MS/MMA = 1:2; 1:1; 2:1; 10:1) were prepared by the same procedure.

5.3.5 Preparation of Poly(4-methylstyrene-*co*-*n*-butyl methacrylate)

The same procedure was used as described as 5.3.4. Copolymers with different feed molar ratios (4MS/BMA = 1:2; 1:1; 2:1; 10:1) were synthesized by the same procedure.

5.3.6 Preparation of Poly(4-methylstyrene-*co*-dodecyl methacrylate)

The first part of the preparation of the copolymer of 4MS/DMA was the same as in 5.3.4, but the work up differed slightly: After the polymerization was completed, 50 mL of dichloromethane was added to dilute the copolymer solution. Then it was poured into 1500 mL of methanol at -78°C to give a very viscous shiny gum. The methanol was decanted, and the gum was transferred into a 100 mL round flask. The organic solvents were removed by rotary evaporation under reduced pressure (60°C - 70°C, water bath). Then the copolymer was washed several times with methanol to extract unreacted monomer. Finally, the methanol residues were collected and the methanol removed by rotary evaporation under vacuum in a oven at 80°C overnight. The very viscous, colourless copolymer was obtained almost quantitatively (35 g, 94%). Copolymers with different feed molar ratios (4MS/DMA = 1:2; 1:1; 2:1) were synthesized by the same procedure.

5.3.7 Oxidative Functionalization of Copolymers of 4-Methylstyrene (4MS) and Alkyl Methacrylate by Cobalt(II) Acetate/Sodium Bromide/Air (General Procedure)

Poly(4MS-co-MMA) 1.0 g (containing 4-methylstyrene 0.61 g, 5.16 mmol) was dissolved in 30 mL of cyclohexane in a 100 mL three-neck round bottom flask fitted with a condenser, an air inlet, magnetic stirring, and a thermometer reaching below the liquid level. After 30 mL of glacial acetic acid was added to the flask, a clear solution formed. The flask was heated in an oil bath to 60°C. Air was bubbled through the reaction mixture for 10 minutes, then 0.129 g (0.516 mmol) of cobalt(II) acetate tetrahydrate was added. The solution became pink. Sodium bromide 0.053 g (0.516 mmol) was added to the flask. The reaction time was counted from this point. This oxidation reaction was run for a certain time (0.5 hour; 2 hours; 7 hours), and then 20 mL of reaction solution was withdrawn using a 100 mL syringe, and poured into 200 mL of methanol (dry ice bath), to obtain a white precipitate. The copolymer was collected by filtration, and washed with cold methanol ten times. It was purified by redissolving in dichloromethane and precipitation with cold methanol. Finally, it was dried in a vacuum oven under reduced pressure at 60°C overnight. The yield was 90%.

The oxidation procedures for the copolymer of 4MS/BMA and 4MS/DMA were similar to the above procedure.

5.3.8 Oxidative Functionalization of Poly(4-Methylstyrene-*co*-Methyl Methacrylate) by Cobalt (III) Acetate/Lithium Chloride/Nitrogen

Poly(4MS-*co*-MMA) 2.00 g (containing 4-methylstyrene 0.996 g, 8.43 mmol) was dissolved in a mixture of 45 mL benzene and 45 mL glacial acetic acid in a 250 mL three-neck round bottom flask. The flask was equipped with a condenser, a nitrogen inlet, magnetic stirring, and a thermometer reaching below the liquid level. The flask was heated in an oil bath to 50°C under nitrogen. Lithium chloride (2.858 g, 67.4 mmol) was added. After all of the lithium chloride had dissolved, cobalt (III) acetate (3.977 g, 16.86 mmol) was added immediately. The reaction was run for two hours from the time of adding the cobalt salt. At that time, the color of the solution became deep green. The reaction mixture was cooled and filtered, and the benzene component was removed on a rotary evaporator under reduced pressure. The remaining solution of oxidized polymer and cobalt salt in acetic acid was poured into 200 mL of a mixture of methanol and water (4:1 v/v). After standing overnight, the white precipitate was collected by filtration, washed with a 4:1 methanol/water mixture, and dried under vacuum at 60°C overnight. A white solid was obtained. Yields were typically around 90% (1.81 g).

5.3.9 Oxidative Functionalization of Copolymer of 4-Methylstyrene and α-Methylstyrene (αMS)

5.3.9.1 Introduction of Acetoxymethyl Groups

The copolymer of 4-methylstyrene and α-methylstyrene 0.90 g (containing 4-methylstyrene 0.60 g, 5.0 mmol) was dissolved in a mixture of 18 mL glacial acetic acid and 18 mL benzene in a 100 mL three-neck flask fitted with a condenser, a nitrogen inlet, magnetic stirring, and a thermometer reaching below the liquid level. The temperature was raised to 80°C, and 2.74 g (5.0 mmol) of ceric ammonium nitrate (dried at 85°C for 1 hour and stored in a desiccator) was added to the flask all at once. During the reaction, the color of the solid changed from orange to light yellow or colourless, and the color of the solution changed from yellow to pale yellow. After two hours the reaction mixture was cooled, and filtered, and the benzene component was removed on a rotary evaporator at reduced pressure. The remaining solution of oxidized polymer and ceric salts in acetic acid was precipitated into 200 mL of a mixture of methanol and water (4:1 v/v). After standing overnight, the white precipitate was filtered, washed with a 4:1 methanol/water mixture, and dried under vacuum at 60°C overnight. The yield was 0.87 g (92%).

5.3.9.2 Introduction of Chloromethyl Groups

The copolymer of 4-methylstyrene and α-methyl methacrylate 5.40 g (containing 4-methylstyrene 3.60 g, 30.00 mmol) was dissolved in the mixture of 108 mL benzene and 108 mL glacial acetic acid in a 250 mL three-neck round bottom flask. It was equipped with a condenser, a nitrogen inlet, magnetic stirring, and a thermometer reaching below the liquid level. The flask was heated in an oil bath at 50°C under nitrogen. Lithium chloride (10.17 g, 240 mmol) was added. After all of the lithium chloride was dissolved, 14.16 g Cobalt (III) acetate (60 mmol) was added immediately. The reaction time was counted from the time of adding the cobalt salt. The oxidation reaction was run for two and a half hours. The colour became deep green. The reaction mixture was cooled and filtered, and the benzene component was removed on a rotary evaporator under reduced pressure. The remaining solution of oxidized polymer and cobalt salt in acetic acid was poured into 300 mL of a mixture of methanol and water (4:1 v/v). After standing overnight, the white precipitate was collected by filtration, washed with a 4:1 methanol/water mixture, and dried under vacuum at 60°C overnight. The yield was quantitative (5.61 g).

5.3.9.3 Introduction of Aldehyde and Carboxylic Acid Groups

The copolymer of 4-methylstyrene and α-methylstyrene 3.54 g (containing 4-methylstyrene 2.30 g, 20.0 mmol) was dissolved in a mixture of 60 mL of cyclohexane and 40 mL of glacial acetic acid in a 250 mL three-neck round bottom flask fitted with a condenser, an air inlet, magnetic stirring, and a thermometer reaching below the liquid level. The flask was heated in a oil bath at 60°C. Air (204 mL/min.) was bubbled through it for 10 minutes, then 0.498 g (2.00 mmol) of cobalt(II) acetate tetrahydrate was added. The solution became deep pink. Sodium bromide 0.206 g (2.00 mmol) was added to the flask. The colour of the solution became blue immediately. The reaction time was counted from this point. The oxidation reaction was run for six hours. During which time, the colour changed to black. After removing cyclohexane by rotary evaporation under reduced pressure, the residue was poured into 200 mL of methanol/water mixture (4:1). The copolymer was collected by filtration and washed with water and methanol ten times, then it was dried in a vacuum oven under reduced pressure at 60°C overnight. The yield was quantitative (3.21 g).

5.3.10 Determination of Oxidation Yield, Copolymer Structure, and Copolymer Composition by ^{1}H NMR

Most NMR spectra were measured in deuteriochloroform solution on a Bruker AC200 or AC300 NMR instrument. A 1:1 mixture of deuteriochloroform and deuterio acetone was used for highly oxidized poly(4-methylstyrene). Chemical shifts are in ppm relative to tetramethylsilane at zero ppm for proton chemical shifts, and the signal of carbon deuterio chloroform at 77.0 ppm.

Oxidation yields for the formation acetoxymethyl, chloromethyl, aldehyde and carboxylic acid groups), the copolymer structure and composition were determined by proton NMR spectroscopy.

5.3.11 Determination of Molecular Weight of Copolymer by SEC

Molecular weights were determined on a Waters size exclusion chromatography (SEC) system using three Waters Ultramicrostyragel columns in series. It was calibrated using narrow-disperse polystyrene standards.

5.4 RESULTS AND DISCUSSION

Previous work [33,34,35] involved a range of new functional copolymers bearing aldehyde and carboxylic acid groups which had been prepared by functionalization of poly(4-methylstyrene), using cobalt (II) acetate tetrahydrate/sodium bromide/oxygen or air. These polymers contained up to 20% of aldehyde and up to 90% of carboxylic acid groups and had number average molecular weights from 2,000 to 16,500. Figure 5.1 shows the relationship of present oxidation and reaction time on molecular weight in heptane/acetic acid.[35]

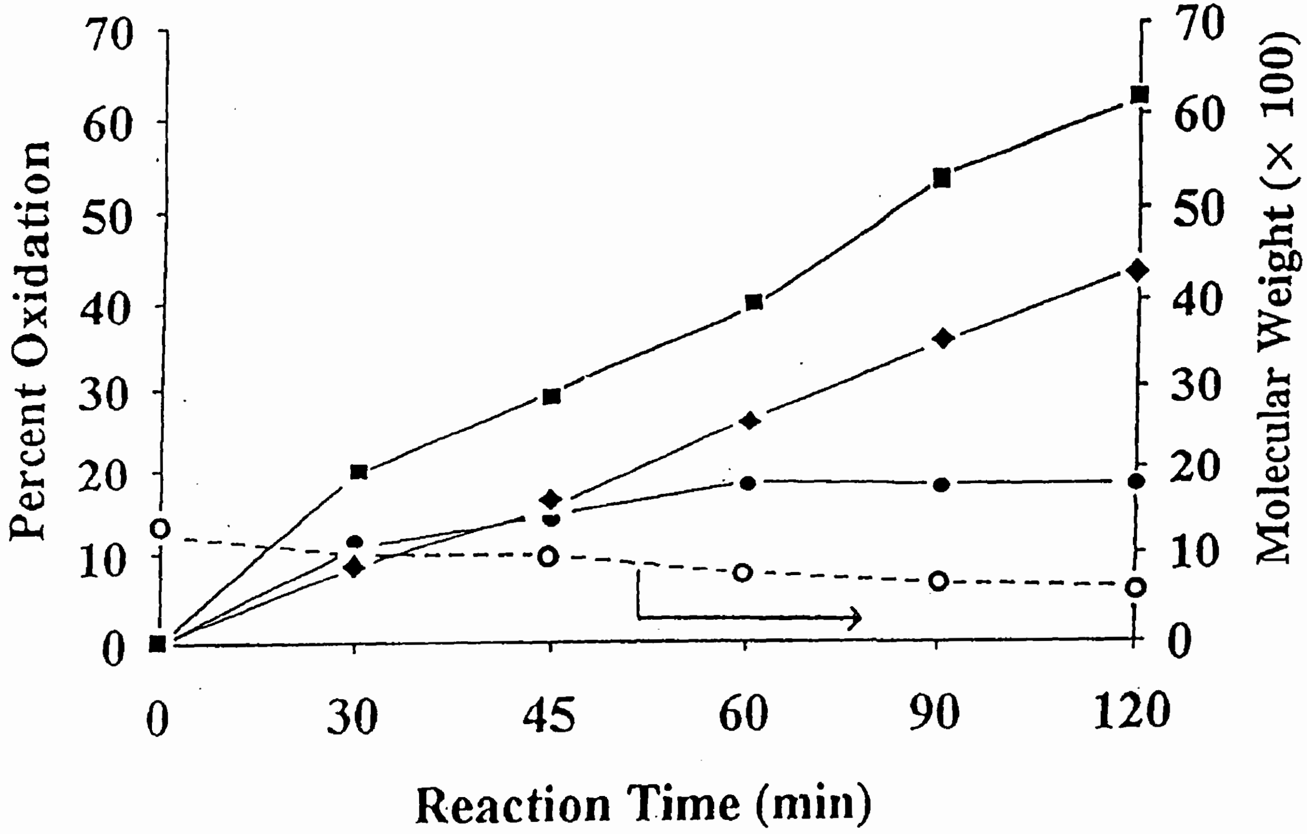


Figure 5.1 Oxidation rate and backbone cleavage in heptane/acetic acid. Reaction conditions: 3 g poly(4-methylstyrene) in 150 mL acetic acid/heptane 1:1, 10 mol% catalyst, 80°C, oxygen flow rate: 400 mL min^{-1}.

- ● - % aldehyde; - ◆ - % carboxylic acid; - ■ - % total oxidation.

From Figure 5.1, it can be seen that with increasing reaction time, the oxidation yield (both aldehyde and carboxylic acid) increased. After two hours' oxidation, up to 62% total oxidation yield (44% carboxylic acid and 18% aldehyde) was obtained. However, substantial backbone cleavage of the polymer occurred. The number average molecular weight of the polymers decreased from 12,000 to 6,000.

In the second chapter and third chapter of this thesis,[36,37] using cerium (IV) and cobalt (III) oxidation systems, different functionalities (acetoxy, nitrate, chloromethyl, and aldehyde groups) could be introduced into poly(4-methylstyrene). At the same time, some reduction in molecular weight of polymers was observed as well. In Chapter 4, a mechanism of backbone cleavage during ceric ammonium nitrate/nitrogen oxidation was proposed.[38] The backbone cleavage problem indicates that not only does the benzylic methyl carbon get oxidized, but oxidation also occurs at the backbone benzylic methine carbon. Backbone cleavage reduces the molecular weight of the polymers, increases the polydispersity, and especially, prevents applications of the method to block copolymers of 4-methylstyrene.

The challenges were how to minimize backbone cleavage during polymer functionalization, how to extend these oxidation processes to copolymers, and to find new applications for these functional copolymers. If an alternating copolymer of 4-methylstyrene can be made in which the comonomer is an α-substituted olefin, this α-substituted group could provide enough steric hindrance in the backbone to prevent the oxidant from attacking the methine carbon of the backbone and thus protecting it from oxidation. Consequently the copolymer of 4-methylstyrene and α-methylstyrene was studied,[39] and it was found that for near alternating copolymers (1:1.5 ratio), no backbone cleavage took place during oxidation.

This result indicated the α-substituted group does protect the polymer main chain from attack by the oxidation. Figure 5.2 shows that after 24 hours oxidation, the total oxidation yield reached 97%, the molecular weight of the 4-methylstyrene and α-methylstyrene copolymer remained relatively constant.

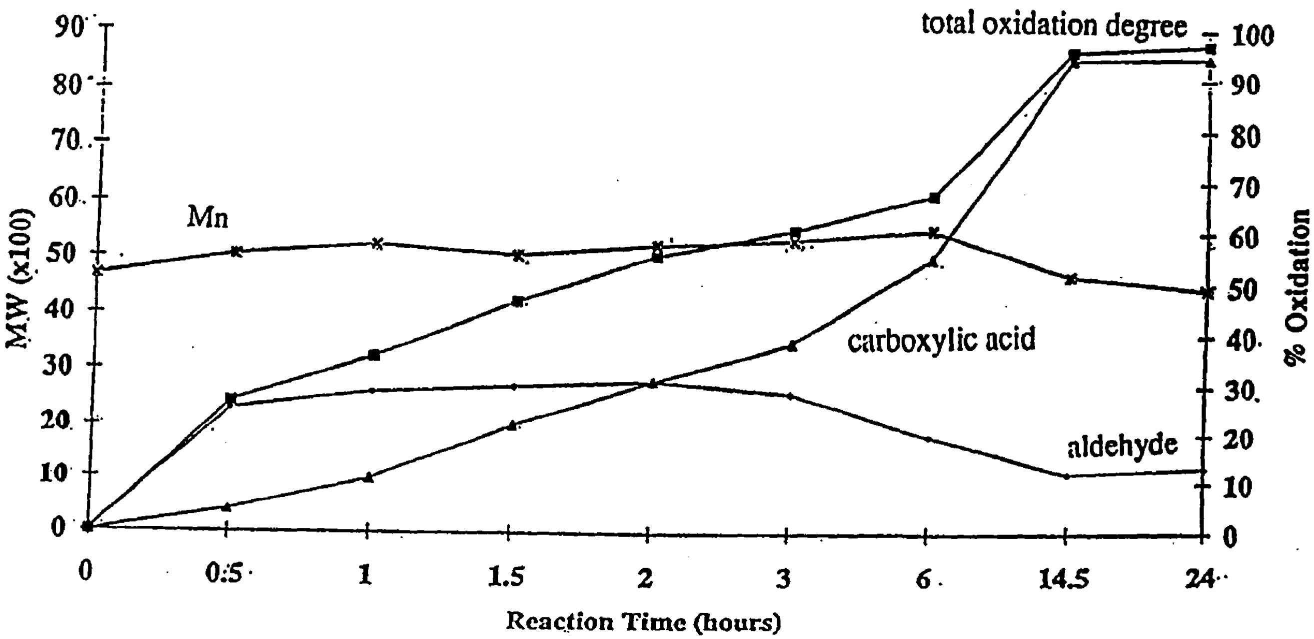
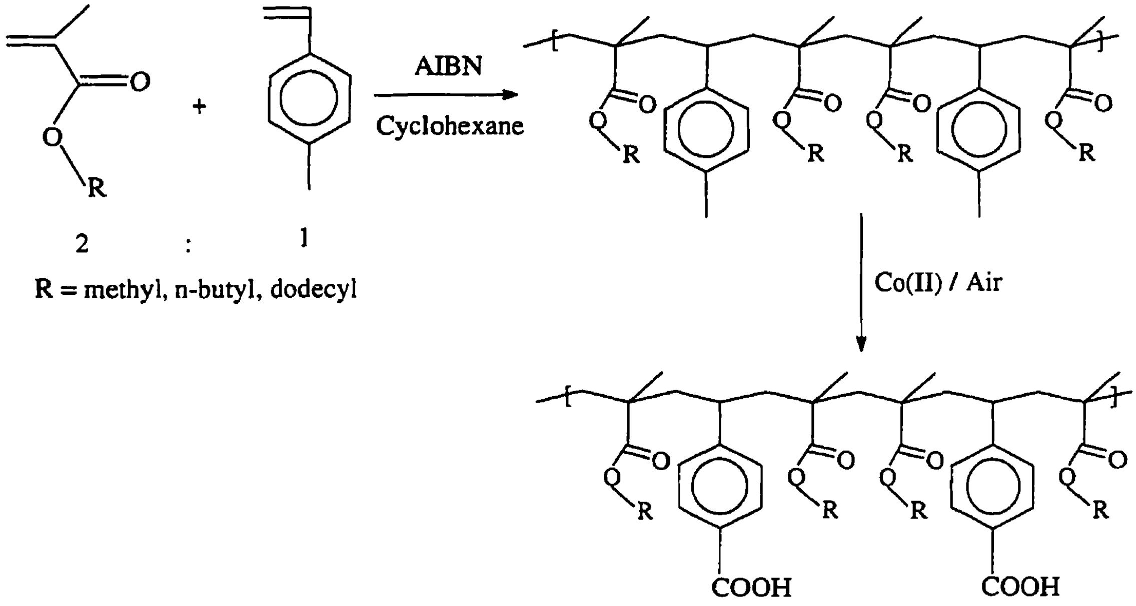


Figure 5.2 Oxidation of poly(4-methylstyrene-co-α-methylstyrene)

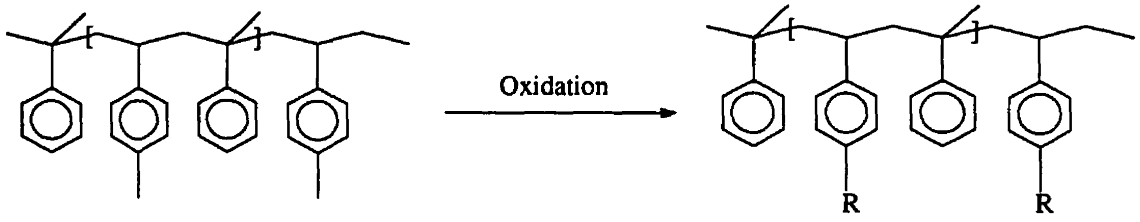
- • - % aldehyde; - - % carboxylic acid; - ▪ - % total oxidation; - x - Mn.

- • - % aldehyde; -▲- % carboxylic acid; - ▪ - % total oxidation; - x - Mn.

If the α-substituted group provided steric protection of the backbone against the oxidation, it was conceivable other α-substituted monomers, such as methyl methacrylate, butyl methacrylate, and dodecyl methacrylate should have same effect. These alkyl methacrylates were chosen as comonomers to prepare copolymers with 4-methylstyrene. Different functional groups were introduced into these copolymers, and their resistance to backbone oxidation was studied.



Also, different functionalities were introduced to copolymers of 4-methylstyrene and α-methylstyrene.



R = CHO, COOH, CH_2OOCCH_3, CH_2Cl

5.4.1 Selective Functionalization of Copolymer of 4-Methylstyrene and α-Methylstyrene

5.4.1.1 Characterization of Functional 4-Methylstyrene/α-Methylstyrene Copolymer

^1H NMR spectroscopy was used to determine the structure of functional 4-methylstyrene/α-methylstyrene copolymer and to calculate the oxidation yield. For the copolymer of 4-methylstyrene and α-methylstyrene, there are no signals in the region 4.00 - 5.50 ppm and in the region 7.50 - 10.00 ppm. Signals in the 4.00 - 5.50 ppm correspond to the benzylic protons (such as benzyl nitrate, benzyl acetate, benzyl chloride) and the signals in the region 7.50 - 10.00 ppm are characteristic of the ortho protons of aromatic aldehydes and carboxylic acids.

After ceric ammonium nitrate oxidation, the peaks at 5.0 ppm and 5.25 ppm indicated the presence of benzyl acetate and benzyl nitrate respectively. Chloromethyl protons resulting from obtained in cobalt (III) acetate/lithium chloride oxidation of copolymers appear at 4.48 ppm.

During cobalt (II) acetate/sodium bromide/air oxidation, the 4-methyl groups in 4-methylstyrene/α-methylstyrene copolymer were converted to aldehyde and carboxylic acid groups, resulting in the appearance of additional peaks at 9.86 ppm (proton of aldehyde) and at 7.50 ppm and 7.80 ppm (ortho protons of aromatic ring to aldehyde and carboxylic acid respectively). For example, Figure 5.3 shows the ^1H NMR spectrum of 4-methylstyrene/α-methylstyrene copolymer containing chloromethyl groups. The peak at 4.48 ppm indicates the methylene proton adjacent to the chlorine. The ^1H NMR spectrum of the copolymer containing acetoxymethyl and nitrooxymethyl groups is shown in Figure 5.4. The signals at 5.00 ppm and 5.25 ppm are the benzylic protons of the acetoxy and nitrooxy groups respectively. These clearly distinguishable signals and their corresponding relative areas enable the ^1H NMR spectra of the copolymers to be used to determine the oxidation yield. An example of this is shown below:

$$\text{-acetoxymethyl \%} = \frac{\text{integration of protons at 5.00 ppm} \times 2}{\text{integration of aromatic protons} \times 8/13} \times 100$$

$$\text{-carboxylic acid \%} = \frac{\text{integration of protons at 7.50-7.80 ppm} \times 2}{\text{integration of aromatic protons} \times 8/13} \times 100 - \text{aldehyde\%}$$

Note: The ratio 8/13 means the fraction of aromatic protons of 4-methylstyrene in total aromatic protons of 4-methylstyrene/α-methylstyrene copolymer (the molar ratio of 4MS/αMS copolymer is 2:1).

