1986

Synthesis of Poly(vinylcatechols).

Saad Moulay

Louisiana State University and Agricultural & Mechanical College

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The Louisiana State University and Agricultural and Mechanical Col.

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SYNTHESIS OF POLY(VINYLCATECHOLS)

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by
Saad Moulay
B.S., Université d'Alger (U.S.T.A.), 1979
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TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS.....	ii
LIST OF TABLES.....	viii
LIST OF FIGURES.....	x
LIST OF SCHEMES.....	xiii
ABSTRACT.....	xv
INTRODUCTION.....	1
A. Polymer Reagents in Organic Synthesis.....	1
I. Polymer Transfer Agents.....	4
II. Polymer Catalysts.....	9
1. Polymer-bound transition metal complexes.....	11
2. Immobilized enzymes.....	15
III. Polymers as Protecting Groups.....	17
B. Redox Polymers.....	22
I. Synthesis of Redox Polymers.....	24
1. Condensation polymers.....	24
2. Attachment of redox units onto preformed polymers.....	33
3. Vinyl polymers.....	40
II. Properties of Redox Polymers.....	54
1. Condensation polymers.....	54
2. Vinyl polymers.....	56
III. Applications.....	58
C. Objectives.....	60
RESULTS AND DISCUSSION.....	62
A. Monomer Syntheses.....	63
B. Polymerization Reactions of Monomers.....	69
I. Homopolymerization.....	69
1. Free radical initiation.....	69
2. Dilatometric study of the homopolymerization of monomer 30.....	71
3. Cationic polymerization.....	73
4. Anionic polymerization.....	74

II. Copolymerization Reactions of Monomers 30 and 31 with Styrene and Methyl Methacrylate..	77
III. Graft Copolymerization on Poly(vinylcatechol) Precursors.....	90
C. Thermal Stability of the Poly(vinylcatechol) Precursors.....	94
D. Chemical Modification of Poly(vinylcatechol) Precursors.....	99
I. Chloromethylation Reaction.....	100
II. Quaternization of Chloromethylated Poly(6-vinyl-1,4-benzodioxane).....	102
III. Synthesis and Chloromethylation of Model Compounds.....	103
IV. Lithiation Reaction.....	104
V. Bromination Reaction.....	105
VI. Cyanogenation Reaction.....	116
VII. Aminomethylation Reaction.....	123
VIII. Sulfonation Reaction.....	128
IX. Sulfomethylation Reaction.....	130
E. Removal of the Blocking Groups.....	131
F. Oxidation of Poly(vinylcatechols) to the Corresponding Poly(benzoquinones).....	140
G. Potentiometric Titration of Poly(3-vinylcatechol).	141
EXPERIMENTAL METHODS.....	154
A. General Information.....	154
B. Syntheses of Monomers.....	155
Method A: Dehydration of 5-(1'-hydroxyethyl)- 1,3-benzodioxole.....	158
a. Preparation of 5-(1'-hydroxyethyl)- 1,3-benzodioxole	158
b. Dehydration of 5-(1'-hydroxyethyl)- 1,3-benzodioxole.....	158
Method B: Decarboxylation of 3,4- methylenedioxycinnamic acid.....	159
Method C: Wittig methenation of piperonal.....	159

Method D: Wittig reaction of substituted ylides with formaldehyde.....	160
a. Preparation of 3,4-methylenedioxybenzyl chloride.....	160
1. With thionyl chloride.....	160
2. With hydrochloric acid.....	161
b. Preparation of 3,4-methylenedioxybenzyl- triphenylphosphonium chloride.....	161
c. Preparation of 5-vinyl-1,3-benzodioxole.	161
C. Synthesis of 2,3-Methylenedioxybenzaldehyde	
Method A: McLean-Whelan's procedure.....	162
Method B: Miller's procedure.....	162
D. Polymerization Reactions of Monomers.....	163
1. Homopolymerization.....	163
a. Free radical initiation.....	163
b. Anionic initiation.....	163
c. Cationic initiation.....	165
2. Dilatometric study of 2,3-dimethoxystyrene...	165
3. Copolymerization	166
a. Copolymerization of 2,3-dimethoxystyrene	
a-1. With styrene.....	166
a-2. With methyl methacrylate.....	167
b. Copolymerization of 6-vinyl-1,4- benzodioxane.....	167
4. Preparation of polystyrene graft on poly(2,3-dimethoxystyrene).....	167
E. Chemical Modification of Poly(vinylcatechol)	
Precursors.....	168
1. Bromination.....	168
2. Cyanogenation.....	168
3. Chloromethylation.....	169
4. Quaternization of chloromethylated poly(6-vinyl-1,4-benzodioxane).....	169
5. Lithiation.....	170
6. Phthalimidomethylation.....	171