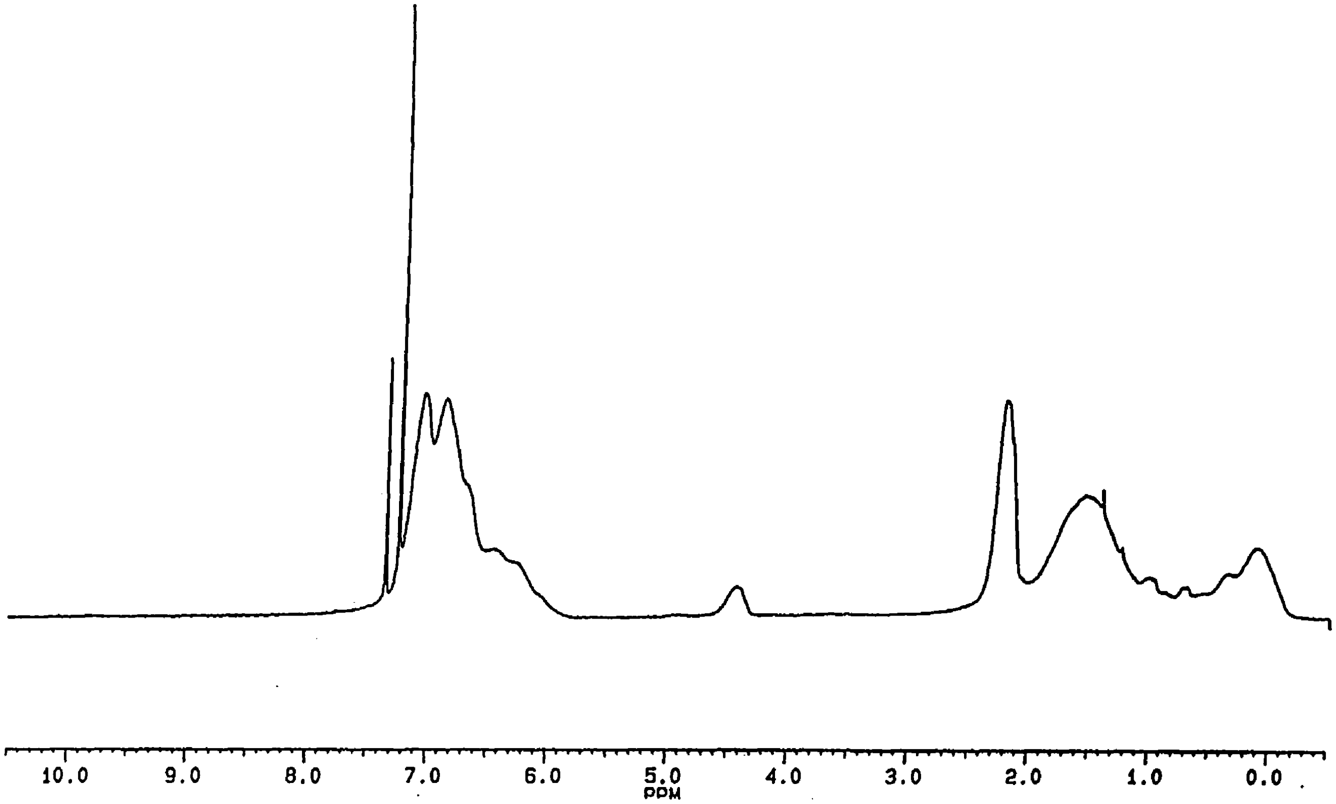


Figure 5.3 ^{1}H NMR spectrum of copolymer of 4-methylstyrene and α-methylstyrene (containing 13.0 % of chloromethyl group)

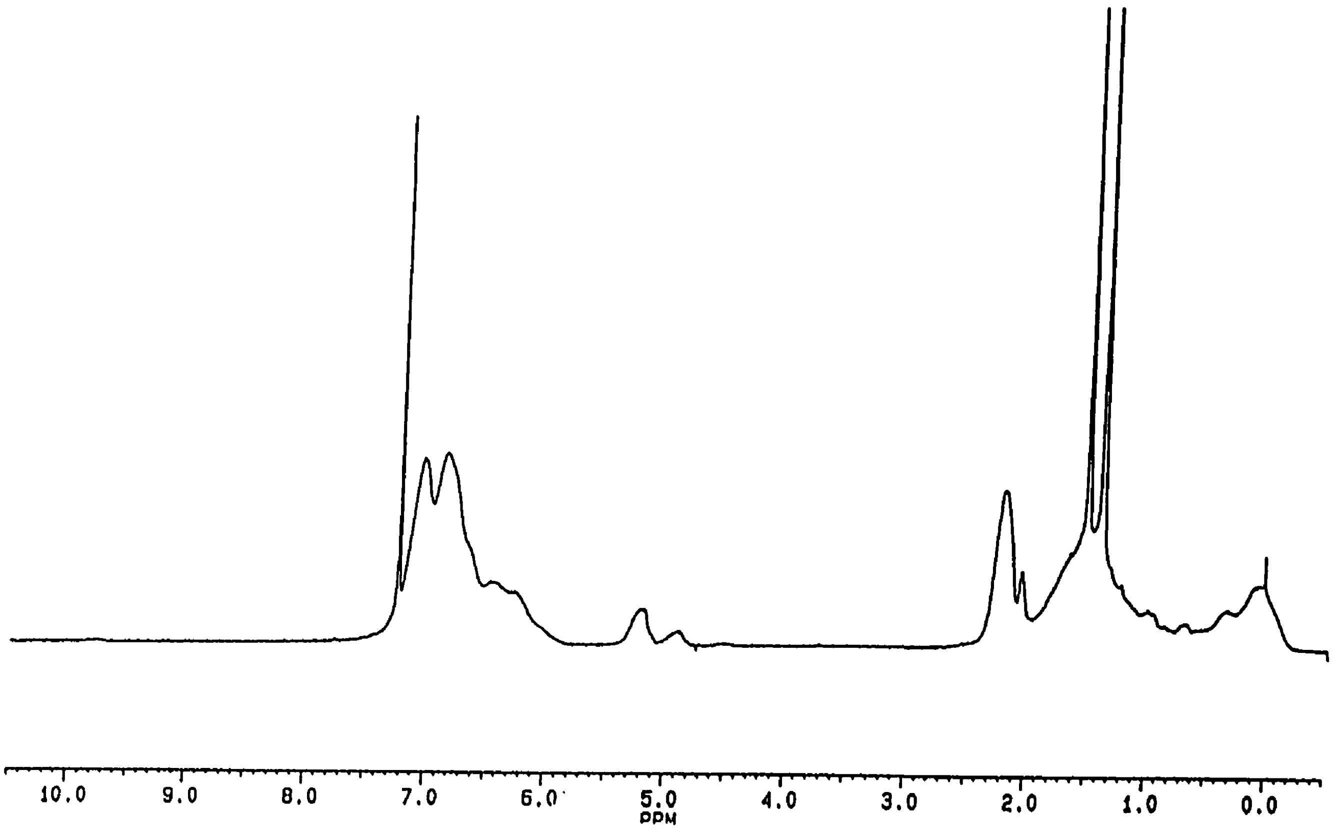


Figure 5.4 ^{1}H NMR spectrum of copolymer of 4-methylstyrene and α-methylstyrene (containing 3.8 % of acetoxy and 10.3 % of nitrooxy groups)

5.4.1.2 Introduction of Functional Groups into the Copolymer of 4-Methylstyrene/α-Methylstyrene

For the copolymer of 4-methylstyrene and α-methylstyrene, different functional groups were introduced into the 4-methylstyrene structure units. Tables 5.1, 5.2, and 5.3 show the results where the % functionality is relative to 4-methylstyrene.

Table 5.1 Introduction of Acetoxymethyl Groups

Run#	Copolymer	Ce(IV) (mmol)	Cosol.	Ace.%	Nit.%	Tot.%	Mn	Mw/Mn
61	0.90g	5.0	cyclohexane	3.80	10.3	14.1	3,500	2.60
64	0.90g	5.0	benzene	11.2	30.3	41.5	3,700	2.39

Experiment Conditions: Cosolvent 18 mL; HOAc 18 mL; 2 hours; 80°C; N_2

Table 5.2 Introduction of Chloromethyl Groups

Run#	Copolymer	Co(III) (mmol)	LiCl (mmol)	Cosol.	-CH2Cl%	Mn	Mw/Mn
62	0.90g	10.0	40	Cyclohexane 18 mL	No	-	-
65	0.90g	10.0	40	Benzene 18 mL	13.0	3,200	3.38
68	5.40g	60	240	Benzene 108 mL	15.8	3,300	2.24

Experiment Conditions: HOAc 23 mL (62, 65); 108 mL (68); 2 hours, 60°C, N_2 (62); 2 hours, 50°C, N_2(65); 2.5 hours, 50°C, N_2(68);

Table 5.3 Introduction of Aldehyde and Carboxylic Acid Groups

Run#	Copolymer	Co(II) (mmol)	NaBr (mmol)	Reaction Time(Hrs)	-CHO%	-COOH%	Mn	Mw/Mn
78	3.54g	2.0	2.0	1.0	11.5	21.6	4,000	2.61
75	3.54g	2.0	2.0	6.0	-	64.8	3,900	2.05

Experiment Conditions: HOAc 60 mL; Cyclohexane 60 mL; Air 204 mL/min.; 60°C.

Table 5.1 indicates that acetoxy groups could be introduced into 4-methylstyrene/α-methylstyrene copolymers. The oxidation system is the same as those of poly(4-methylstyrene) described in chapter 2; that is: copolymer 0.90 g (containing poly(4-methylstyrene) 5.0 mmol); ceric ammonium nitrate 5.0 mmol; nitrogen; 80°C; 2 hours, and a cosolvent. With different cosolvents, different results were obtained for the same experimental conditions. Thus 14% of total oxidation was obtained by using cyclohexane as a cosolvent; while 42% of oxidation was obtained by using benzene, indicating that benzene is a much better cosolvent than cyclohexane.

As noted in the discussion in Chapter 2, all nitrate groups could be displaced by acetoxy groups by refluxing the polymer in the mixture of acetic acid and xylene for 24 hours.

Table 5.2 shows chlorination of 4-methylstyrene/α-methylstyrene copolymer was carried out by cobalt (III) under nitrogen. The amount of oxidant (cobalt(III) acetate) was twice the number of moles of 4-methylstyrene unit, and cyclohexane and benzene were used as cosolvents from Table 5.2. The following two points can be made:

1) Using cyclohexane as a cosolvent, no oxidation took place. The reason for this is possibly the poor solubility of lithium chloride in the mixed solvent. After the copolymer and lithium chloride were added into the mixed solvent, two clear layers were observed.

2) When the process was scaled up, almost the same results were obtained (comparison 68 and 65). Because the oxidation reaction took longer for 68 (0.5 hour longer), a little higher yield (13-15.8%) was obtained.

The result of cobalt (II) acetate tetrahydrate/sodium bromide oxidation is listed in Table 5.3. With increasing reaction time, the aldehyde groups were further oxidized and converted to carboxylic acids (78, and 76). A mixture of aldehyde and carboxylic acid was obtained for a one hour oxidation, however, up to 65% of carboxylic acid was obtained after six hours of oxidation (under the same temperature and reagent conditions).

For all of these three oxidation processes, the polymer yield was near quantitative (more than 90%) and no reduction in molecular weight was observed. Under the isolation conditions, a small part of the copolymer with low molecular weight was lost and this resulted in a small increase in the molecular weight and a narrowing in the molecular weight distribution.

5.4.2 Oxidation of Poly(methyl methacrylate)

Poly(methyl methacrylate) was produced by a free radical polymerization in solution using AIBN as an initiator. The resulting polymer had a molecular weight of 36,500 and a polydispersity of 1.37, its ^{1}H NMR spectrum can be found in Figure 5.5. The peaks are narrower than those for poly-4-methylstyrene, but proton-proton J coupling is still not observable. Again, there are different stereochemical environments around the carbon which result in broadening. The signal from the backbone is split into a number of different peaks arising primarily from the tacticity of the polymer chain. The methyl protons from the backbone appear between 0.75 ppm and 1.3 ppm, the methylene protons appear in the range of 1.7 ppm to 1.9 ppm, and the methoxy protons are far enough away from the backbone to give a very sharp peak at 3.5 ppm.

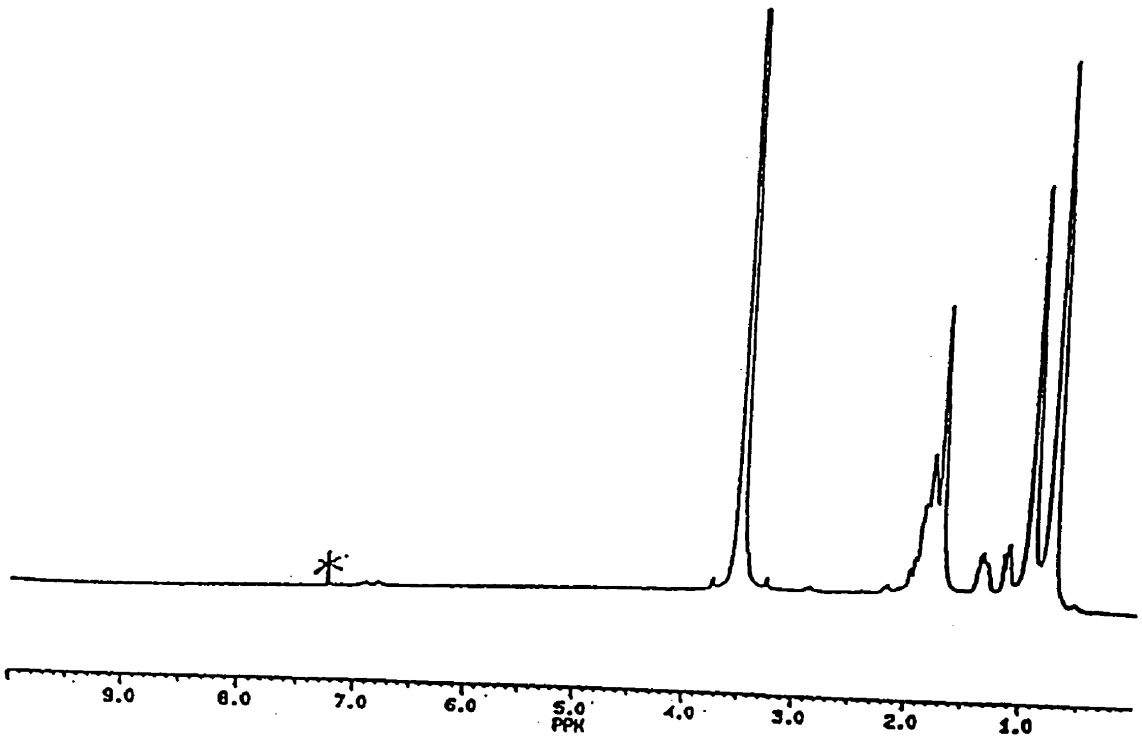


Figure 5.5 ^{1}H NMR spectrum of poly(methyl methacrylate)

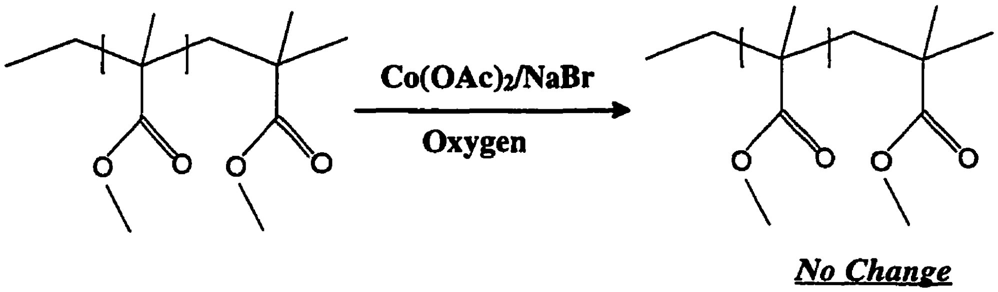


Figure 5.6 Attempted Oxidation of Poly(methyl methacrylate)

Poly(methyl methacrylate) was subjected to the cobalt catalyzed oxidation procedure mentioned earlier. The homopolymer, having no labile hydrogens should not change during the oxidation. The same procedure was followed as for poly(4-methylstyrene), with the exception that the homopolymer was isolated by precipitation from methanol that was cooled in a dry ice/acetone bath and stirred with an off-centre vortex. These conditions were used so that the polymer would not be soft and sticky and therefore easier to collecte by filtration. The isolated polymer was then characterized by both proton NMR and GPC and the results obtained are given in Table 5.4.

Table 5.4 Results For Poly(methyl methacrylate) Oxidations

Reaction Time (hours)	Mn	Mw/Mn	Total Oxidation Degree (%)
0.0	36,500	1.37	0%
3.0	35,300	1.36	0%

Experiment Conditions: PMMA 1.30 g; $Co(OAc)_2{\bullet}4H_2O$ 0.3250 g; NaBr 0.1343 g; HOAc 24 mL; Methylethylketone 36 mL; 80°C; Oxygen bubbled.

Figure 5.7 shows the overlap of the GPC plots for poly(methyl methacrylate) and the product from the attempted oxidation. After oxidation there was no molecular weight shift noted. If cobalt catalyzed oxidation had taken place there should have been a change in the NMR spectrum or a reduction in molecular weight from the GPC data. From the proton NMR spectra of products from the two reaction runs showed no new peaks after oxidation and the molecular weight decrease was minimal, and well within error limits, so the degree of oxidation is 0% for both reaction times. These results showed that the α-methyl groups of poly(methyl methacrylate) do protect the backbone from oxidation. It also showed that other alkyl methacrylates should have the same ability and be inert to cobalt (II)/oxygen oxidation.

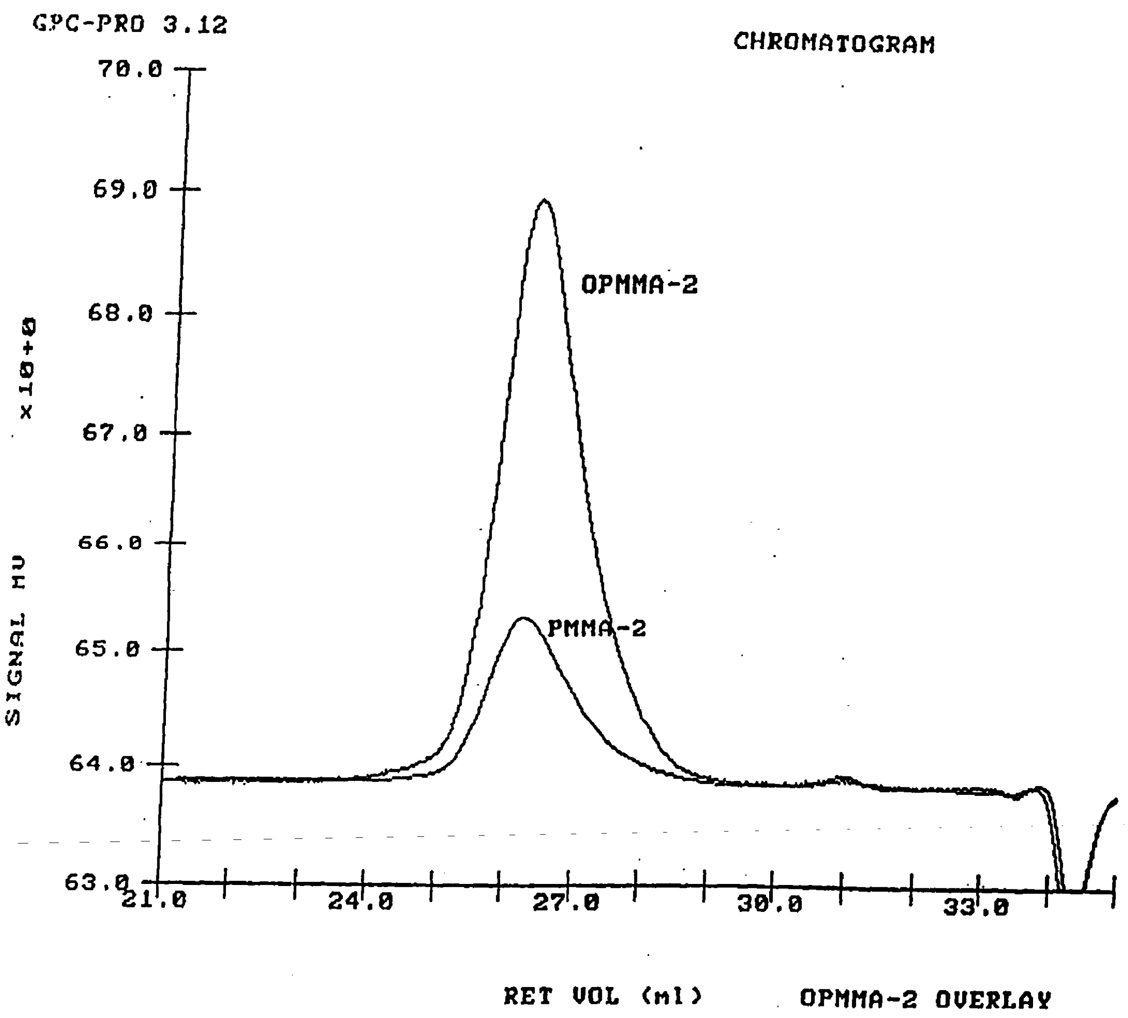


Figure 5.7 The overlap of poly(methyl methacrylate) and oxidized poly(methyl methacrylate)

5.4.3 Solution Copolymerization of 4-Methylstyrene and Alkyl Methacrylate

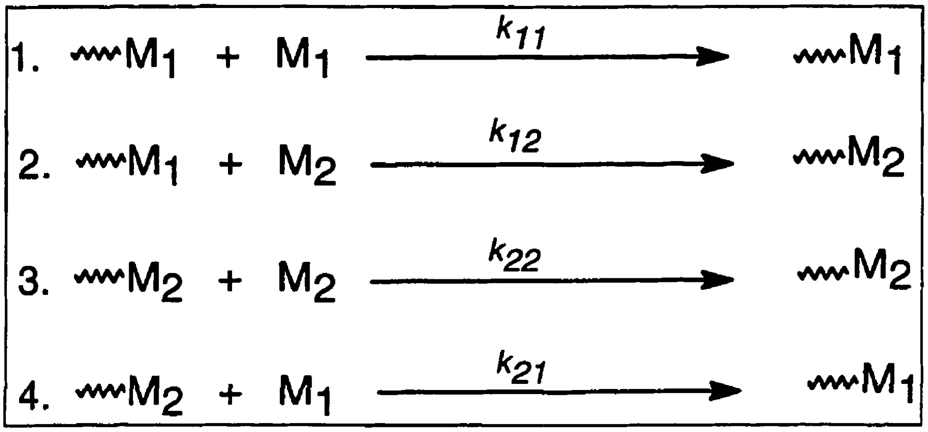
Copolymers of 4-methylstyrene/alkyl methacrylate were synthesized with different feed molar ratio by free radical polymerization at 60°C under nitrogen using AIBN as initiator.

5.4.3.1 Reactivity Ratios

The process of free radical copolymerization is similar to that of homopolymerization as described above. The main difference lies in the fact that the reactivities of the monomers are usually different.

Copolymers can be classified as having random, block, or alternating comonomer sequences. A block type arrangement seems unlikely to eliminate backbone cleavage since there will be large segments of each type of polymer. This means that there would be sections of 4-methylstyrene that would have no protection in the backbone. Likewise, a random structure would have some block sections of each type of homopolymer purely by chance. The alternating structure is the most promising for eliminating backbone cleavage, as each 4-methylstyrene unit would be sandwiched between two sterically demanding, bulky methylmethacrylate units. This concept was confirmed by experimental date obtained for 4-methylstyrene/α-methylstyrene copolymers.

Reactivity ratios have been determined for many pairs of comonomers, in order to measure their relative reactivities in copolymerization. The first attempt to deal with this was made by Dostal,[40] who assumed that the rate of addition of a monomer to a radical is independent of the size and nature of the radical chain and is influenced only by the nature of the radical end group. The four proposed reactions in this classical "terminal" model are seen in following.



$$\begin{aligned}
&1.\ \sim\!M_1 + M_1 \xrightarrow{k_{11}} \sim\!M_1\\
&2.\ \sim\!M_1 + M_2 \xrightarrow{k_{12}} \sim\!M_2\\
&3.\ \sim\!M_2 + M_2 \xrightarrow{k_{22}} \sim\!M_2\\
&4.\ \sim\!M_2 + M_1 \xrightarrow{k_{21}} \sim\!M_1
\end{aligned}$$

By making the assumption of steady-state conditions, the four elementary reactions above lead to a equation describing the instant copolymer composition:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]\,(r_1[M_1] + [M_2])}{[M_2]\,([M_1] + r_2[M_2])}$$

In this equation, the copolymer composition, $d[M_1]/d[M_2]$, is the molar ratio of the two monomer units in the copolymer. $d[M_1]/d[M_2]$ is related to the concentration of the two monomers in the feed, $[M_1]$ and $[M_2]$, and the parameters r_1 and r_2. The parameters r_1 and r_2 are the reactivity ratios and provide a measure of the preference a radical has for reacting with its own monomer rather than with the comonomer in the mixture:

$r_1 = k_{11}/k_{12}$ $\qquad$ $r_2 = k_{22}/k_{21}$

The reactivity ratios may be determined by an analysis of the change in composition of the feed (or of the copolymer) during the very early stages of polymerization. Authors such as Cowie[41] and Odian[42] have discussed the significance of reactivity ratios. If the reactivity ratio for the first monomer is greater than one, the monomer tends to produce homopolymers, or block polymers. When the reactivity ratios for both of the two monomers are approximately equal to one then the copolymerization conditions are said to be "ideal" and a random copolymer is produced. When the reactivity ratios of the two monomers are both less than one, then an alternating copolymer tends to be produced. Reactivity ratios will vary for each monomer depending on the type of polymerization technique employed.

The reactivity ratios for methylmethacrylate and 4-methylstyrene are 0.405 and 0.440 respectively for a free radical polymerization.[28] Since both reactivity ratios are less than one, a tendency towards an alternating copolymer structure should result. In addition, since the reactivity ratios are both similar in magnitude, the copolymer composition will mimic that of the feed ratio.

Table 5.5 Radical Reactivity Ratio [28,11,12,13]

M_1	M_2	r_1	r_2
MMA	4MS	0.405	0.44
MMA	St	0.49	0.48
BMA	St	0.40	0.56
DMA	St	0.36	0.56

St, styrene; 4MS, 4-methylstyrene; MMA, methyl methacrylate; BMA, butyl methacrylate; DMA, dodecyl methacrylate.

The reactivity ratios of 4-methylstyrene/butyl methacrylate and 4-methylstyrene/ dodecyl methacrylate have not been reported in chemical literature (Table 5.5). However, the reactivity ratios for styrene/butyl methacrylate and styrene/dodecyl methacrylate can be found. As well, the values for the reactivity ratios of 4-methylstyrene/methyl methacrylate and styrene/methyl methacrylate, are similar. Hence, we assume the reactivities ratios of 4MS/ BMA and 4MS/DMA are similar to those of St/BMA and St/DMA.

Hence, their copolymers will also tend to form alternating copolymers and their copolymer composition should mimic the feed molar ratio.

5.4.3.2 Characterization of Poly(4-methylstyrene-*co*-alkyl methacrylate) and Functional Poly(4-methylstyrene-*co*-alkyl methacrylate)

5.4.3.2a Poly(4-methylstyrene-*co*-methyl methacrylate) and Functional Poly(4-methylstyrene-*co*-methyl methacrylate)

Characterization of copolymers and functional copolymers was carried out by proton NMR spectroscopy.

Figure 5.8 shows the ^{1}H NMR spectrums of poly(4-methylstyrene), poly(methyl methacrylate), and poly(4-methylstyrene-co-methyl methacrylate). For poly(4-methylstyrene) (see Figure 5.8 (A)), the detail of each peak assignment was discussed in section 2.4.1.1. For poly(methyl methacrylate) (see Figure 5.8 (B)), the NMR spectrum was described in section 5.4.2. The proton NMR spectrum of poly(4-methylstyrene-co-methylmethacryate) is shown in Figure 5.8 (C). Aromatic protons of 4-methylstyrene appear at 6-7 ppm (broad with a shoulder), the 4-methyl proton appears at 2.24 ppm, α-methylene protons of methyl methacrylate at 0.75-1.0 ppm, the methoxy protons at 2.8-3.5 ppm, the methylene hydrogen at 1.0-1.9 ppm, and the methine hydrogen at 1.9 ppm.

The NMR spectrum of the oxidized copolymer of 4-methylstyrene and methyl methacrylate is shown in Figure 5.9 (B). Comparing (A) and (B), because the methyl groups were selectively oxidized to aldehyde and carboxylic acid groups, this results in the additional peaks in 9.8 ppm and 7.50, 7.80 ppm corresponding to aromatic protons ortho to aldehyde and carboxylic acid.

After cobalt(III) acetate/lithium chloride oxidation, the chloromethyl groups were introduced into 4-methylstyrene units of copolymer, it is confirmed by an additional peak at 4.48 ppm in the proton NMR spectrum (Figure 5.10 (B)).

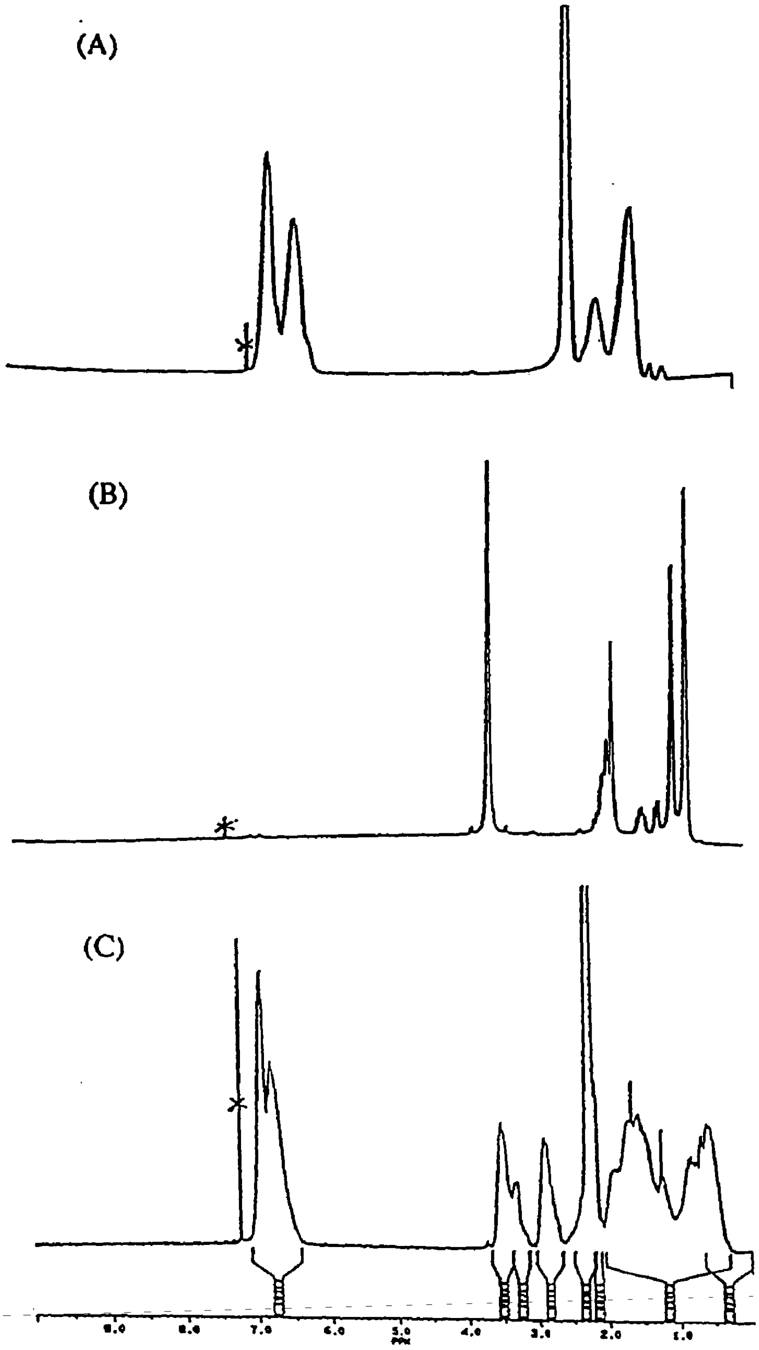


Figure 5.8 ^{1}H NMR spectra of poly(4-methylstyrene) (A), poly(methyl methacrylate) (B), and poly(4-methylstyrene-co-methyl methacrylate) (1:1) (C).

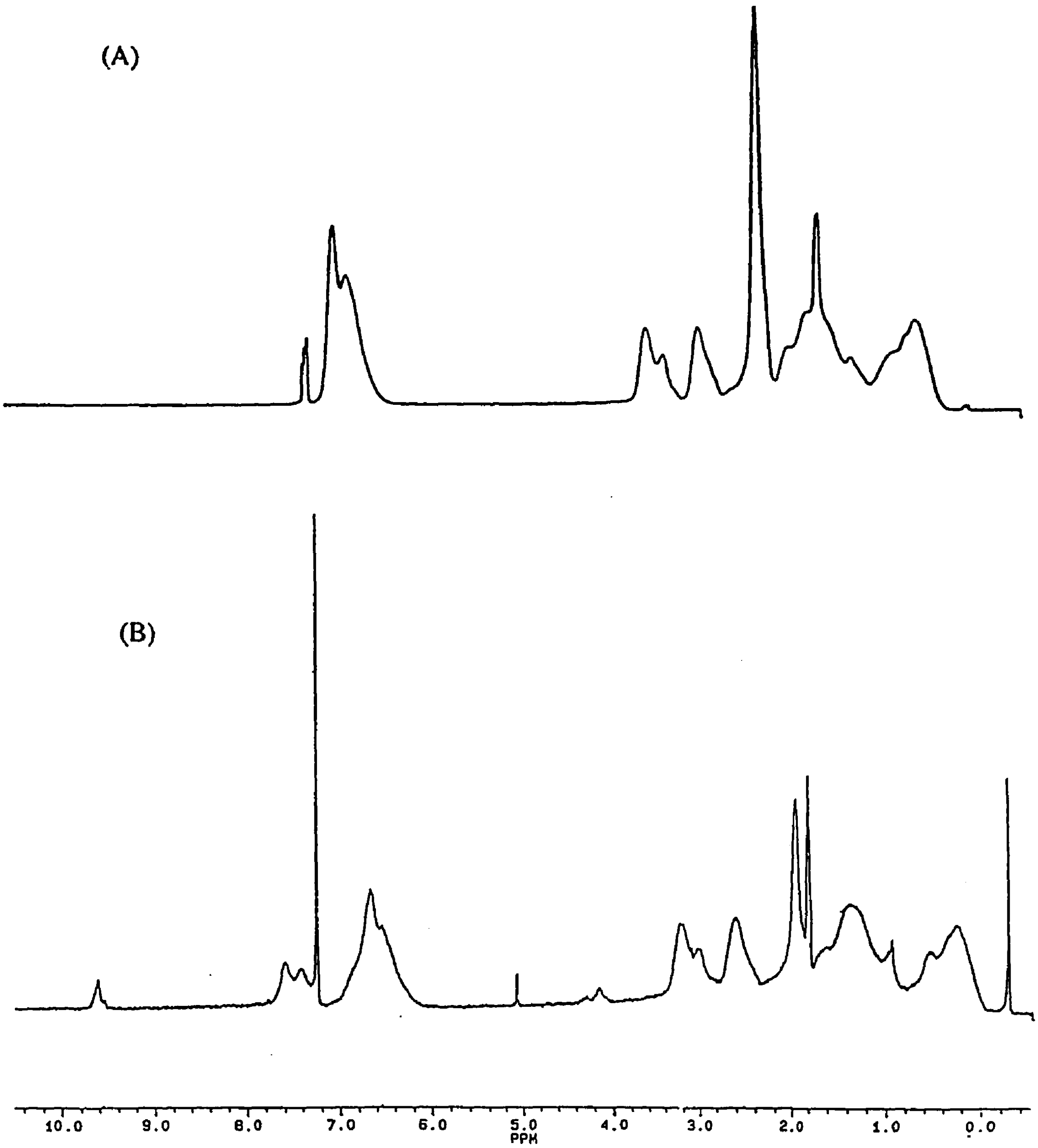


Figure 5.9 ^{1}H NMR spectra of copolymer of 4-methylstyrene and methyl methacrylate after Co(II) oxidation: (A) Copolymer of 4-methylstyrene and methyl methacrylate. (B) Oxidized copolymer (containing 17.7 % of aldehyde and 29.5 % of carboxylic acid groups).

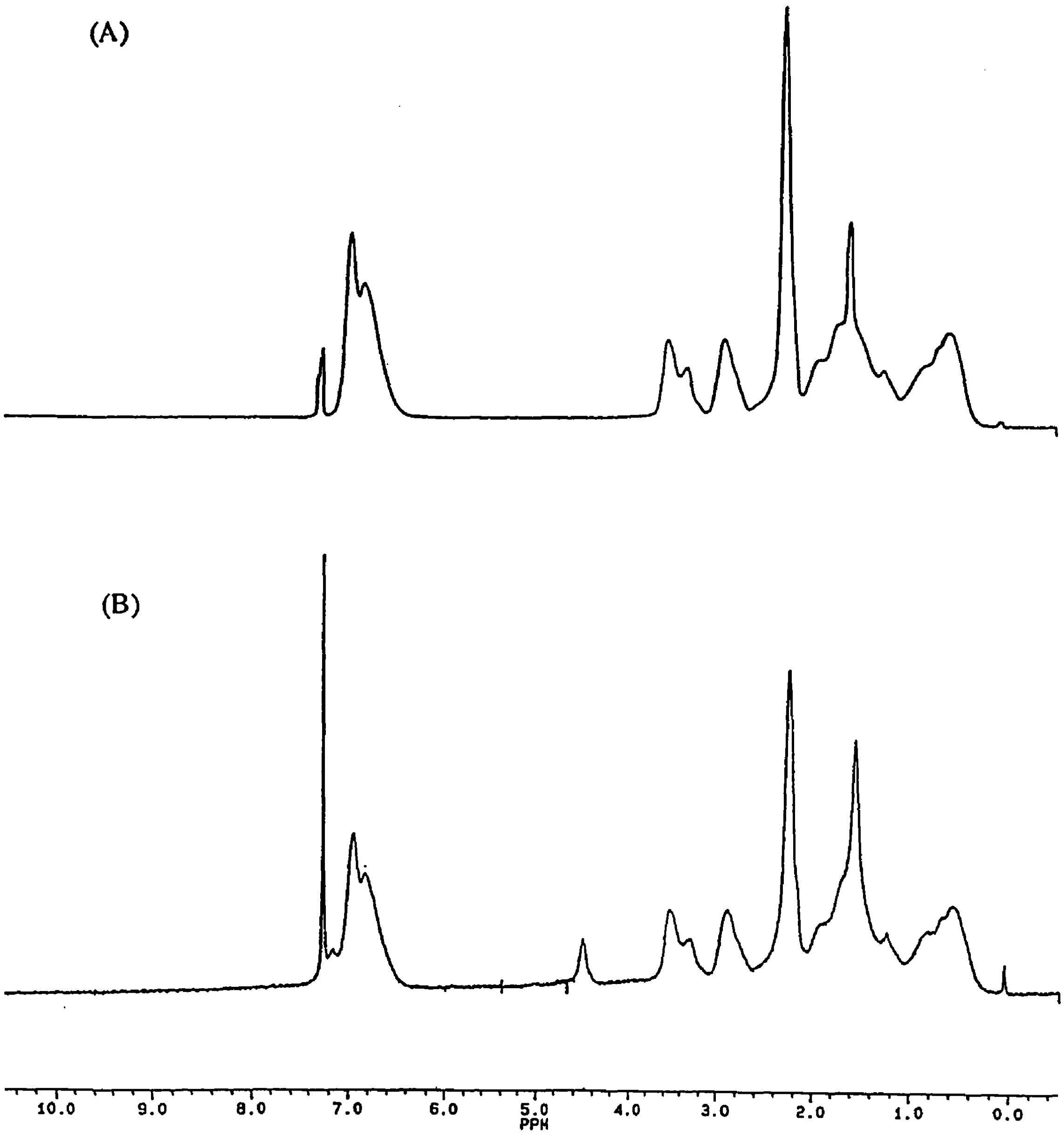


Figure 5.10 ^1H NMR spectra of copolymer of 4-methylstyrene and methyl methacrylate after Co(III) oxidation: (A) Copolymer of 4-methylstyrene and methyl methacrylate. (B) Oxidized copolymer (containing 24.2 % of chloromethyl groups).

5.4.3.2b Poly(4-methylstyrene-*co*-*n*-butyl methacrylate) and Functional Poly(4-methylstyrene-*co*-*n*-butyl methacryate)

Characterization of poly(4-methylstyrene-*co*-*n*-butyl methacrylate) by proton NMR are as follows:

6.0-7.0 ppm	broad with a shoulder	aromatic H of 4-methylstyrene
2.24 ppm	single peak	4-methyl H of 4-methylstyrene
1.9 ppm		methine H of 4-methylstyrene
0.3-1.0 ppm		α-methyl H of butyl methacrylate
2.8-4.0 ppm		methoxyl H of butyl methacrylate
1.0-1.9 ppm		methylene H of BMA, and 4MS

For functional copolymers of 4MS/BMA, there are additional peaks at 9.8 ppm (aldehyde H), 7.8 ppm (ortho protons to carboxylic acid), and 7.5 ppm (ortho protons to aldehyde).

5.4.3.2c Poly(4-methylstyrene-*co*-*n*-butyl methacrylate) and Functional Poly(4-methylstyrene-*co*-*n*-butyl methacryate)

Characterization of poly(4-methylstyrene-co-dodecyl methacrylate) by proton NMR is as follows:

6.0-7.0 ppm	broad with a shoulder	aromatic H of 4-methylstyrene
2.24 ppm	single peak	4-methyl H of 4-methylstyrene
1.9 ppm		methine H of 4-methylstyrene
0.2-0.7 ppm		α-methyl H of dodecyl methacrylate

2.7-4.1 ppm	methoxyl H of dodecyl methacrylate
1.0-2.0 ppm	methylene H of DMA, and 4MS

For functional copolymer of 4MS/BMA, there are additional peaks at 9.8 ppm (aldehyde H), 7.8 ppm (ortho protons to carboxylic acid), and 7.5 ppm (ortho protons to aldehyde).

5.4.4 Structure and Composition of Copolymers of 4-Methylstyren/Alkyl Methacrylate

5.4.4.1 Structure and Composition of Copolymers of 4MS/MMA

Nuclear Magnetic Resonance (NMR) spectroscopy was used to study the two homopolymers (poly(4-methylstyrene) and poly(methyl methacrylate)) as well as the various copolymers produced.

The proton NMR spectrum for poly(4-methylstyrene) shows a sharp peak at 2.3 ppm which is characteristic of the methyl group, and two broad peaks which are characteristics of aromatic protons. These peak are absent in the proton NMR spectrum for poly(methyl methacrylate). The proton NMR spectrum for poly(methyl methacrylate) shows a sharp peak at 3.5 ppm which is characteristic of the methoxy group. As well, this peak represents three protons and is absent in the proton NMR spectrum of poly-4-methylstyrene (we have discussed in section 5.4.3.2).

These two peaks (aromatic and methoxy or 4-methyl and methoxy) were used to determine the ratio of 4-methylstyrene units to methyl methacrylate units in the copolymers that were produced.

Table 5.6 Comparison of Feed Molar Ratio and Copolymer Composition

Run#	Feed Molar Ratio				Copolymer Composition	
	4MS	MMA	4MS%	MMA%	4MS%	MMA%
h-3	1	2	33	67	38	62
h-1	1	1	50	50	48	52
h-2	2	1	67	33	63	37
h-4	10	1	90	10	86	14

Table 5.6 shows that the overall copolymer composition is almost identical to the feed ratio. It means the copolymer composition mimics the feed ratio at these high conversions.

Overall, each copolymer before oxidation contains three possible types of environments around any given 4-methylstyrene unit. It can be surrounded by two methylmethacrylate units, by two 4-methylstyrene units or by one of each. It is expected that the reactivity ratios favour the alternating sequence and so the environment where two methylmethacrylate units surround the 4-methylstyrene is high for all cases. From the reactivity ratios for the two monomers, as well as from the monomer feed ratios, a table can be constructed showing the probabilities of structural arrangement (in a qualitative way). Table 5.7 outlines these probabilities for the environments around a given 4-methylstyrene unit. Because the reactivity ratios for both monomers are less than one, each monomer tends to copolymerize with the other, hence the alternating sequence would be preferred.

Table 5.7 Probabilities of Environments for 4-Rstyrene*

Ratio MMA:4-MS	MMA-4RS-MMA	MMA-4RS-4RS	4RS-4RS-4RS
2:1	**Very High**	Low	Very Low
1:1	High	Low	Low
1:2	High	**Very High**	Low

* R = methyl, aldehyde or carboxylic acid

After oxidation the number of environments increase as some of the methyl groups in the 4-methylstyrene units change from methyl to aldehyde and carboxylic acid. It is expected that the environment where the 4-methylstyrene unit is surrounded by two methylmethacrylate units after oxidation gives sharper signals than either of the other two environments. To check this expectation a comparison of the two "very high" probabilities are done. That is the 2:1 copolymer containing two methyl methacrylates on either side is compared with the 1:2 copolymer with one methylmethacrylate and one 4-methylstyrene on either side.