a. With N-methylolphthalimide and trifluoromethanesulfonic acid.....	171
b. With n-butyllithium and N- bromomethylphalimide.....	171
7. Hydrazinolysis.....	172
8. Quaternization of aminomethylated poly(2,3-dimethoxystyrene).....	173
9. Attempt of phthalimidoethylation of poly(2,3-dimethoxystyrene).....	173
10. Sulfonation.....	174
11. Sulfomethylation.....	174
F. Synthesis of Model Compounds.....	175
1. Synthesis of 5-methyl-1,3-benzodioxole, Clemmensen reduction of piperonal.....	175
2. Acylation reaction of 1,3-benzodioxole.....	176
3. Synthesis of 5-ethyl-1,3-benzodioxole, Clemmensen reduction of 5-acetyl-1,3- benzodioxole.....	176
4. Chloromethylation attempt of 5-methyl-1,3- benzodioxole.....	176
G. Removal of Blocking Groups.....	177
1. Deblocking of poly(3,4-dimethoxystyrene).....	177
2. Deblocking of poly(2,3-dimethoxystyrene).....	177
3. Removal of blocking group of poly(5-vinyl- 1,3-benzodioxole).....	178
a. With boron trichloride.....	178
b. With boron trichloride and dodecyl mercaptan.....	178
4. Attempt of deblocking poly(6-vinyl-1,4- benzodioxane).....	179
a. With boron trichloride and dodecyl mercaptan.....	179
b. With hydroiodic acid.....	179
H. Oxidation of Poly(vinylcatechols) to Poly(vinyl- benzoquinones).....	180
I. Potentiometric Titration.....	180

REFERENCES.....	204
VITA.....	216

LIST OF TABLES

Table	Page
1. Polymer Transfer Agents in Organic Synthesis.....	5
2. Quaternary Ammonium Resins $\text{P}-\text{N}^+-\text{A}^-$ in Organic Synthesis.....	10
3. Polymer-Bound Catalysts.....	14
4. Properties of Some Polycondensates of Phenol- Formaldehyde with Redox Units.....	55
5. Examples of Redox Polymers and Their Redox Potentials.....	145
6. Yields and Physical Properties of Monomers.....	182
7a. ^1H NMR and IR of Monomers.....	183
7b. Mass Spectra Results of Monomers.....	184
8. Yields and ^1H NMR Results of sec-Phenylethyl Alcohol Derivatives.....	185
9. Yields, Physical Properties and Mass Spectra of Benzyl Chloride and Benzyltriphenyl- phosphonium Chloride Derivatives.....	186
10. Elemental Analysis of Polymers.....	187
11. Summary of Polymerization Data.....	188
12. Copolymerization of 2,3-Dimethoxystyrene (M_1) with Styrene (M_2).....	189
13. Copolymerization of 2,3-Dimethoxystyrene (M_1) with Methyl Methacrylate (M_2).....	190

14. Copolymerization of 6-Vinyl-1,4-benzodioxane (M ₁) with Styrene (M ₂).....	191
15. Copolymerization of 6-Vinyl-1,4-benzodioxane (M ₁) with Methyl Methacrylate.....	192
16. Reactivity Ratios and Q-e Parameters of Copolymerizations.....	193
17. Copolymerization Parameters of Some Substituted Styrene Monomers.....	83
18. TGA Results.....	96
19. DTA Results.....	97
20. Results of Lithiation-Silylation of Polymers.....	194
21. Results of Bromination of Polymers.....	195
22. Results of Cyanogenation of Brominated Polymers.....	196
23. Results of Phthalimidomethylation of Polymers.....	197
24. Characterization Data of Amidomethylated Polymers.....	198
25. Results of Hydrazinolysis Reactions.....	199
26. Results of Sulfonation of Polymers.....	187
27a. Results of Titration of Catechol at 23°C.....	200
27b. Results of Titration of Poly(3-vinylcatechol) at 23°C.....	201
28a. Results of Titration of Catechol at 35°C.....	202
28b. Results of Titration of Poly(3-vinylcatechol) at 35°C.....	203