Looking at the NMR spectra in Figure 5.8, Figure 5.13, it is found that all the 4-methylstyrene signals in the 2:1 oxidized copolymer are sharper than the corresponding 4-

methylstyrene signals in the 1:2 oxidized copolymer. These signals include the unoxidized methyl groups, the aldehyde protons, and the aromatic protons (from the unoxidized 4-methylstyrene units and the aldehyde containing units). This arises because in the 2:1 copolymer there is only one configuration for the 4-methylstyrene units which is independent of the degree of oxidation of the copolymer (whether the R group is a methyl, an aldehyde or a carboxylic acid group). This is seen in Figure 5.11.

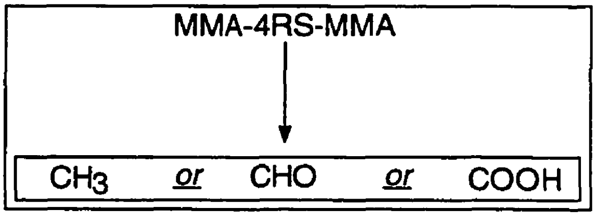


Figure 5.11 Environments After Oxidation for 2:1 Copolymer, Poly(methylmethacrylate-*co*-4-methylstyrene)

In the 1:2 copolymer there are three different configurations of the copolymer arrangement for each central 4RS. This gives rise to more environments and so the peaks are broadened in the NMR spectra. The types of configurations are seen in Figure 5.12.

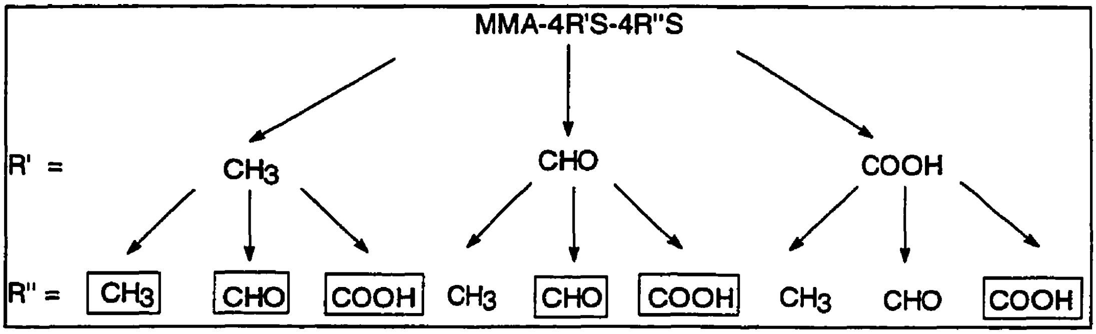


Figure 5.12 Environments after oxidation for 1:2 copolymer, Poly(methylmethacrylate-*co*-4-methylstyrene)

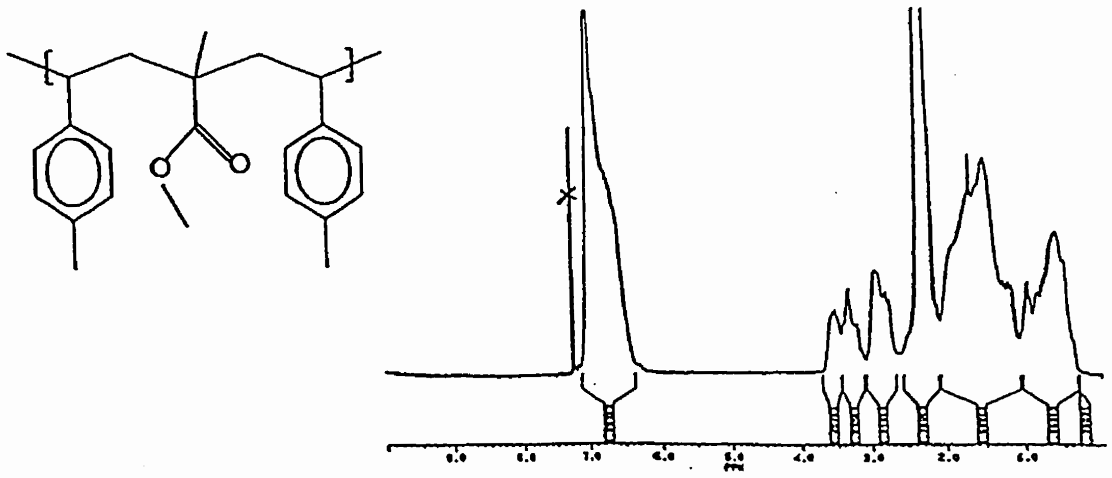
Comparing the NMR spectra of the three copolymers before oxidation the aromatic hydrogens are sharper for the 2:1 copolymer and broaden slightly for the 1:1 copolymer. Figure 5.13 shows that the 1:2 copolymer has very broad peaks. Again, this can be explained with the lower number of environments for the 2:1 copolymer than the 1:2 copolymer.

Based on the above discussion, for the copolymer of 4MS/MMA with 10:1 (4MS/MMA) feed ratio, the very high probability is that there is a short 4-methylstyrene block which is connected with MMA:

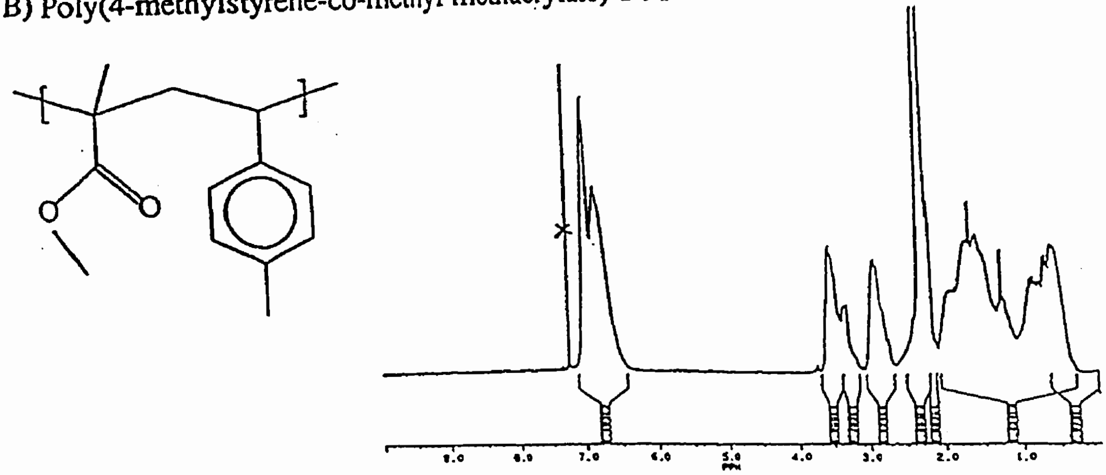
-MMA-4MS-4MS-4MS-4MS-4MS-4MS-4MS-4MS-4MS-4MS-4MS-MMA-

After oxidation, the NMR spectrum should show much broader peaks than the other three copolymers (1/2; 1/1; 2/1 for 4MS/MMA), and be close to an oxidized homopolymer. This is in Figure 5.14.

A) Poly(4-methylstyrene-co-methyl methacrylate) 2 : 1



B) Poly(4-methylstyrene-co-methyl methacrylate) 1 : 1



C) Poly(4-methylstyrene-co-methyl methacrylate) 1 : 2

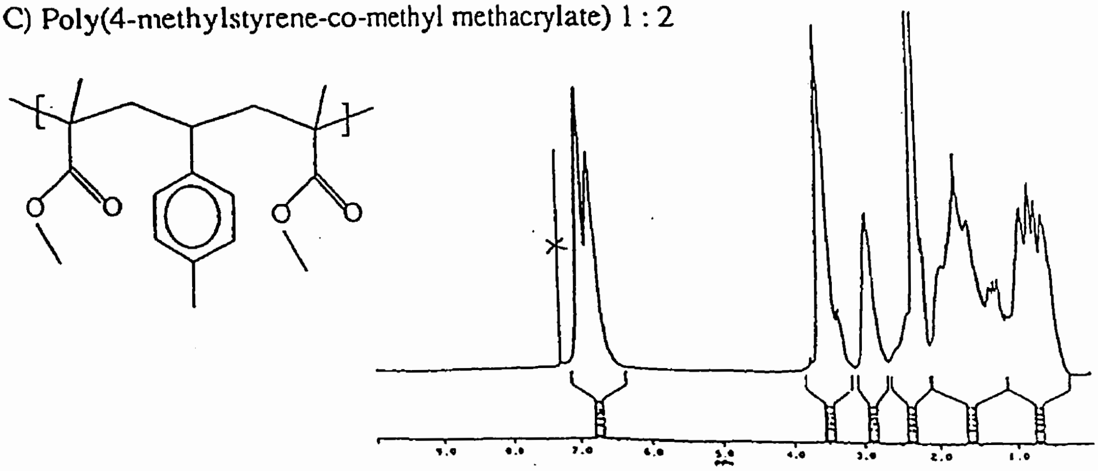


Figure 5.13 Comparison of ¹HNMR spectra of copolymers of 4-methylstyrene and methyl methacrylate with different feed ratio

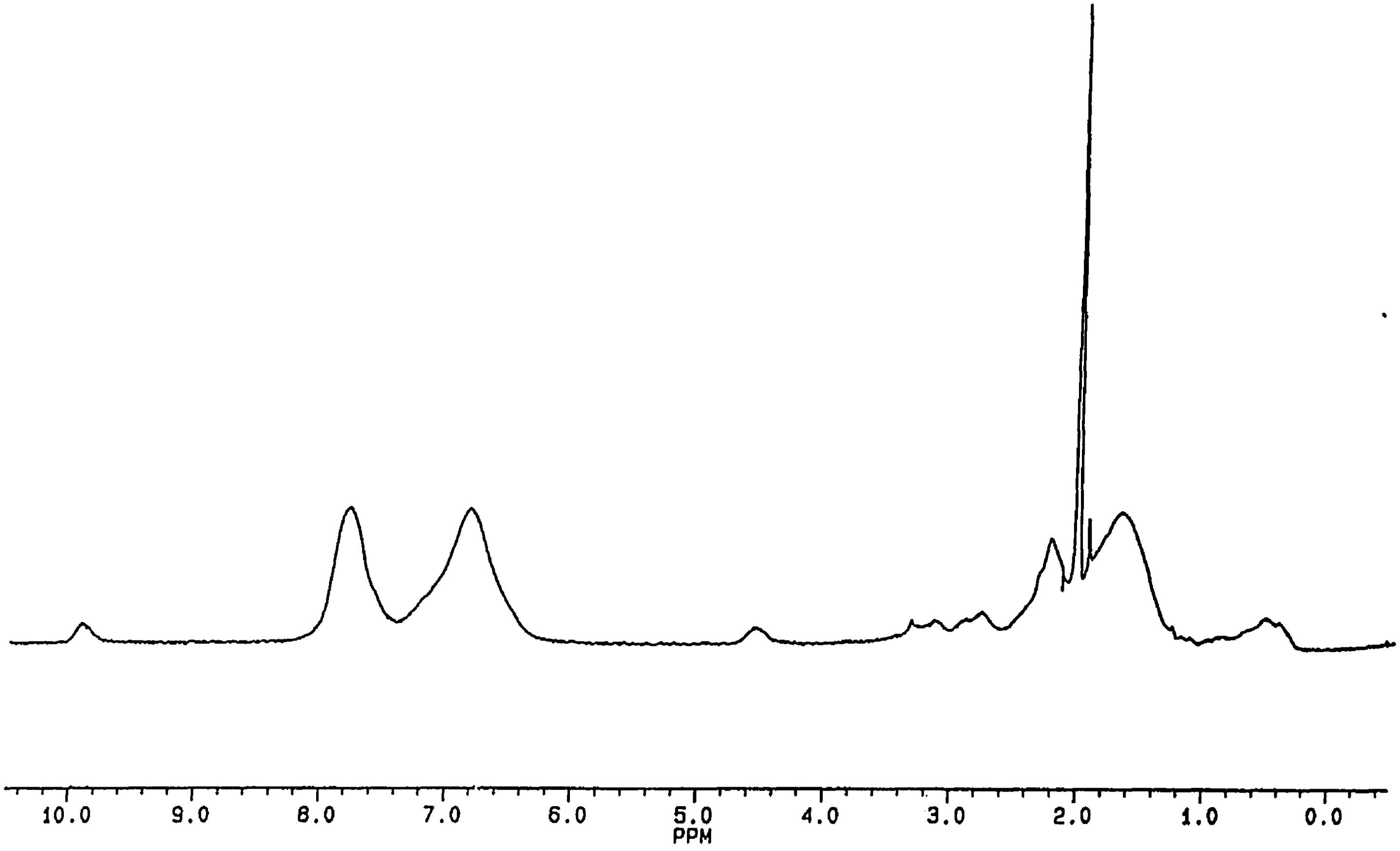


Figure 5.14 ¹HNMR spectra of copolymers of 4-methylstyrene and methyl methacrylate with 10:1 feed ratio after Co(II) oxidation

5.4.4.2 Structure and Composition of Copolymer of 4MS/BMA

The structure and copolymer composition of the copolymer of 4MS/BMA were similarly determined by proton NMR spectroscopy. The method used to determine copolymer composition was the same as that used for the copolymer of 4MS/MMA. The integration ratio of aromatic protons and methyleneoxy protons were related to the mole ratio of 4-methylstyrene units to *n*-butyl methacrylate units. The following table is the comparison of feed ratio and copolymer composition.

Table 5.8 Comparison of Feed Molar Ratio and Copolymer Composition

Run#	Feed Molar Ratio				Copolymer Composition	
	4MS	BMA	4MS%	BMA%	4MS%	BMA%
f-4	1	2	33	67	32	68
f-1	1	1	50	50	49	51
f-3	2	1	67	33	59	41
f-5	10	1	90	10	85	15

Table 5.8 indicates that the copolymer compositions mimic the feed ratio. For the comonomer sequence, an argument similar to copolymer of 4-methylstyrene and methyl methacrylate can be made. Based on the consideration of the probable environment of 4RSt (R = methyl, aldehyde, and carboxylic acid), and the environment after oxidation, for each feed ratio of the copolymer of 4MS/BMA, the idealized structure of the copolymers are:

4MS : BMA	Structure
1 : 2	-BMA-BMA-4MS-BMA-BMA-4MS-BMA-BMA-4MS-
1 : 1	-BMA-4MS-BMA-4MS-BMA-4MS-BMA-4MS-BMA-
2 : 1	-BMA-4MS-4MS-BMA-4MS-4MS-BMA-4MS-4MS-
10 : 1	-BMA-4MS-4MS-4MS-4MS-4MS-4MS-4MS-4MS-4MS-4MS-

5.4.4.3 Structure and Composition of Copolymer of 4MS/DMA

The proton NMR spectrums of the copolymer of 4MS/DMA and the functional copolymer of 4MS/DMA were carefully studied. The same conclusions were obtained (Table 5.9):

Table 5.9 Comparison of Feed Molar Ratio and Copolymer Composition

Run#	Feed Molar Ratio				Copolymer Composition	
	4MS	DMA	4MS%	DMA%	4MS%	DMA%
i-1	1	2	33	67	30	70
i-2	1	1	50	50	40	60
i-3	2	1	67	33	58	42

1). The copolymer composition is close to the feed mole ratio.

2). For the copolymers with 1:2 and 1:1 (4MS/DMA) feed ratios, the copolymer structures tend to those in which the 4-methylstyrene unit is surrounded by dodecyl methacrylate units. However, the structure of copolymers with 2:1 and 10:1 (4MS/DMA) feed ratio have short 4-methylstyrene blocks (two or ten 4-methylstyrene units).

5.4.5 Oxidative Functionalization of Copolymer of 4-Methylstyrene/Alkyl Methacrylate by Cobalt (II) Acetate/Sodium Bromide/Air

5.4.5.1 Functionality and Resistance of Copolymer Backbone to Oxidation for Poly(4MS-*co*-MMA)

The copolymers with four different feed ratios were oxidized by the cobalt (II) acetate catalyzed procedure. Each copolymer was separately dissolved in an equal volume of glacial acetic acid and cyclohexane, to which cobalt diacetate tetrahydrate ($Co(OAc)_2 \bullet 4H_2O$) was added. The solution became pink. The mixture was heated at a temperature of 60°C after air was continuously bubbled through it for 10 minutes. The sodium bromide was added immediately. The reaction time was counted at this point. The mixture was constantly stirred for the duration of the reaction. The colour of the solution changed from pink to dark pink, then purple and finally black. Different reaction times were set. The isolated copolymer were then characterized by both NMR and GPC. The results obtained can be seen in the Table 5.10, Table 5.11, Table 5.12 and Table 5.13.

Table 5.10 Results for Poly(4MS-co-MMA) Oxidation (4MS/MMA = 1:2)

Run#	Reaction Time (Hours)	-CHO%	-COOH%	Tot.%	Mn	Mw/Mn
h-3OA	0.50	6.3	5.4	11.7	15,300	1.90
h-3OB	2.0	24.3	14.2	38.5	15,500	1.95
h-3OC	7.0	26.9	32.6	59.5	14,800	1.91

note: all functionality is relative to 4-methylstyrene.

Experimental Conditions: Copolymer: Mn 15,700; Mw/Mn 1.74; Copolymer 3.00g (containing 4MS 12.70 mmol); $Co(OAc)_2 \bullet 4H_2O$ 1.270 mmol; NaBr 1.270 mmol; HOAc 100 mL; Cyclohexane 120 mL; 60°C,; Air 204 mL/min.

Table 5.11 Results for Poly(4MS-co-MMA) Oxidation (4MS/MMA = 1:1)

Run#	Reaction Time (Hours)	-CHO%	-COOH%	Tot.%	Mn	Mw/Mn
h-1OA	0.50	7.1	5.8	12.9	17,200	1.88
h-1OB	2.0	20.6	17.7	38.3	16,500	1.90
h-1OC	6.0	21.0	68.7	89.7	16,700	1.96

Experimental Conditions: Copolymer: Mn 16,300; Mw/Mn 1.91; Copolymer 3.00g (containing 4MS 15.48 mmol); $Co(OAc)_2 \bullet 4H_2O$ 1.548 mmol; NaBr 1.548 mmol; HOAc 100 mL; Cyclohexane 100 mL; 60°C,; Air 204 mL/min.

Table 5.12 Results for Poly(4MS-co-MMA) Oxidation (4MS/MMA = 2:1)

Run#	Reaction Time (Hours)	-CHO%	-COOH%	Tot.%	Mn	Mw/Mn
h-2OA	0.50	19.5	9.3	28.8	20,200	1.73
h-2OB	2.0	17.9	31.3	49.2	16,000	1.93
h-2OC	7.0	12.9	57.3	70.2	13,400	2.04

Experimental Conditions: Copolymer: Mn 19,200; Mw/Mn 1.65; Copolymer 3.00g (containing 4MS 18.35 mmol); $Co(OAc)_2 \bullet 4H_2O$ 1.835 mmol; NaBr 1.835 mmol; HOAc 100 mL; Cyclohexane 100 mL; 60°C,; Air 204 mL/min.

Table 5.13 Results for Poly(4MS-co-MMA) Oxidation (4MS/MMA = 10:1)

Run#	Reaction Time (Hours)	-CHO%	-COOH%	Tot.%	Mn	Mw/Mn
h-4OA	0.50	9.2	4.2	13.4	17,400	2.42
h-4OB	2.0	19.0	43.1	62.1	7,200	2.29
h-4OC	7.0	15.2	64.5	79.7	6,400	1.91

Experimental Conditions: Copolymer: Mn 21,300; Mw/Mn 2.26; Copolymer 3.00g (containing 4MS 21.57 mmol); $Co(OAc)_2 \bullet 4H_2O$ 2.157 mmol; NaBr 2.157 mmol; HOAc 100 mL; Cyclohexane 100 mL; 60°C,; Air 204 mL/min.

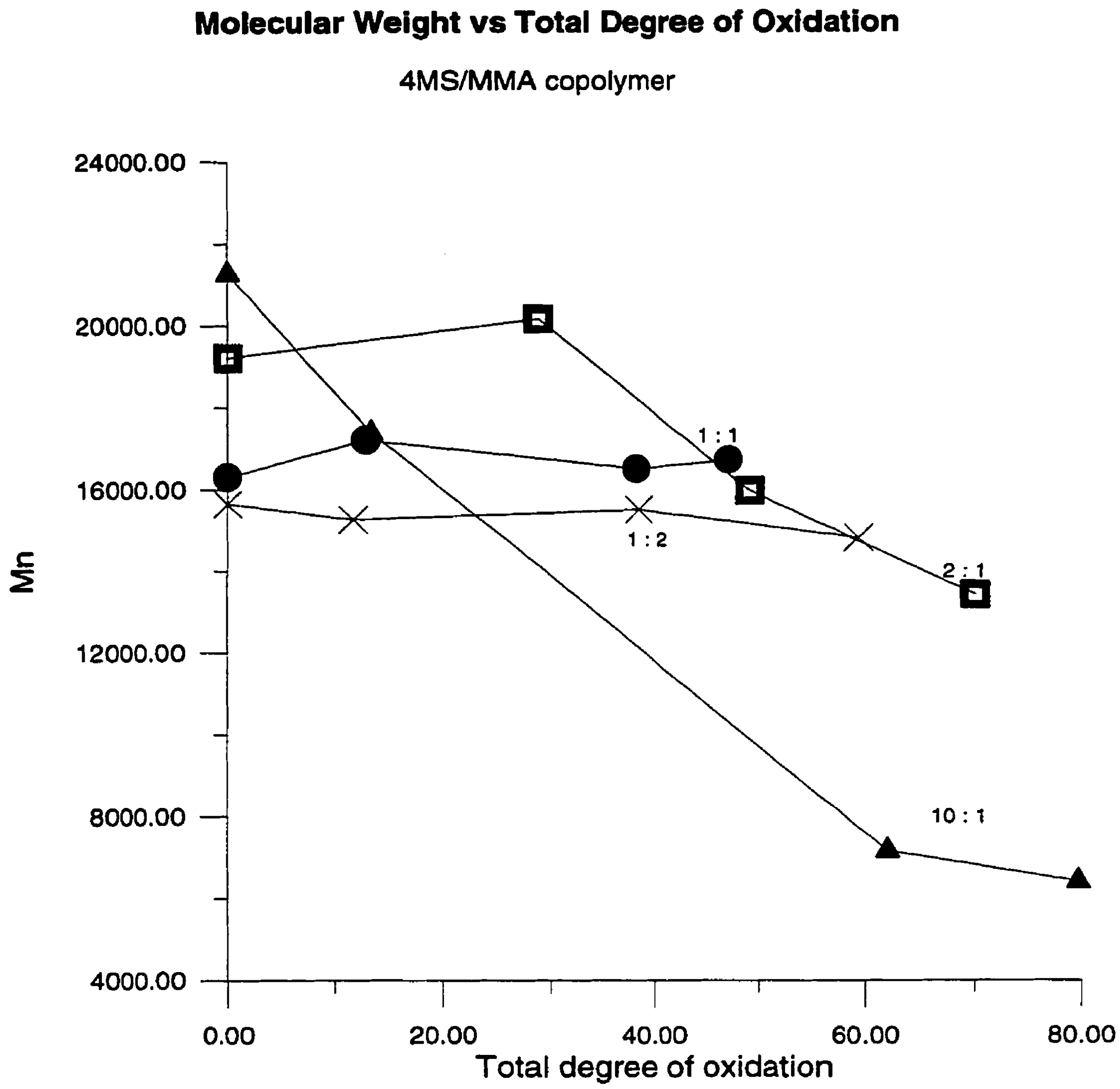


Figure 5.15 Relationship of molecular weight and oxidation yield for copolymers of 4-methylstyrene and methyl methacrylate (data from Table 5.10, 5.11, 5.12 and 5.13)

Figure 5.15 shows molecular weight vs total oxidation degree for 4MS-MMA copolymers with different feed molar ratios. Cobalt (II) acetate catalyzed oxidation converted some of the 4-methyl units to aldehyde and carboxylic acid functional groups. The alkyl methacrylate units were not affected by the oxidation (see discussion in 5.4.2).

Table 5.10, Table 5.11, Table 5.12, Table 5.13, and Figure 5.15 indicates:

1) Both the total oxidation yield, and the carboxylic acid fraction, increased with increasing reaction time.

2) Oxidation did not take place at the backbone of copolymers as no reduction in molecular weight was in evidence for the copolymers with feed ratio (4MS/MMA = 1:2, and 1 : 1). After seven hours of oxidation, up to 60% of oxidation yield was obtained (h-3OC), but the molecular weight of oxidized copolymer showed no significant change (15,700 - 14,800).

3) However, oxidation did take place at the backbone for these copolymers with feed ratio (4MS/MMA) 2:1 and 10:1. For example, the molecular weight of starting copolymer (10:1) was 21300, after seven hours oxidation, it went down to 6,400. For 2:1 feed ratio (4MS/MMA), at the same conditions, the change in molecular weight was from 19200 to 13400.

4) In general, the greater the 4-methylstyrene content, the greater the oxidation yield, and the bigger the reduction of molecular weight after oxidation.

The idealized structure of alternating copolymers for 4-methylstyrene and methyl methacrylate is that one 4-methylstyrene and one methyl methacrylate are connected to each other and the 4-methylstyrene units are surrounded by two methyl methacrylate units.

For a 1:1 4MS/MMA molar ratio, we assume the copolymer structure is close to ideal alternation, so the α-methyl group sterically protects the backbone from oxidation.

For 1:2 4MS/MMA molar ratio, we also assume that each 4-methylstyrene unit surrounded by two methyl methacrylate units; again, steric hindrance protects the back bone.

For 2:1 4MS/MMA molar ratio, the copolymer structure may contain the following sequences: MMA-MMA-MMA, MMA-4MS-MMA, MMA-4MS-4MS, and 4MS-4MS-4MS. The latter two sequences are sensitive to backbone cleavage, so a little backbone cleavage took place.

For 10:1 molar ratio of copolymer, we can see there are short 4MS blocks (statistic distribution) on the polymer chain (see 5.4.4.1). The protection of MMA became minimized, and much backbone cleavage occurred. After seven hours oxidation, the molecular weight of the copolymer decreased from 21,300 to 6,400.

Functionality and resistance of copolymer backbone to oxidation for poly(4MS-co-MMA) depends on comonomer ratio in the copolymer. The greater the 4-methylstyrene content, the greater the functionality we can get, and the poorer the resistance of the backbone to oxidation. This conclusion results from the sequence length of the 4-methylstyrene unit in the copolymer: if the 4-methylstyrene unit is surrounded by two methyl methacrylate units, the α-methyl groups gives excellent protection to the backbone. In contrast, if there is a short 4-methylstyrene block in the copolymer chain, the backbone cleavage unavoidably took place.

5.4.5.2 Functionality and Resistance of Copolymer Backbone to Oxidation for Poly(4MS-co-BMA)

To study the functionality and resistance of copolymer backbone to oxidation for poly(4MS-co-BMA), the oxidation yield for each separate run was calculated by using NMR data, and the molecular weight of oxidized copolymers was measured by size exclusion chromatography. All of the results are shown in Table 5.14, Table 5.15, Table 5.16 and Table 5.17.

Table 5.14 Results for Poly(4MS-co-BMA) Oxidation (4MS/BMA = 1:2)

Run#	Reaction Time (Hours)	-CHO%	-COOH%	Tot.%	Mn	Mw/Mn
f-4BOA	0.50	10.3	3.8	14.1	22,100	2.07
f-4BOB	2.0	10.8	8.3	19.1	22,200	2.36
f-4BOC	7.0	22.3	13.9	36.2	22,200	2.19

Experimental Conditions: Copolymer: Mn 21,300; Mw/Mn 2.13; Copolymer 3.00g (containing 4MS 9.06 mmol); $Co(OAc)_2{\bullet}4H_2O$ 0.906 mmol; NaBr 0.906 mmol; HOAc 100 mL; Cyclohexane 100 mL; 60°C,; Air 204 mL/min.

Table 5.15 Results for Poly(4MS-co-BMA) Oxidation (4MS/BMA = 1:1)

Run#	Reaction Time (Hours)	-CHO%	-COOH%	Tot.%	Mn	Mw/Mn
f-1BOA	0.75	10.8	8.8	19.6	22,500	2.00
f-1BOB	2.0	23.9	19.2	43.1	27,500	1.92
f-1BOC	7.0	17.0	38.9	55.9	25,400	1.97

Experimental Conditions: Copolymer: Mn 23,900; Mw/Mn 1.72; Copolymer 3.00g (containing 4MS 13.45 mmol); $Co(OAc)_2 \bullet 4H_2O$ 1.345 mmol; NaBr 1.345 mmol; HOAc 100 mL; Cyclohexane 100 mL; 60°C; Air 204 mL/min.

Table 5.16 Results for Poly(4MS-co-BMA) Oxidation (4MS/BMA = 2:1)

Run#	Reaction Time (Hours)	-CHO%	-COOH%	Tot.%	Mn	Mw/Mn
f-3BOA	0.25	10.2	-	10.2	27,600	1.83
f-3BOB	2.0	14.5	35.3	49.8	19,500	1.92
f-3BOC	7.0	11.4	57.9	69.3	18,300	1.95

Experimental Conditions: Copolymer: Mn 25,000; Mw/Mn 1.65; Copolymer 3.00g (containing 4MS 16.75 mmol); $Co(OAc)_2 \bullet 4H_2O$ 1.675 mmol; NaBr 1.675 mmol; HOAc 100 mL; Cyclohexane 100 mL; 60°C; Air 204 mL/min.

Table 5.17 Results for Poly(4MS-co-BMA) Oxidation (4MS/BMA = 10:1)

Run#	Reaction Time (Hours)	-CHO%	-COOH%	Tot.%	Mn	Mw/Mn
f-5BOA	0.50	14.9	10.9	25.8	11,200	2.66
f-5BOB	2.0	17.4	38.2	55.6	7,500	2.14
f-5BOC	7.0	17.5	57.0	74.5	5,300	2.18

Experimental Conditions: Copolymer: Mn 22,900; Mw/Mn 2.13; Copolymer 3.00g (containing 4MS 21.4 mmol); $Co(OAc)_2 \bullet 4H_2O$ 2.14 mmol; NaBr 2.14 mmol; HOAc 100 mL; Cyclohexane 100 mL; 60°C; Air 204 mL/min.

These results indicate again:

1) Oxidation yield increased with reaction time.

2) No oxidation took place at the backbone of copolymers with the feed ratio 1:2 and 1:1 (4MS/BMA). However, there is no backbone protection of copolymers with feed ratio 2:1 and 10:1 (4MS/BMA).

3) The reduction in molecular weight of copolymer with 10:1 feed ratio was greater than those copolymer with 2:1 feed ratio.

5.4.5.3 Functionality and Resistance of Copolymer Backbone to Oxidation for Poly(4MS-co-DMA)

Poly(4-methylstyrene-co-dodecyl methacrylate) with three different feed ratio were synthesized and oxidized by cobalt (II) acetate/sodium bromide/air system. Table 5.18, Table 5.19, and Table 5.20 show the results of oxidation.

Table 5.18 Results for Poly(4MS-co-DMA) Oxidation (4MS/DMA = 1:2)

Run#	Reaction Time (Hours)	-CHO%	-COOH%	Tot.%	Mn	Mw/Mn
i-2AOA	0.50	-	-	-	31,400	1.95
i-2AOB	2.0	<2.0	-	<2.0	31,900	1.90
i-2AOC	7.0	6.5	12.0	18.5	36,800	2.91

Experimental Conditions: Copolymer: Mn 31,700; Mw/Mn 1.87; Copolymer 2.44g (containing 4MS 5.03 mmol); $Co(OAc)_2•4H_2O$ 0.503 mmol; NaBr 0.503 mmol; HOAc 100 mL; Cyclohexane 100 mL; 60°C; Air 204 mL/min.

Table 5.19 Results for Poly(4MS-co-DMA) Oxidation (4MS/DMA = 1:1)

Run#	Reaction Time (Hours)	-CHO%	-COOH%	Tot.%	Mn	Mw/Mn
i-1AOA	0.50	-	-	-	23,300	1.92
i-1AOB	2.0	14.4	-	14.4	24,100	1.99
i-1AOC	7.0	17.3	-	17.3	24,199	2.60

Experimental Conditions: Copolymer: Mn 23,700; Mw/Mn 1.94; Copolymer 2.69g (containing 4MS 6.53 mmol); $Co(OAc)_2•4H_2O$ 0.653 mmol; NaBr 0.653 mmol; HOAc 100 mL; Cyclohexane 100 mL; 60°C,; Air 204 mL/min.

Table 5.20 Results for Poly(4MS-co-DMA) Oxidation (4MS/DMA = 2:1)

Run#	Reaction Time (Hours)	-CHO%	-COOH%	Tot.%	Mn	Mw/Mn
i-3AOA	0.50	-	-	-	38,200	2.27
i-3AOB	2.0	29.7	4.7	34.4	26,100	2.07
i-3AOC	7.0	9.8	39.0	48.8	20,100	1.97

Experimental Conditions: Copolymer: Mn 34,900; Mw/Mn 1.66; Copolymer 2.74g (containing 4MS 9.81 mmol); $Co(OAc)_2•4H_2O$ 0.9814 mmol; NaBr 0.981 mmol; HOAc 100 mL; Cyclohexane 100 mL; 60°C; Air 204 mL/min.

From these results, similar conclusions can again be made as for the 4MS/BMA copolymers. Different length of ester of alkyl methacrylate in copolymers affect the oxidation yield too. Table 5.21 shows these effects.

Table 5.21 Effect of Alkyl Length of Alkyl Methacrylate in Copolymer on Oxidation

Length of Ester of Alkyl methacrylate	Oxidation Yield		
	0.5 hour	2 hours	7 hours
1 carbon	28.9	49.2	70.2
4 carbon	10.2	49.8	69.2
12 carbon	-	34.4	48.8

Comparisons of the oxidation behavior between 4MS/MMA, 4MS/BMA, and 4MS/DMA copolymers shows that the longer the alkyl group, the slower the oxidation takes place. Apparently, the longer alkyl group block the way the catalysts attack the methyl groups. In summary, oxidation can be extended to copolymers, in fact, this may be used to prevent or reduce backbone cleavage.

5.4.6 Chlorination of Copolymer of 4-Methylstyrene and Methyl Methacrylate

Chlorination of poly(4-methylstyrene-co-methyl methacrylate) was carried out by cobalt (III) acetate/lithium chloride/nitrogen oxidation process. The oxidation reaction ran for 2 hours.

The following shows the results of chlorination:

h-1ch1	1 : 1 (4MS/MMA)	2 hours reaction	25.2% of -CH_2Cl
h-3ch1	1 : 2 (4MS/MMA)	2 hours reaction	24.2% of -CH_2Cl

It indicates that chloromethyl groups could be introduced into copolymers of 4-methylstyrene, and our new process of chlorination works for copolymers. Also it shows the good reproducibility for the chlorination process.

5.4.7 Potential Application of Functional Polymers

5.4.7.1 Potential Application of Functional Poly(4-methylstyrene)

Poly(4-methylstyrene) containing acetoxymethyl functional groups can be used as a crosslinking agent for many elastomers (SBS, SIS and so on). Poly(4-acetoxymethylstyrene) is crosslinked by photo-proton generation process. If the copolymer of styrene- butadiene-styrene is mixed with a little acetoxylated poly(4-methylstyrene), when it is exposed in photo radiation, it would be crosslinked. These kinds of rubber may find specific applications.

Chlorination process could be applied in chloromethylation of crosslinked styrene resins. First, we can make crosslinked 4-methylstyrene resins (copolymerization of 4-methylstyrene and divinyl benzene), then chlorinate this resin with a Co(III) acetate/lithium chloride/nitrogen oxidation. The advantages of this procedure are:

1) the degree of chlorination is easy to control.

2) use of the carcinogenic agent chloromethyl alkyl ether is prevented.

Highly oxidized poly(4-methylstyrene) (with aldehyde and carboxylic acid groups) is soluble in aqueous base. This may find application in water treatment.

5.4.7.2 Potential Application of Functional Copolymer of 4-Methylstyrene

Poly(methyl methacrylate-*co*-4-methylstyrene) made in the ratios of 1:1, or 2:1 and subjected to cobalt catalyzed oxidation do not suffer from backbone cleavage. The methyl group in the 4-methylstyrene units can be converted to functional groups of carboxylic acid and aldehydes. These two features give the copolymers some interesting properties. Some of these applications include:

i) additives for lubricating oils and
ii) bone implant adhesives.

These applications are now briefly explained.

Poly(methyl methacrylate) is used in the biomedical field as a bone implant adhesive. The problem with bone implants is the length of time that is required for new bone to grow around the implant and to be firmly secured in place. If the oxidized copolymer of methylmethacrylate and 4-methylstyrene is used, the adhesive qualities of the methylmethacrylate would exist; however, the carboxylic acid groups from the 4-methylstyrene units would provide a site for new bone growth. Calcium phosphates which are needed for new bone growth have been shown to be attracted to the carboxylic acid groups.[43]

The 4MS/αMS copolymers are useful in adhesives, sealants, and molding compounds. For example, the 4MS/αMS copolymers are useful in pressure sensitive adhesives, construction adhesives, assembly adhesives, sheet molding compounds, compression molding compounds, injection molding compounds, and extrusion molding compounds.[44]

Carboxylic acid groups improve the hydrophilic property of functional 4MS/αMS copolymers. This should enhance their adhesive strength of adhesive and find more specific applications for them.

5.5 CONCLUSION

Copolymers of 4-methylstyrene/methyl methacrylate, 4-methylstyrene/n-butyl methacrylate, and 4-methylstyrene/dodecyl methacrylate with different feed ratio (4MS/alkyl methacrylate (AMA) = 1:2, 1:1, 2:1, or 10:1) were prepared by free radical polymerization. These copolymers were characterized by proton NMR and SEC techniques.

The structure of these copolymers were discussed with regard to the information provided by ^{1}H NMR. The idealized comonomer sequence of copolymer of 4MS/AMA mimic the feed ratios. For a 1:2 (4MS/AMA) feed ratio, there is one 4MS unit surrounded by two AMA units. For a 1:1 (4MS/AMA) feed ratio, one 4MS unit connect one AMA alternately. For a 2:1 feed ratio, the structure sequence is converse as those of 1:2 copolymer. In the 10:1 copolymer, there is a short 4MS block in the main chain.

The functionalities of these copolymers by Co(II)/NaBr/air oxidation were studied. The cobalt(II)/sodium bromide oxidation introduced aldehyde, and carboxylic acid groups into 4-methyl side chain of copolymers. Increasing the reaction time increased the yield of carboxylic acid and total oxidation yield. The greater the 4-methylstyrene content in copolymers, the greater oxidation yield obtained. Up to 70 % of aldehyde and carboxylic acid groups could be formed.

The resistance of the copolymer backbone to oxidation were investigated too. For 1:2 and 1:1 (4MS/AMA) copolymers, there was no backbone cleavage occurring during oxidation. For 2:1 and 10:1 copolymers, backbone cleavage took place. It depended on the 4-methylstyrene content in the copolymers: the greater the 4MS content, the bigger the reduction in molecular weight.

Chlorination of the 4-methylstyrene/methyl methacrylate copolymer was carried out by a Co(III)/LiCl system. Up to 24 % of chloromethyl groups could be introduced into the copolymer.

Oxidative functionalizations of 4-methylstyrene/α-methylstyrene copolymer were studied as well. Different functional groups (including aldehyde, carboxylic acid, acetoxy, and chloromethyl groups) were formed in the 4-methyl position by different oxidation processes.

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CHAPTER 6

THERMAL PROPERTIES OF FUNCTIONAL HOMOPOLYMERS AND COPOLYMERS OF 4-METHYLSTYRENE

6.1 AIM OF THE RESEARCH

Functional poly(4-methylstyrene)s prepared by either ceric(IV) or cobalt (III) oxidation as described in Chapter 2 and 3 have different functional groups attached to the 4-methyl side chain (e.g. acetoxy, nitrooxy, chloromethyl, and formyl groups). Functional copolymers of 4-methylstyrene and butyl methacrylate oxidized by cobalt (II)/sodium bromide as described in Chapter 5 contain aldehyde and carboxylic acid. These copolymers should have interesting thermal properties due to the presence of the plasticizing butyl (and other alkyl) groups and the polar acid groups. In terms of polymer applications, it is desirable to study their thermal properties further.

Copolymers of 4-methylstyrene/butyl methacrylate and 4-methylstyrene/dodecyl methacrylate were prepared by free radical solution polymerization using AIBN as an initiator.

The purpose of this research is to study the thermal properties of functional poly(4-methylstyrene) and functional copolymers by thermogravimetry, and to measure the glass transition temperature of copolymers of 4-methylstyrene/butylmethacrylate and /dodecyl methacrylate by differential scanning calorimetry (DSC).

6.2 A SURVEY: THE STUDY OF THERMAL PROPERTIES FOR FUNCTIONAL POLYMERS

Functional polymers based on styrenic resins have many applications. Their fundamental properties (Tg, Mn, and degradation temperature) have been studied for many years.[1]

It is well known that polystyrene thermally degrades mainly to monomer with some dimer (2,4,-diphenyl-1-butene) and trimer (2,4,6-triphenyl-1-hexene) in the absence of oxygen. The main features of thermal degradation of polystyrene include: random initiation of the main chain, depolymerization, termination, and intramolecular hydrogen transfer followed by β-scission, which generate monomer, dimer, trimer, and other volatile species (see section 6.4.1). No crosslinked residue occurs. However, certain aspects of the thermal degradation mechanism still remain the subject of discussion.[2-10]

Unfortunately, research on thermal properties for poly(4-methylstyrene) is very rare. In 1994, Cascaval and Neagu studied the thermal degradation behavior of copolymers of 4-methylstyrene and divinylbenzene using pyrolysis-gas chromatography and thermogravimetry techniques.[11] The pyrolysis products, consisted mainly of volatile aliphatic and aromatic hydrocarbons, and their composition vary with copolymer composition and pyrolysis temperature.

The study of thermal behavior of styrene divinylbenzene copolymers containing functional groups $-CH_2X$ ($X = H, Cl, I, OCOCH_3, OH, NH_2, CN$) in the para position has been carried out using pyrolysis-GC-MS by several research groups.[12,13]

Davies studied the effects of pendant functional groups (chloromethyl, sulfide, sulfoxide, sulfone, aldehyde) on thermal stability of linear polystyrene. Different pendant groups have different effects on polystyrene stability.[14] For example, initial decomposition temperatures of polystyrene bearing different pendent groups are: $-CH_2Cl$ 230°C; $-CH_2SC_2H_5$ 265°C; -H 270°C; $-CH_2SO_2C_2H_5$ 300°; -CHO 340°C.

Three types of chloromethyl-substituted polystyrene networks were prepared by different methods by S. Tsuge and his coworkers.[15] For the chloromethylated styrene-divinylbenzene copolymers the thermal behavior was studied by TGA, pyrolysis-GC. They suggested that dehydrochlorination occurred around 200°C, the residue with a methylene crosslinked structure underwent further degradation around 400°C and left involatile residue between 420-450°C.

Boinon et *al.* found that the thermal behaviors of poly(2-chloromethylstyrene) and poly(3-chloromethylstyrene) are quite different. However, the major volatile products released during the degradation are hydrogen chloride and the starting monomer, as found by means of dynamic and isothermal thermogravimetric analysis and GC-MS spectroscopy.[16] They also studied the kinetics and mechanism of thermal degradation for pure poly(chloromethylstyrene) by GC-MS spectropcopy. They reported that in the first stage, hydrogen chloride and the monomer were obtained.[17]

The study of the thermal properties of oxidized poly(4-methylstyrene) and the oxidized copolymer of 4-methylstyrene have not been described yet, although extensive study of the oxidation of poly(4-methylstyrene) has been carried out for several years.[18, 19,20]

6.3 EXPERIMENTAL METHODS

6.3.1 Materials and Their Purification

In this study, reagent grade 4-methylstyrene (4MS) monomer was purchased from Deltech Corp. It was purified by passing it through an alumina column to remove inhibitors prior to polymerization.

2,2-Azobisisobutyronitrile (AIBN) was purchased from Kodak and used as received. Glacial acetic acid, trichloroacetic acid, benzene, cyclohexane, were purchased from Aldrich and used as received. Ceric ammonium nitrate was purchased from SIGMA. It was dried at 85°C for one hour and stored in a desiccator before use. Lithium chloride was purchased from Fisher Scientific and used as received.

Cobalt (III) acetate was prepared as described in Chapter 3.

6.3.2 Radical Solution Polymerization of 4-methylstyrene)

Poly(4-methylstyrene) was prepared by radical solution polymerization at 60°C using AIBN as an initiator and toluene as a solvent under nitrogen. It was described in Chapter 2.

6.3.3 Functionalization of Poly(4-methylstyrene)

Different functional groups were introduced into poly(4-methylstyrene) by novel oxidation processes.

Acetoxy and nitrooxy groups were selectively introduced into poly(4-methylstyrene) using ceric ammonium nitrate as an oxidant, the mixture of glacial acetic acid and benzene as a solvent, under nitrogen at 80°C. The nitrooxy groups were displaced by acetoxy groups by refluxing the polymer in acetic acid for ten hours. The detailed procedure was described in Chapter 2.

Chloromethyl groups were introduced into poly(4-methylstyrene) using cobalt (III) acetate/lithium chloride as an oxidant, the mixture of glacial acetic acid and benzene as a solvent, under nitrogen at 50°C. It was described in Chapter 3.

6.3.4 Preparation of Poly(4-methylstyrene-co-alkyl methacrylate)

Copolymers of 4-methylstyrene/methyl methacrylate, /n-butyl methacrylate, and / dodecyl methacrylate were prepared by a solution free radical polymerization. AIBN was used as an initiator, cyclohexane as a solvent. The detailed experimental procedure was given in Chapter 5.

6.3.5 Functionalization of Poly(4-methylstyrene-co-alkyl methacrylate)

Functionalization of copolymers of 4-methylstyrene/alkyl methacrylate was carried out in a mixed solvent using Co(II) acetate tetrahydrate/sodium bromide/air oxidation system. The experiments were performed as in section 5.3.7.

6.3.6 DSC Measurements for Functional Homopolymers of 4-Methylstyrene

Differential Scanning Calorimetry (DSC) experiments were carried out using a DuPont 2100 instrument at a heating rate of 15°C/min in an atmosphere of flowing nitrogen (25 mL/min) and 5-10 mg of sample.

6.3.7 TGA Measurements for Functional Copolymers of 4-Methylstyrene

The thermogravimetric analysis experiments were carried out using a NETZSCH STA ANALYSIS instrument under the following operational conditions: heating rate 5.5°C /min in an atmosphere of nitrogen or air (flowing rate of 30 mL/min), 25-40 mg samples.

6.4 RESULTS AND DISCUSSION

6.4.1 Thermogravimetric Analysis of Poly(4-methylstyrene)

First, we studied the thermal properties of the parent polymer poly(4-methylstyrene), which provides the baseline data for other functional polymers.

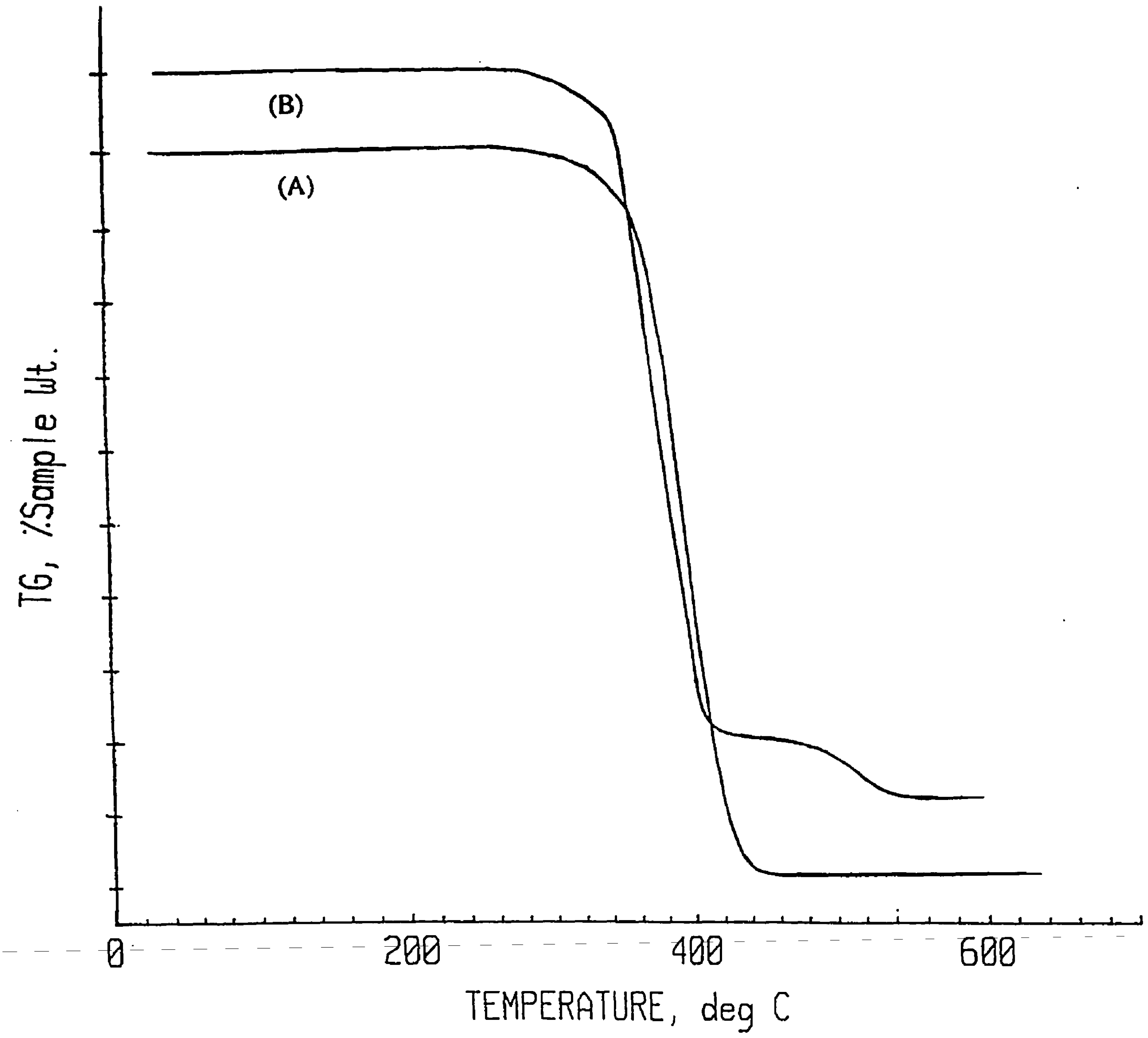


Figure 6.1 Thermograms of poly(4-methylstyrene) in nitrogen (A) and in air (B). Each plot begins at 100% on the mass axis, with each division representing a 10% mass loss

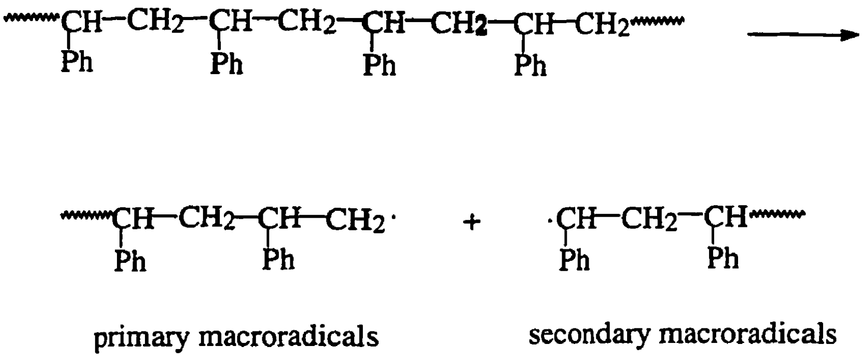
Figure 6.1 shows the dynamic thermogravimetric analysis (TGA) curves recorded for the poly(4-methylstyrene) (P4MS) homopolymer in nitrogen (curve (A)) and air (curve (B)). The degradation in nitrogen in the range 200 - 600°C, proceeded in one stage, with the entire weight loss occurring between 240°C and 440°C. The temperature corresponding to the maximum rate of degradation was 396°C.

In contrast, the degradation of poly(4-methylstyrene) in air proceeded in two separate stages. The first 91.5% of the weight loss occurred between 240°C to 410°C. The maximum rate of depolymerization took place around 378 °C. The weight loss in the second stage was around 8%, and occurred between 410°C - 540°C.

The pyrolysis products of poly(4-methylstyrene) from temperatures of 200 to 600°C in air was studied by Cascaval and Neagu.[11]by the pyrolysis-gas chromatography technique. They found that the degradation of poly(4-methylstyrene) proceeds into two stages. The first stage of weight loss (290-500°C) occurred due to primarily depolymerization. The second stages of degradation (520-600°C) is due to the secondary decomposition reaction i.e. cracking and gastification processes. The pyrolysis products consist of volatile aliphatic and aromatic hydrocarbons, which include: C1-C4 highly volatile hydrocarbons, benzene, toluene, ethylbenzene, styrene, ethyltoluene, 4-methylstyrene, ethylstyrene, naphthalene and two unknown peaks.

Thermal degradation of polystyrene has been investigated for many years. It is well known that polystyrene thermally degrades mainly to monomers with some dimer (2,4-diphenyl-1-butene), and trimer (2,4,6-triphenyl-1-hexene) in the absence of oxygen.[21,22,23,24]

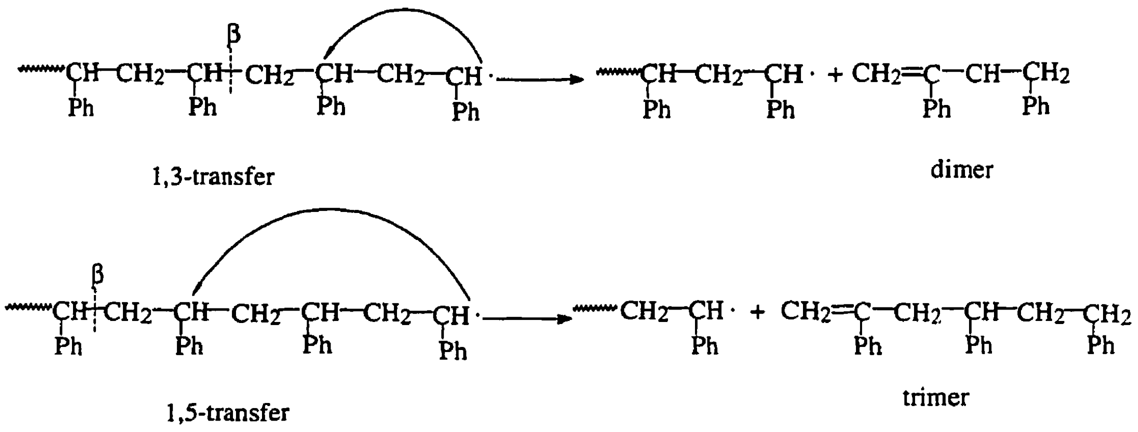
The thermal degradation of polystyrene at elevated temperatures is initiated by a random scission of the main chain to give primary and secondary macro radicals.



$$\sim\underset{Ph}{CH}-CH_2-\underset{Ph}{CH}-CH_2-\underset{Ph}{CH}-CH_2-\underset{Ph}{CH}-CH_2\sim \longrightarrow \sim\underset{Ph}{CH}-CH_2-\underset{Ph}{CH}-CH_2\cdot + \cdot\underset{Ph}{CH}-CH_2-\underset{Ph}{CH}\sim$$

Both macroradicals chiefly depolymerize to the monomer.

In addition, the macroradicals can engage in hydrogen abstraction. The formation of the dimer and the trimer have been interpreted by intramolecular 1,3-and 1,5-transfer from the terminal group of the secondary macroradicals to the reactive tertiary carbon followed by β-scission.[7, 25-29]

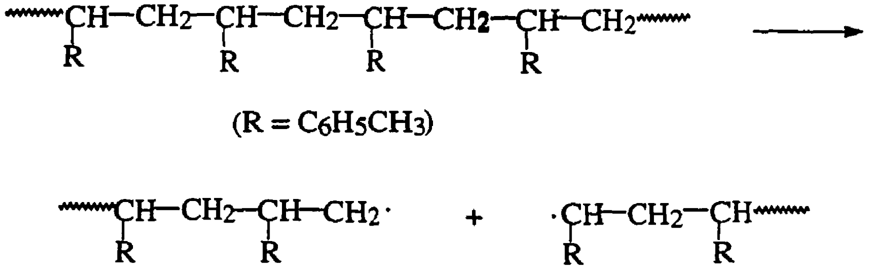


$$\sim\underset{Ph}{CH}-CH_2-\underset{Ph}{CH}-CH_2-\underset{Ph}{CH}-CH_2-\underset{Ph}{CH}\cdot \longrightarrow \sim\underset{Ph}{CH}-CH_2-\underset{Ph}{CH}\cdot + CH_2=\underset{Ph}{C}-CH-\underset{Ph}{CH_2}$$

$$\sim\underset{Ph}{CH}-CH_2-\underset{Ph}{CH}-CH_2-\underset{Ph}{CH}-CH_2-\underset{Ph}{CH}\cdot \longrightarrow \sim CH_2-\underset{Ph}{CH}\cdot + CH_2=\underset{Ph}{C}-CH_2-\underset{Ph}{CH}-CH_2-\underset{Ph}{CH_2}$$

The thermal decomposition of poly(4-methylstyrene) possibly proceeds as the following: In the absence of oxygen, the thermal degradation of poly(4-methylstyrene) is initiated by a random scission of the main chain, which then depolymerizes to the monomer, termination, and hydrogen intramolecular transfer, followed by β-scission to form dimer, trimer, and other products.[30]

First, it is initiated by the random scission of the main chain to form primary and secondary macroradicals.



$$\sim\underset{R}{CH}-CH_2-\underset{R}{CH}-CH_2-\underset{R}{CH}-CH_2-\underset{R}{CH}-CH_2\sim \longrightarrow$$

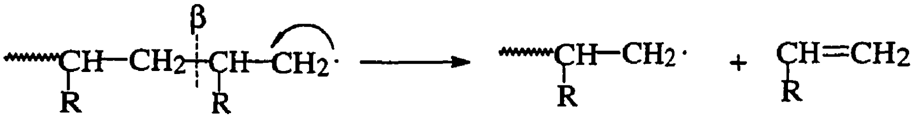
(R = $C_6H_5CH_3$)

$$\sim\underset{R}{CH}-CH_2-\underset{R}{CH}-CH_2\cdot \quad + \quad \cdot\underset{R}{CH}-CH_2-\underset{R}{CH}\sim$$

R1 R2

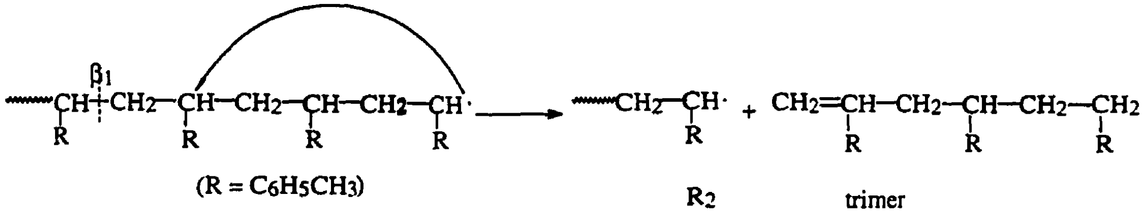
primary macroradicals secondary macroradicals

The primary radicals exclusively undergo depolymerization, which leads to the formation of monomers.

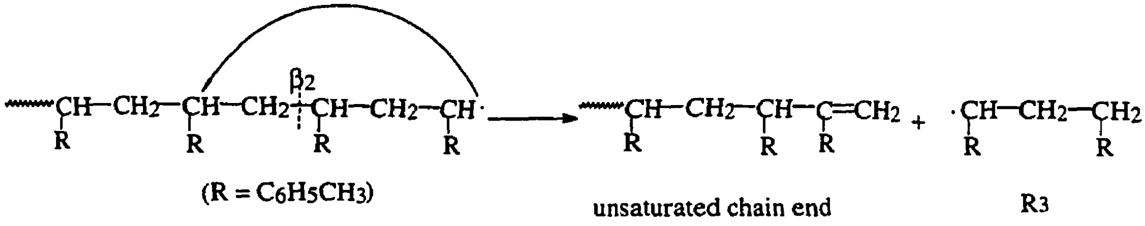


$$\sim\underset{R}{CH}-CH_2\overset{\beta}{\vdots}\underset{R}{CH}-CH_2\cdot \longrightarrow \sim\underset{R}{CH}-CH_2\cdot \quad + \quad \underset{R}{CH}=CH_2$$

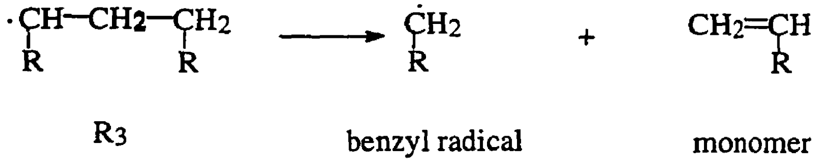
On the other hand, the secondary macroradicals undergo the intramolecular 1,5 transfer followed by β-scission. Thus a trimer and R2 radicals are produced by the scission at β1



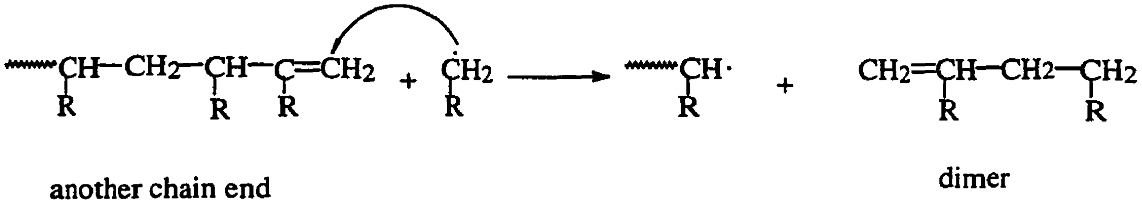
or a 1,3 ditolyl propyl radicals (R3) and an unsaturated polymer chain-end are given by the scission at β2



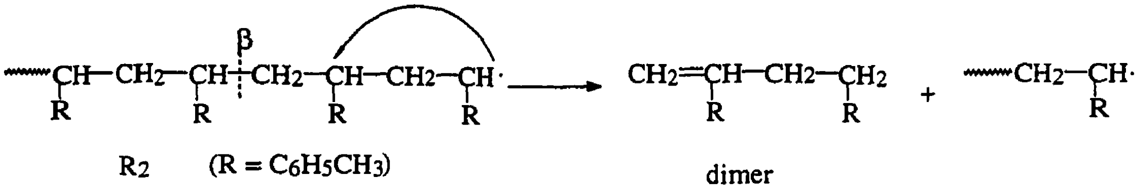
The R3 radicals should give rise to 1,3 ditolyl propane by hydrogen abstraction, and the R3 radicals might undergo further decomposition to form a monomer and a benzyl radical.



This benzyl radical can give rise to xylene by hydrogen abstraction. Most probably the other way is that the benzyl radical in this condensed molten phase attacks the other unsaturated chain ends formed by the β-scission described above and then the dimer is formed by β-scission to the double bond.



On the other hand, dimer formation is carried out through 1,3 transfer of R2 macroradicals followed by β-scission. This has been proposed by many researcher about applications for polystyrene.[7, 25, 27, 31]



6.4.2 Thermal Properties of Poly(4-methylstyrene) Containing Chloromethyl Groups

Poly(4-methylstyrene) was chlorinated using cobalt(III) acetate/lithium chloride/ nitrogen as an oxidation system, and benzene/acetic acid as a mixed solvent (Chapter 3.2). The degree of the chlorination could be controlled between 0 and 21%. Two samples with 12.5% (10) and 21.0% (18) of chloromethyl groups were respectively used to study their thermal properties.

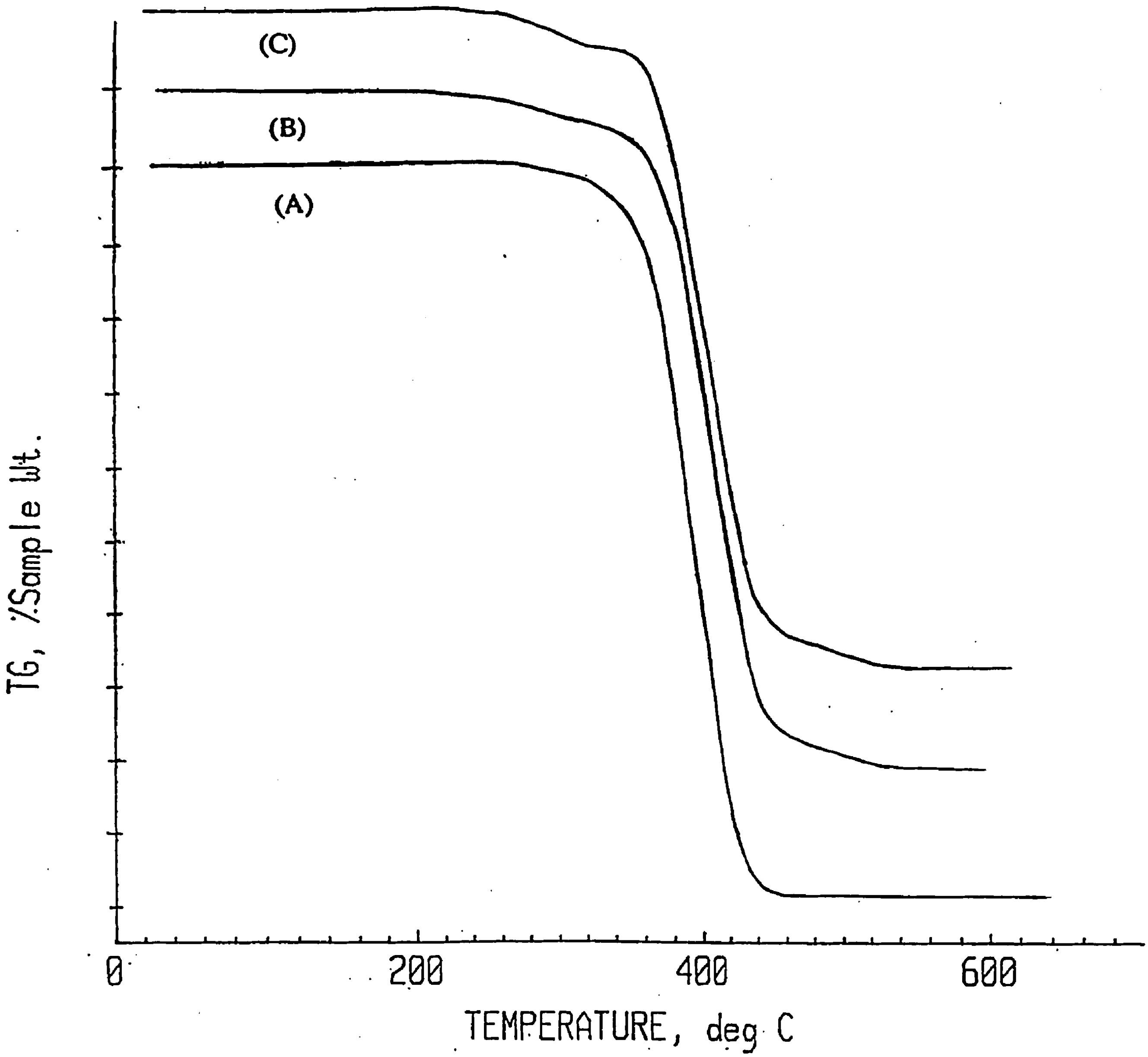


Figure 6.2 Thermograms in nitrogen of poly(4-methylstyrene) (A), sample 10 (containing 12.5% of chloromethyl group) (B), and sample 18 (containing 21% of chloromethyl group) (C). Each plot begins at 100% on the mass axis, with each division representing a 10% mass loss

Figure 6.2 shows the thermogravimetric analysis curves (TGA) of poly(4-methylstyrene) (A), chlorinated poly(4-methylstyrene) incorporating 12.5% (B) and 21% (C) chloromethyl groups respectively.

Thermograms show an onset of the mass loss at 200°C, at a heat rate of 5°C/min. This indicates that no volatile species remained trapped in the polymer matrix after the chlorination reaction. Mass loss (Figure 6.2 (B)) occurred in two stages: 4.0% mass loss over the range 200 - 335°C, followed by a more rapid mass loss of 86% over the range 335 - 540°C, leaving an 8% involatile residue.

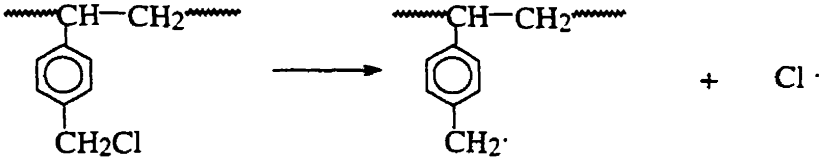
If we compare poly(4-methylstyrene) to sample 10, we can see that the curve shifts to high temperature range. The temperature corresponding to the maximum rate of decomposition for chlorinated poly(4-methylstyrene) is 405°C, which is a few degree higher than that of poly(4-methylstyrene).

The TGA curve (C) for poly(4-methylstyrene) containing 21% chloromethyl groups has the same pattern of thermal decomposition as the curve (B) (12.5% chloromethyl). The only difference between (B) and (C) is in the first stage, there (C) shows 6% mass loss compared to 4% for (B). Apparently, the initial first weight loss, occurring around 200°C, increases as the degree of chlorination increases. The main degradation for both (B) and (C) occurred around 405°C and the amount of residue increased (from 8% to 9%) as the degree of chlorination increased.

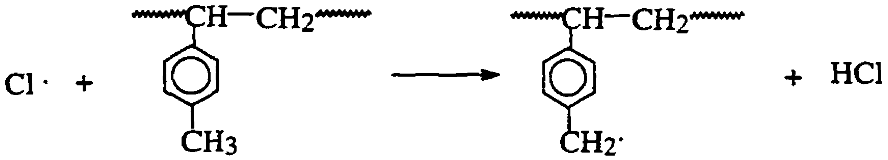
Chlorination thus leads to an increased susceptibility to thermal degradation in comparison to poly(4-methylstyrene) itself (onset of 200 vs 240°C, under identical conditions). This is not a surprising result since introduction of the chloromethyl groups provides new reactive sites for radical formation. A dehydrohalogenation is a likely source of the 4.0% (or 6.0%) mass loss occurring over the range 200- 335°C.[14] Thus quantitative loss of hydrogen chloride from (B) and (C) would result in 3.40% and 6.1% mass loss (21% of chlorination corresponding to 6.1% (18) of the mass loss theoretically).

These results suggest that the dehydrochlorination occurs (inter or intramolecular) around 200°C, leaving behind a possibly cross-linked structure that undergoes further degradation around 400°C. The accompanying cross-linking could account for the involatile residue (8% for (B), 9% for (C)).[15]

Dehydrochlorination: It appeared that with polymer containing para-
(200 - 335°C) chloromethyl groups, most chemical change are initiated
by cleavage of the C-Cl bond:



Then, chlorine radicals abstract hydrogen from the methyl group to form benzyl radical. Then these methylene radicals could generate an ethylene cross-linked structure.



Major weight loss : Random initiation by scission of C-C bonds, depolymerization (around 405°C) and termination reaction or intramolecular transfer.

As well hydrogen abstraction from the tertiary carbon of the main chain would lead to methylene crosslinks.[16]

Figure 6.3 shows the difference between the thermal decompositions of samples under nitrogen and air. Curve (A) again shows TGA of P4MS under nitrogen. The curve (C) is the thermogram of this sample under air.

There were three stages of mass loss. The first two of mass loss followed the same pattern as under nitrogen: a 6.1% of mass loss over the range of 200 -335°C, followed by a rapid mass loss of 65.5% over the range 335 - 420°C. The third stage of mass loss was about 24.5%, It started at 420°C, and finished at 540°C, remaining 4% of mass involatile residue. It indicates: 1). Oxygen promoted the decomposition of chlorinated P4MS. 2) Interior cross-linking reaction occurs. At higher temperature, oxygen enhances random main chain scission: Thermal oxidation reduces the degree of polymerization much faster than thermal degradation under nitrogen.[32]

The first stage of the mass loss started at 200°C and ended at 335°C. Around 6% of weight loss occurred. It was the same as that of the sample in nitrogen, corresponding to the dehydrochlorination of polymers.

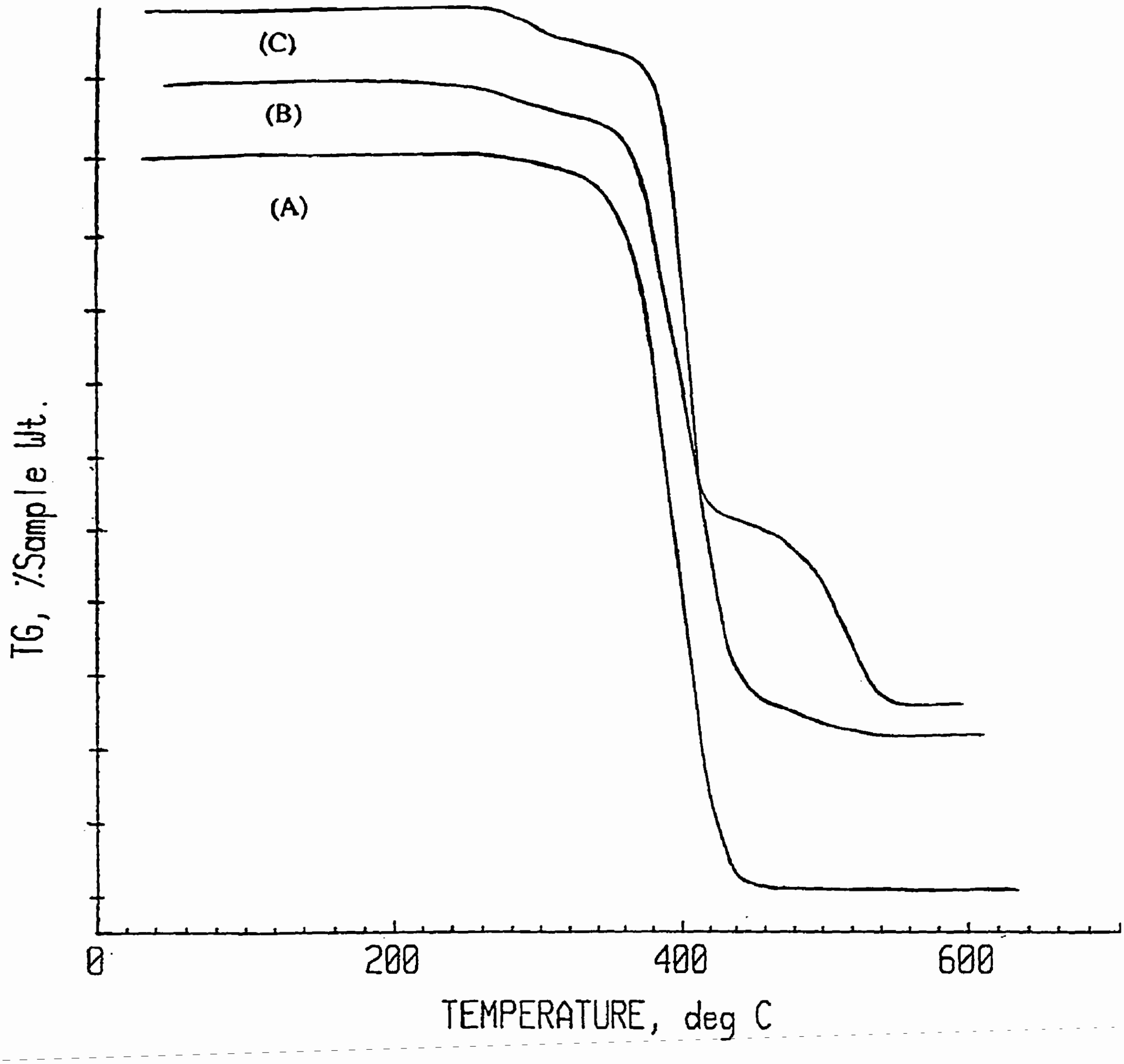


Figure 6.3 Thermograms of poly(4-methylstyrene) in nitrogen (A), sample 18 in nitrogen (B) and in air (C). Each plot begins at 100% on the mass axis, with each division representing a 10% mass loss

In the second stage, the weight loss was around 65.5% over the range of 335 - 420°C. This is a rapid mass loss. This stage indicates the random scission of the main chain and depolymerization.

The third part of the mass loss represented about 24.5%, started at 420°C and finished at 540°C, leaving 4% of involatile residue. The third stage was probably due to the cracking and gasification of compounds. Finally left 4% of mass which is highly cross-linked materials.

Because oxygen was involved in the thermal degradation, the mechanism should be different.

The general mechanism of the promotion of the radical-induced main-chain scission of pyrolysis by oxygen is the following:[13]

$$P\cdot + O_2 \longrightarrow POO\cdot$$

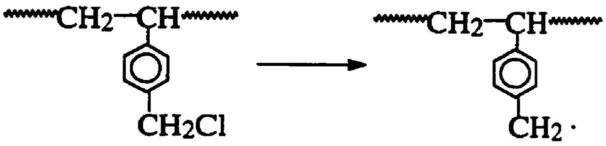
$$2\,POO\cdot \longrightarrow POOOOP$$

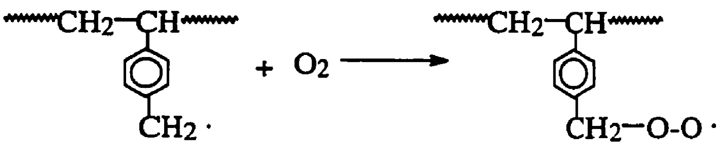
$$POOOOP \longrightarrow 2\,PO\cdot + O_2$$

$$PO\cdot \longrightarrow P_1 + P_2$$

Scheme 1 (main chain scission)

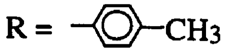
For our system, probably the main-chain scission occurred by the following steps.



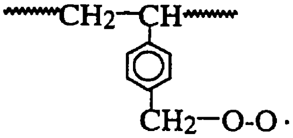


The main-chain scission can be induced by a abstraction of hydrogen from main-chain carbons according to reactions:

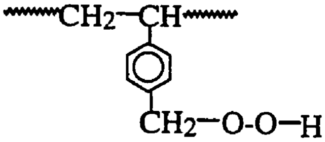
$$\sim CH_2-CH(R)\sim + X\cdot \longrightarrow \sim CH_2-\dot{C}(R)\sim + XH$$



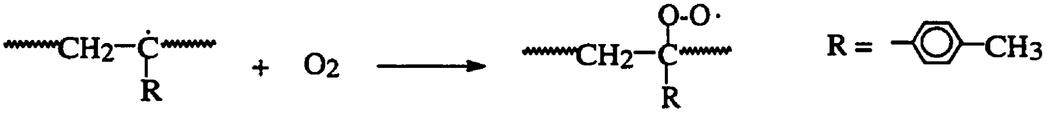
in which X denotes Cl·, Cl-O-O·, or



XH is HCl, Cl-O-O-H or



The latter macroradicals formed are assumed to react with oxygen.



Peroxyl radicals formed this way can undergo reactions described in scheme 1 which enhances random main chain scission.[32]

6.4.3 Thermal Properties of Poly(4-methylstyrene) Containing Acetoxy Groups

When poly(4-methylstyrene) was selectively oxidized by ceric ammonium nitrate/ nitrogen, copolymers containing 4-methylstyrene, vinyl benzyl acetate, and vinyl benzyl nitrate units were obtained.[33] However, the functional group-benzyl nitrate could be displaced by benzyl acetate by refluxing the polymer in acetic acid for ten hours. The thermal properties for both copolymers (4-methylstyrene/vinyl benzyl acetate copolymer and terpolymer) were tested.

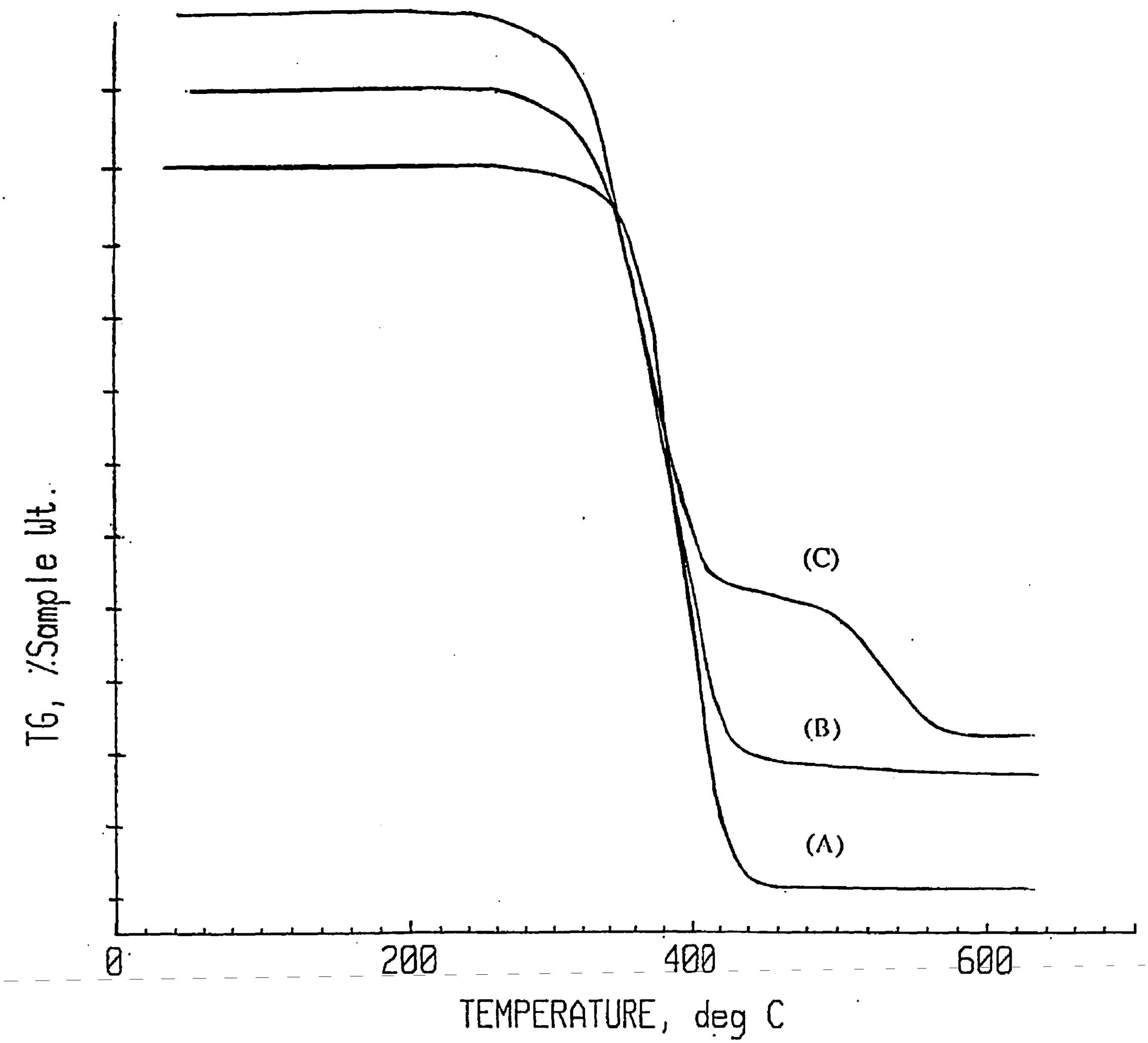


Figure 6.4 Thermograms of poly(4-methylstyrene) in nitrogen (A), a-35 (containing 23.7% of acetoxymethyl group) in nitrogen (B) and in air (C). Each plot begins at 100% on the mass axis, with each division representing a 10% mass loss

Figure 6.4 compares the TGA curves of poly(4-methylstyrene) in nitrogen (A), poly(4-methylstyrene) containing only acetate groups (a-35) in nitrogen (B) and in air (C).

Figure 6.4 (A) is the thermogravimetric curve of poly(4-methylstyrene) in nitrogen. We discussed it before.

Figure 6.4 (B) and (C) are the thermogravimetric curves of acetated poly(4-methylstyrene) in nitrogen and air respectively. We can see that they show patterns similar to those of poly(4-methylstyrene) in nitrogen and air.

For a-35 in nitrogen, the weight loss occurred in one step. It started around 200°C, and ended at 460°C, leaving 6% non-volatile residue.

The onset temperature of the weight loss is 40°C lower than that of poly(4-methylstyrene) (240°C). This is a reasonable result, since it contain the acetoxy groups. The bond dissociation energies [34,35,36] for the following compounds are:

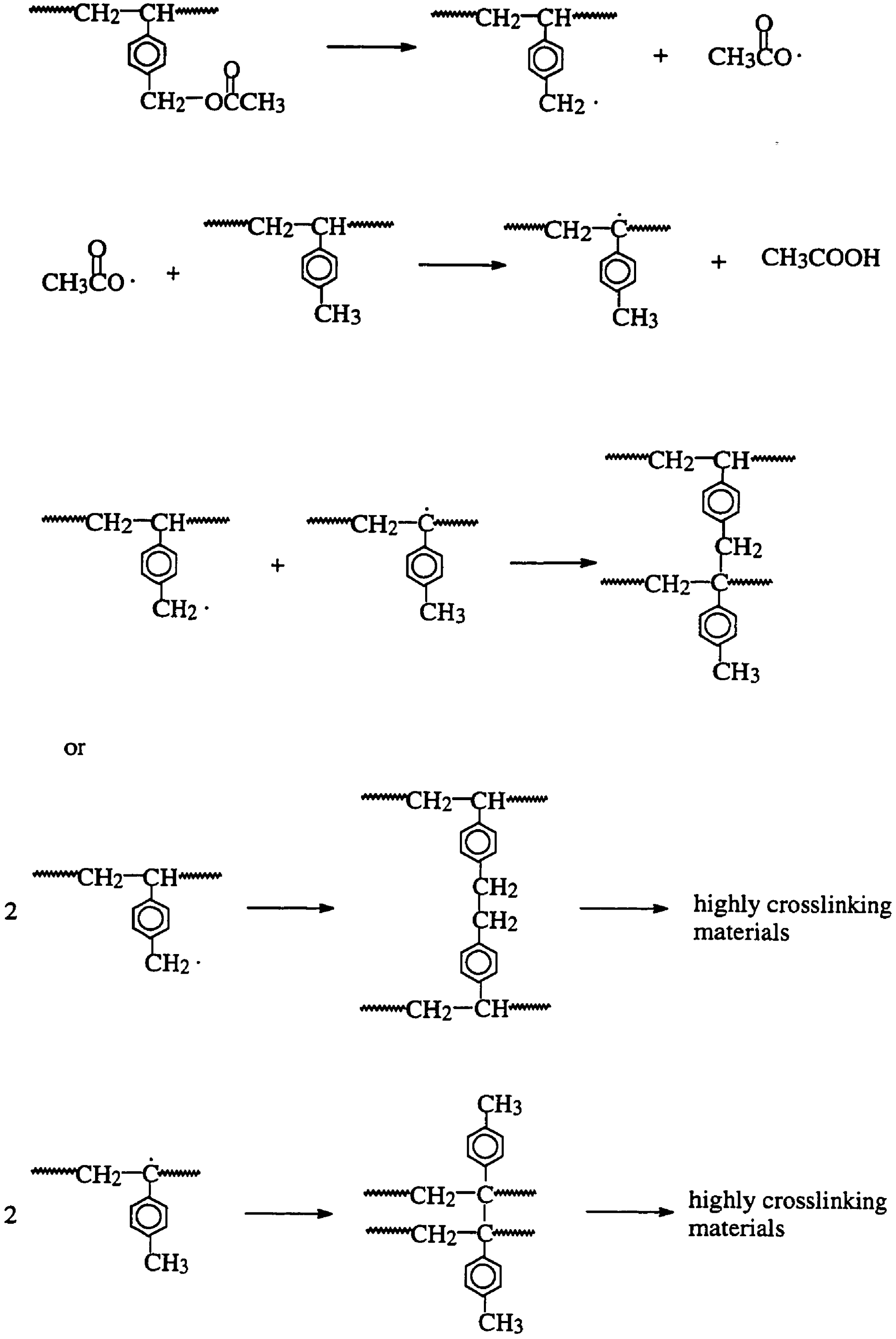
Bond	D(kJ/mol)
$(CH3)_2CH\text{-}H$	395
$(CH3)_3C\text{-}H$	381
$C_6H_5CH_2\text{-}H$	368
C-C	344-355
$H_2C{=}CHCH_2\text{-}H$	361
$H_2C{=}CHCH_2\text{-}Cl$	289
$C_6H_5CH_2\text{-}OCOCH_3$	280
$CH_3\text{-}NO_2$	254.4

$C_6H_5CH_2$-ONO_2	220 (supposed)
C_3H_7-NO_2	246.9
O-NO_2	208.7
C_2H_5O-NO	175.7
C_2H_5O-OC_2H_5	158.6

The bond dissociation energy of benzyl-acetate is much smaller than that of benzyl-H, so the benzyl acetate bond is easy to break. We think the weight loss starting at 200°C is due to the homogeneous cleavage of the benzyl acetate bond, releasing $CH_3COO\cdot$. Thus the final pyrolysis products should contain acetic acid.

The temperature corresponding to maximum degradation rate shifted to lower temperature 372°C (compare to 396°C for poly(4-methylstyrene)).

During thermolysis of acetoxylated poly(4-methylstyrene), the benzyl-acetate bond breaks first, to produce a benzyl radical. This abstracts hydrogen from the tertiary carbon of the backbone, or combines with another benzyl radical to generate cross-linked products. The 6% non-volatile residue may be attributed to highly crosslinking materials (containing aromatic rings).


CH3COOH
or
2
highly crosslinking materials
2
highly crosslinking materials

These crosslinking processes interfere with thermal depolymerization of the backbone, hence leading to the final non-volatile residue.

The thermal degradation of functional poly(4-methylstyrene) in the presence of oxygen (air) is more complex. The weight loss occurs in two distinct steps. The first part of the mass loss 79.4% occurred between 200°C and 420°C. The second part started at 420° and ended at 580°C, leaving around 1% involatile residue. In the first stage, the onset temperature of 200°C, in addition to the releasing of the weights again initial formation of acetoxy radicals, followed by depolymerization. However, either the primary benzyl radical or the tertiary benzyl radical reacts with oxygen to produce peroxide radicals. These peroxide radicals undergo a series of reactions (indicated in scheme 1) to introduce main-chain scission (see discussion in 6.4.2).

At the same time, the oxygen involved in the radical reaction prevented the cross-linking reaction, so the non-volatile residue was just 1% (as compared to 6% of non-volatile material for the same sample in nitrogen.). Alternately, oxygen simply combusts any involatile residues formed.

6.4.4 Thermal Properties of Poly(4-methylstyrene) Containing Nitrooxy and Acetoxy Groups

When poly(4-methylstyrene) was oxidized by ceric ammonium nitrate, the terpolymer containing methyl, acetoxymethyl, and nitrooxymethyl groups was obtained.

The thermogram of this functional polymer is shown in Figure 6.5.

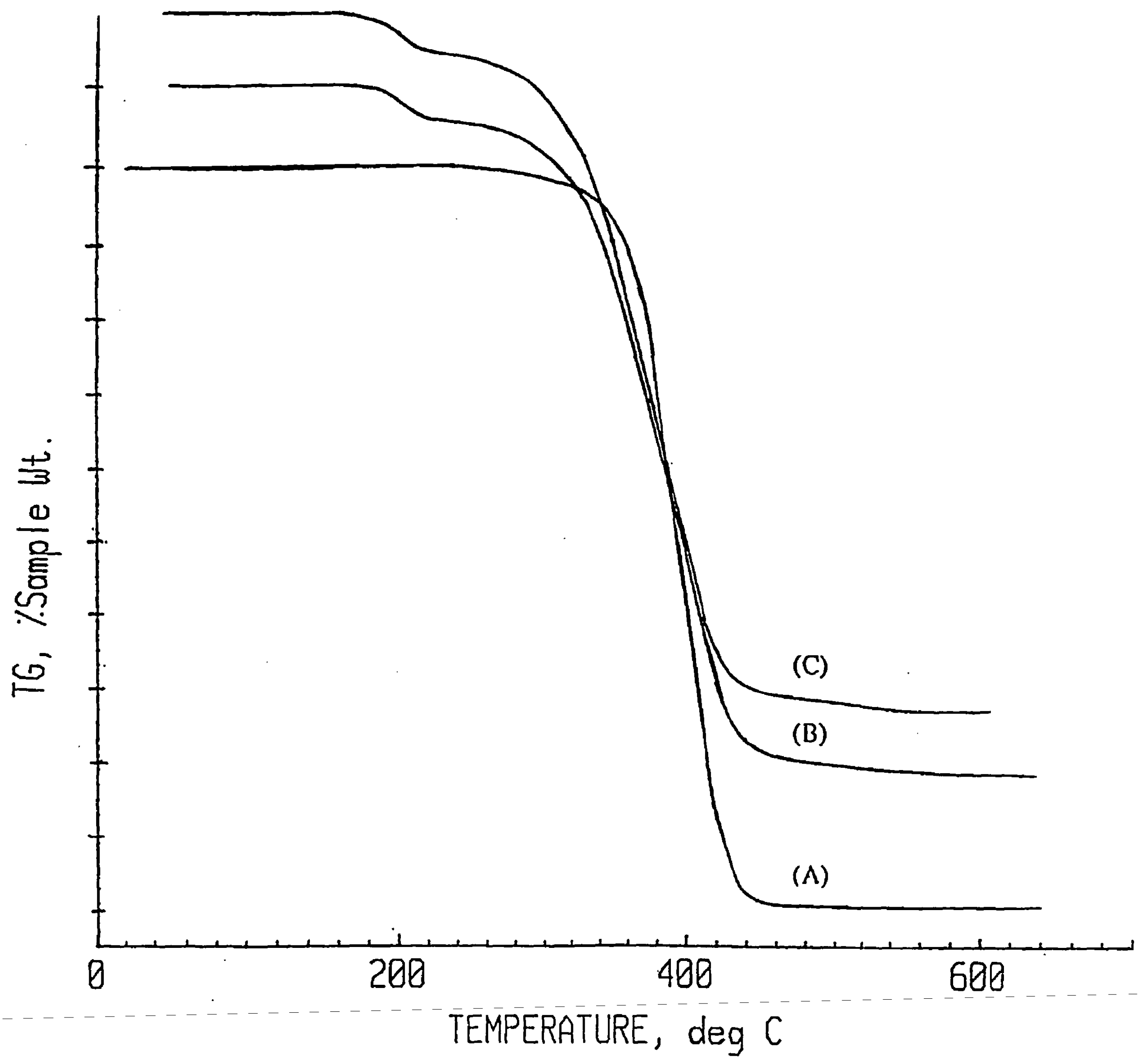


Figure 6.5 Thermograms of poly(4-methylstyrene) (A), a-25 (B), and a-11 (C) (containing 23.6% and 45.2% total oxidation degree respectively) under nitrogen. Each plot begins at 100% on the mass axis, with each division representing a 10% mass loss

division representing a 10% mass loss.

Figure 6.5 (A), (B), and (C) show the weight loss curves of poly(4-methylstyrene), a-25 (acetate 14.3%, nitrate 9.3%) and a-11 (acetate 16.9%, nitrate 28.3%) under nitrogen respectively.

In both cases, thermal degradation occurred in two steps. For a-25 (B), an initial 5.4% mass loss occurred between 148°C and 230°C. The second step of the mass loss is the major degradation step, about 88% of the weight loss occurred in the temperature range 230 - 540°C, leaving 6.5% non-volatile materials.

Supposedly, the bond dissociation energy of benzyl-nitrate is much lower than that of benzyl-chloride (see section 6.4.3). Probably, the degradation at 148°C corresponds to the cleavage of the benzyl-nitrate side chain. Sample a-11 (Figure 6.5(C)) contains more of the nitrooxy group, so the weight loss of the first step is larger than that of sample a-25. For both polymers, after 200°C, the benzyl-acetate bonds started to break. The breaking of the bonds of both benzyl nitrate and benzyl acetate formed benzyl radicals.

For the second step, the maximum rapid weight loss is at about 370°C. It shifted to the lower temperature (compared to poly(4-methylstyrene)). This degradation process likely follows the same process describe above.

6.4.5 Determination of the Glass Transition Temperature for Functional Copolymers by Differential Scanning Calorimetry (DSC)

6.4.5.1 Glass Transition Temperature of Polymers

Glass Transition Temperature. Amorphous polymers can exhibit two distinctly different types of mechanical behavior. For example, polystyrene is a hard, rigid, glassy plastic at room temperature, while polybutadiene is a soft, flexible rubbery material. The temperature, or narrow range of temperature, below which an amorphous polymer is in a glassy state, and above which it is rubbery, is known as the glass transition temperature (Tg). At Tg, a dramatic change occurs in the local movement of the polymer chain which leads to large changes in a host of physical properties. These properties include density, specific heat, mechanical modulus and mechanical energy absorption and their dielectric and acoustical equivalents, rate of gas or liquid diffusion through the polymer, and many other properties as well.

The Determination of Tg. Experimental methods of measuring Tg are based on the change in properties of polymers converted from the glassy to the rubbery state. Two methods are used:

(I) the steady-state method, in which polymer properties are measured under isothermal conditions over a temperature range including Tg;

(ii) the dynamic method, in which polymer properties are measured during heating of the material through the Tg. In this method, Tg is measured by an extrapolation procedure in order to obtain isothermal conditions.

Dynamic methods are more popular, on account of their convenience. The two methods may sometimes give different Tg values. Tg depends not only upon the experimental conditions, such as the heating rate, but also on the thermal history of the polymer sample, e.g. rate of cooling.

These dynamic methods are the following: Dilatometry; buoyancy; expansivity; refractometry; light scattering; NMR; ESR; DSC-DTA measurement; sifting point measurement; dynamic mechanical properties; dielectric constant; ultrasonic; chromatography.

Most commonly, thermal transitions in polymers are studied using differential scanning calorimetry (DSC).[38]

Factors Influencing Tg

Chain Microstructure. Chain flexibility and intermolecular packing distance (chain stiffness), bulkiness, flexibility of the side chain, and polarity of the chain are major parameters influencing Tg.

Intermolecular Bonds. Polymers with strong intermolecular bonds, e. g. chemical crosslinks or hydrogen bonds, exhibit higher values of Tg.

Effects of Solvent and Plasticizers. The presence of low molecular weight compounds (such as solvent, water, and plasticizer) in the amorphous phase of a semicrystalline polymer lowers Tg.

Effect of Molecular Weight. For high molecular weight polymers, Tg is essentially independent of molecular weight, but as the polymer chain length becomes shorter, Tg is likely to decrease appreciably. The following equation shows the relationship between Tg and Mn.

$$Tg = Tg(\infty) - K/Mn$$

where Tg (∞) is the glass-transition temperature in the limit of infinite molecular weight and K a constant reflecting the enhanced free volume around chain ends.

Copolymerization and Polyblend Effects. Amorphous random copolymers exhibit a single Tg which can be predicted by

$$Tg = \frac{KW_1Tg_1 + W_2Tg_2}{KW_1 + W_2}$$

where Tg_1 and Tg_2 are glass transition temperatures of two homopolymers, and W_1 and W_2 are weight fractions of two homopolymers. K is the constant $K = (\alpha_r - \alpha_g)_2(\alpha_r - \alpha_g)_1$. α_1 and α_2 are heat expend coefficient for homopolymer, r rubber state, g glass state.

6.4.5.2 Glass Transition Temperature for 4-Methylstyrene/Butyl Methacrylate Copolymers

For a series of homogeneous copolymers, the Tg values are in the range between the values of the parent homopolymers (Figure 6.6).[39]

A series of copolymers of 4-methylstyrene and butyl methacrylate were prepared by free radical polymerization using AIBN as an initiator and cyclohexane as a solvent under nitrogen. The glass transition temperatures of copolymers of 4-methylstyrene and n-butyl methacrylate were measured by differential scanning calorimetry at a heating rate of 15°C/ min. in an atmosphere of flowing nitrogen and 5-10 mg of sample. Table 6.1 and Figure 6.6 show the results:

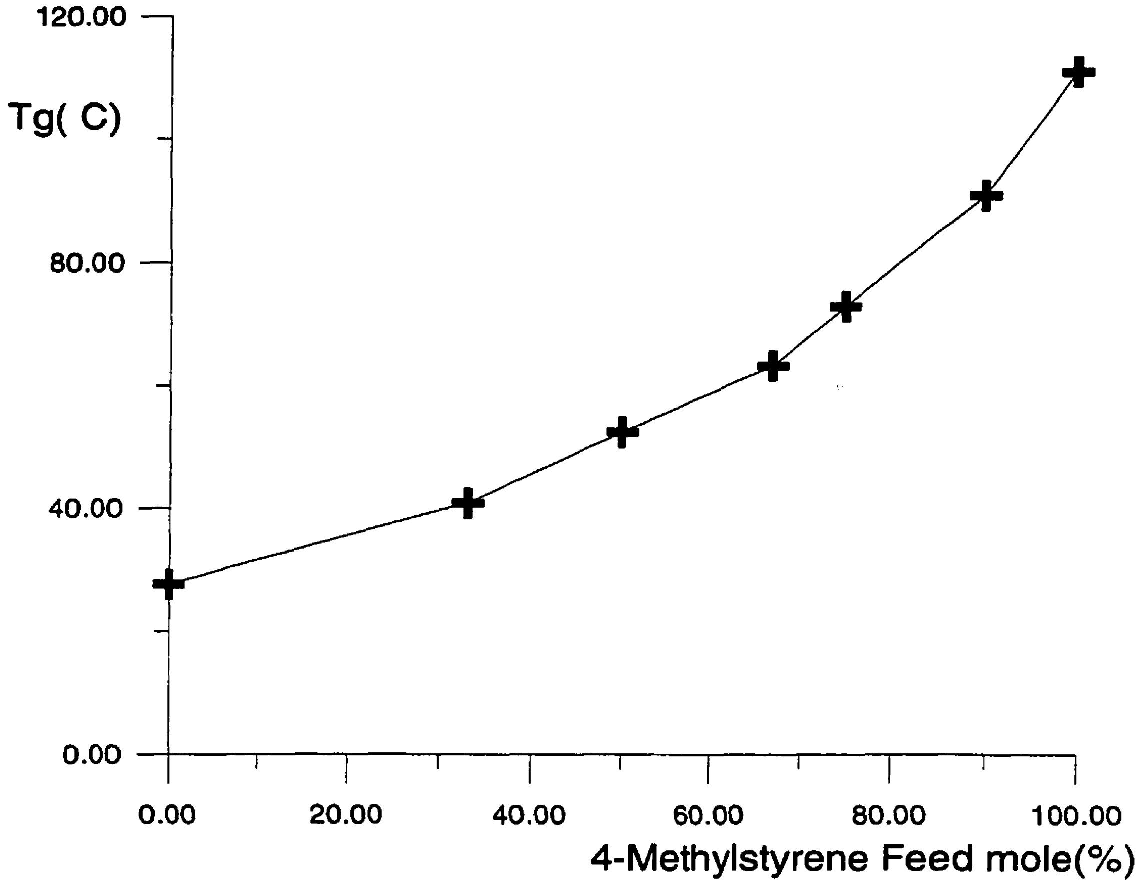


Figure 6.6 Tg and monomer feed ratio for the copolymer of 4MS/BMA.

Table 6.1 Tg of 4-Methylstyrene/Butyl methacrylate Copolymers

Run#	Feed Molar Ratio			Tg (°C)
	(4MS :	BMA)	4MS%	
Poly(4MS)	1	0	100	111
f-5B	10	1	90	91.09
f-6B	3	1	75	72.9
f-3B	2	1	67	63.2
f-1B	1	1	50	52.4
f-4B	1	2	33	40.8
Poly(BMA)	0	1	0	27.7

Mn range of all samples: 21,000 - 25,000.

From Table 6.1 and Figure 6.6, we can see that the Tg of the copolymers lie between the Tg of poly(butyl methacrylate) and the Tg of poly(4-methylstyrene), and there is a very good non-linear relationship between Tg and comonomer feed ratio. Actually, we can control the Tg of the final product-copolymers by adjusting the comonomer feed ratio. It is very useful for polymer applications.

6.4.5.3 Glass Transition Temperature for 4-Methylstyrene/Butyl Methacrylate Copolymers Containing Aldehyde and Carboxylic Acid Groups

Oxidative functionalization of copolymers of 4-methylstyrene and butyl methacrylate were carried out using Co(II) acetate/sodium bromide/air system, to introduce aldehyde and carboxylic acid groups into copolymers. The glass transition temperatures of these functional copolymers were measured by DSC. Table 6.2 shows the results.

Table 6.2 Tg of Functional 4MS/BMA Copolymers

Run#	Total Oxidation Yield (%)*	Tg (°C)
f-4B	0.0	40.8
f-4BOA	14.1	47.5
f-4BOB	36.2	61.2
f-4BOD	80.2	115
f-3B	0.0	63.2
f-3BOA	10.2	64.7
f-3BOB	49.8	107
f-3BOC	69.2	127

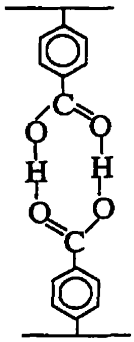
%* oxidation of 4-methyl groups

Mn of all samples are in the range 19,500-27,600.

All of the results indicate that after introduction of aldehyde and carboxylic acid groups, the Tg of the copolymers increased. The higher the oxidation yield, the higher the glass transition temperature of the copolymers.

The carboxylic acid side chains can generate very strong hydrogen bonds between copolymer molecules: in addition, both aldehyde and carboxylic acid groups increase the Tg through dipolar interaction.

carboxylic acid-carboxylic acid



These strong intermolecular bonding result in large intermolecular forces and hence higher glass transition temperatures of these functional copolymers.

6.4.5.4 Glass Transition Temperature for 4-Methylstyrene/Dodecyl Methacrylate Copolymers

The glass transition temperatures of copolymers of 4-methylstyrene and dodecyl methacrylate were measured by differential scanning calorimetry at a heating rate of 15°C/ min. in an atmosphere of flowing nitrogen and 5-10 mg of sample. The number average molecular weight of these copolymers is in the range 23,800 - 34,900. Figure 6.7 is the Tg vs feed molar ratio curve.

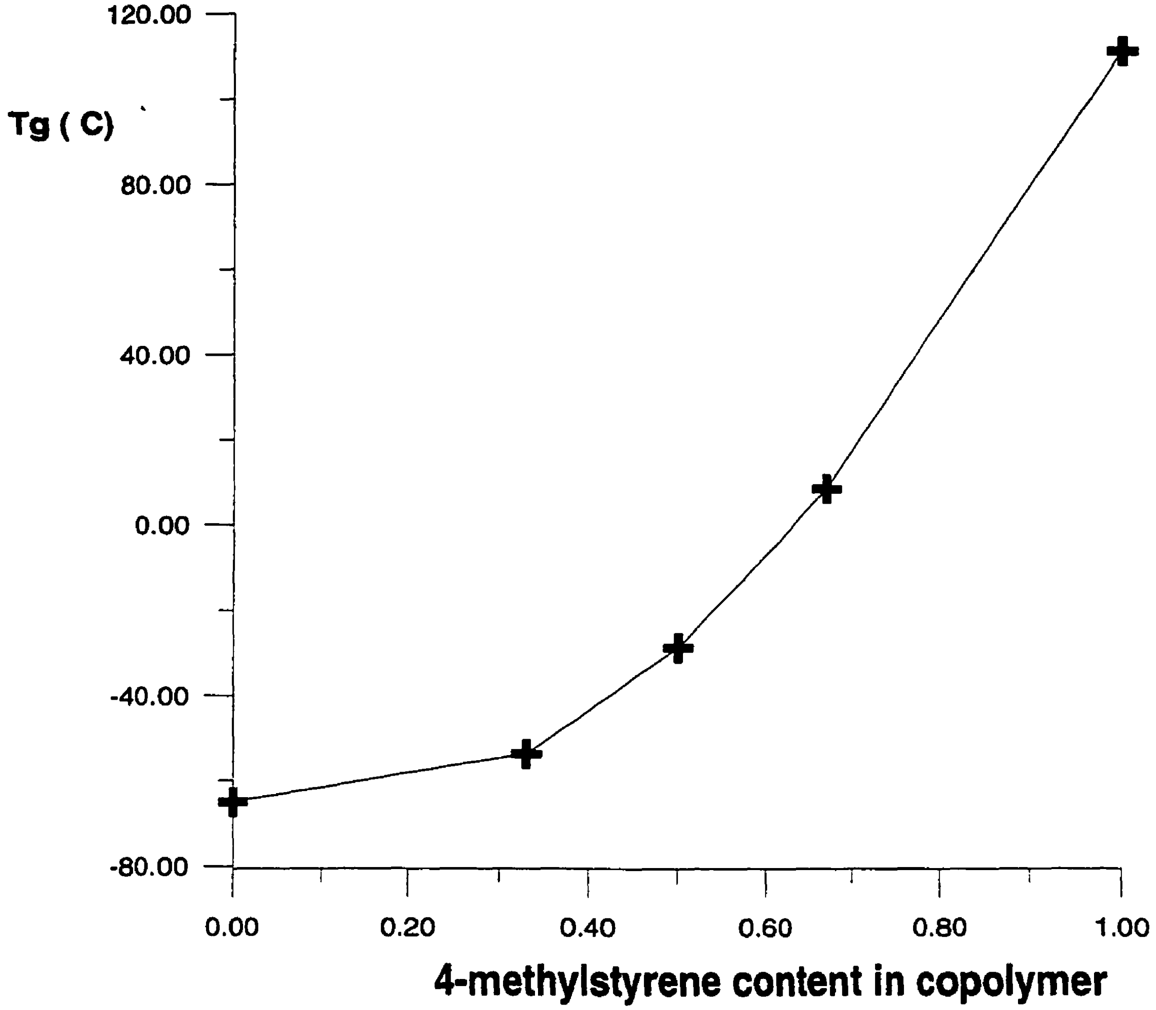


Figure 6.7 Tg and monomer feed ratio for the copolymer of 4MS/DMA.

A similar conclusion as for 4-methylstyrene/butyl methacrylate copolymers is obtained. We can control the Tg of copolymers by controlling the feed comonomer ratio.

6.5 CONCLUSIONS

The thermal properties of poly(4-methylstyrene) containing different functional groups (chloromethyl, acetoxy, and the mixture of acetoxy and nitrooxy) were studied using thermogravimetry in nitrogen and air.

For the chlorinated poly(4-methylstyrene), the thermal decomposition is initiated by the cleavage of the C-Cl bond. The mechanism involves the random scission of the main chain, depolymerization, termination, intramolecular transfer by hydrogen from the tertiary carbon of the main chain, and the accompanying cross-linking reaction.

For the acetoxylated poly(4-methylstyrene), the first step of the mass loss is initiated by the homolytic cleavage of the acetoxy-benzylic bond, then followed by the same pattern as that of degradation of chlorinated polymers.

Supposely, the bond dissociation energy of benzyl-nitrate is much lower than those of benzyl chloride and benzyl acetate, the weight loss of the terpolymers (containing acetoxy, nitrooxy, and 4-methylstyrene) began at a lower temperature than that of the other two polymers.

The introduction of the functional groups increases the susceptibility of poly(4-methylstyrene) too, as all of the functional polymer samples have lower heat resistance than poly(4-methylstyrene) does. Oxygen involved in the reaction makes the thermal degradation of polymers more complex.

The glass transition temperatures of the copolymers of 4-methylstryrene/butyl methacrylate and 4-methylstyrene/dodecyl methacrylate were measured by differential scanning calorimetry. There is a very good relationship between Tg and monomer feed ratios. The Tg of functional copolymers of 4-methylstyrene and butyl methacrylate were measured as well. The higher Tg were found by the functional copolymers, which results from the strong intermolecular dipolar and hydrogen bonding of polymer chains.

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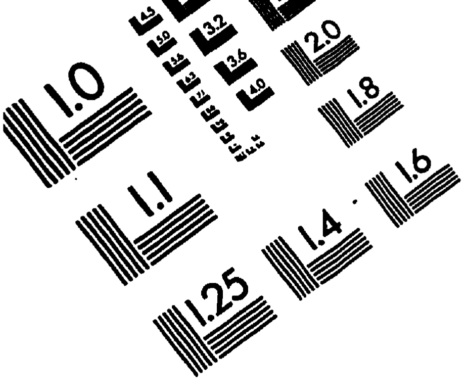

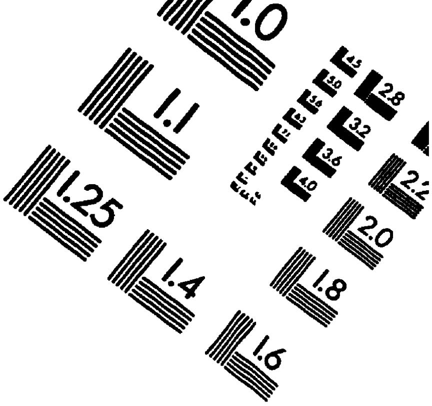

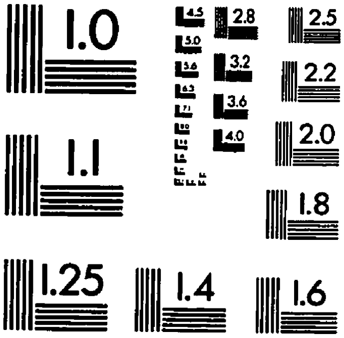

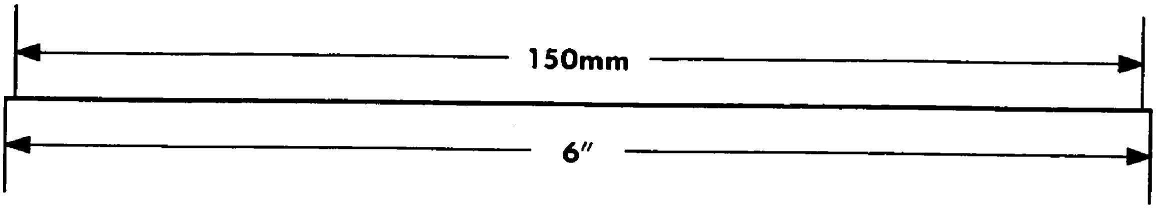

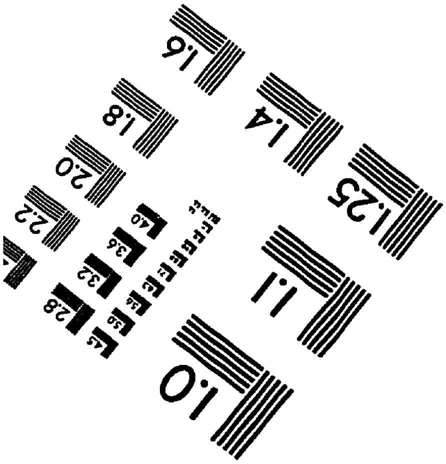

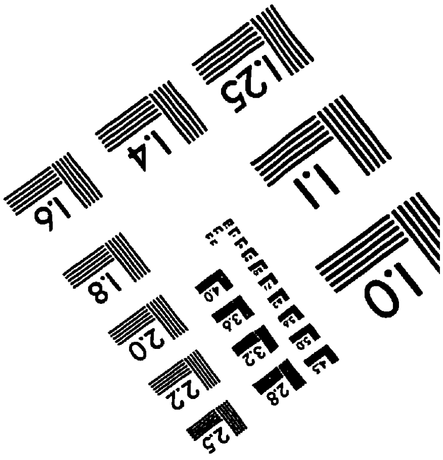

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