LIST OF FIGURES

Figure	Page
1. Plot of contraction in the dilatometer during polymerization of 2,3-dimethoxystyrene.....	72
2. 100 MHz ^1H NMR spectra of partially deblocked poly(3,4-dimethoxystyrene).....	75
3. Method of intersection plot for 2,3-dimethoxystyrene (M_1)-styrene (M_2) copolymerization.....	80
4. Method of intersection plot for 2,3-dimethoxystyrene (M_1)-methyl methacrylate (M_2) copolymerization.....	81
5. Fineman-Ross plot for 2,3-dimethoxystyrene (M_1)-methyl methacrylate (M_2) copolymerization.....	82
6. Plot of the mole fraction of 2,3-dimethoxystyrene (M_1) in the feed versus the mole fraction in the copolymer.....	84
7. Method of intersection plot for 6-vinyl-1,4-benzodioxane (M_1)-styrene (M_2) copolymerization.....	86
8. Fineman-Ross plot for 6-vinyl-1,4-benzodioxane (M_1)-styrene (M_2) copolymerization.....	87
9. Method of intersection plot for 6-vinyl-1,4-benzodioxane (M_1)-methyl methacrylate (M_2) copolymerization.....	88
10. Fineman-Ross plot for 6-vinyl-1,4-benzodioxane (M_1)-methyl methacrylate (M_2) copolymerization.....	89

11.	Plot of the mole fraction of 6-vinyl-1,4-benzodioxane (M_1) in the feed versus the mole fraction in the copolymer.....	91
12.	FT-IR spectrum of the 2,3-dimethoxystyrene - styrene graft copolymer.....	93
13.	Thermal gravimetry analysis (TGA) curves of the poly(vinylcatechol) precursors.....	95
14.	Differential thermal analysis (DTA) curves of the poly(vinylcatechol) precursors.....	98
15.	200 MHz ^{13}C NMR spectrum of silylated poly(5-vinyl-1,3-benzodioxole).....	106
16.	200 MHz ^{13}C NMR spectrum of poly(5-vinyl-1,3-benzodioxole).....	109
17.	200 MHz ^{13}C NMR spectrum of brominated poly(5-vinyl-1,3-benzodioxole).....	110
18.	200 MHz ^{13}C NMR spectrum of poly(3,4-dimethoxy-styrene).....	114
19.	200 MHz ^{13}C NMR spectrum of brominated poly(3,4-dimethoxystyrene).....	115
20.	200 MHz ^{13}C NMR spectrum of poly(2,3-dimethoxy-styrene)....	117
21.	200 MHz ^{13}C NMR spectrum of brominated poly(2,3-dimethoxystyrene).....	118
22.	200 MHz ^{13}C NMR spectrum of poly(2,3-methylene-dioxystyrene).....	119
23.	200 MHz ^{13}C NMR spectrum of brominated poly(2,3-methylenedioxystyrene).....	120

24.	FT-IR spectrum of phthalidimidomethylated poly(2,3-dimethoxystyrene).....	126
25.	FT-IR spectra of poly(2,3-dimethoxystyrene) and poly(3-vinylcatechol).....	135
26.	200 MHz ^1H NMR spectra of poly(3-vinylcatechol) in DMSO- d_6 and DMSO- $\text{d}_6/\text{D}_2\text{O}$	136
27.	Potentiometric titration of catechol and poly(3-vinylcatechol) at 23°C	148
28.	Potentiometric titration of catechol and poly(3-vinylcatechol) at 35°C.....	151
29.	200 MHz ^{13}C NMR spectrum of poly(6-vinyl-1,4- benzodioxane).....	121
30.	200 MHz ^{13}C NMR spectrum of brominated poly(6-vinyl-1,4-benzodioxane).....	122
31.	^1H NMR of Poly(6-vinyl-1,4-benzodioxane).....	138
32.	^1H NMR of poly(6-vinyl-1,4-benzodioxane) after treatment with 57% HI.....	139

LIST OF SCHEMES

Scheme	Page
1. Polymer Transfer Agent.....	4
2. Bromination of Cumene.....	7
3. Mechanism of Bromination of Cumene with PNBS.....	7
4. Oxidation of Primary Amines by Poly(benzoquinone).....	6
5. Polymer Catalyst.....	11
6. Attachment of Enzymes on Sephadex.....	15
7. Attachment of Enzymes on Polystyrene Matrix.....	16
8. Polymer as Protecting Group.....	17
9. Merrifield's Solid State Peptide Synthesis.....	18
10. Solid State Peptide Synthesis with Mobile Mediator.....	20
11. Protection of Hydroxyl Group of Dialcohol by Polymer Matrix.....	21
12. Protection of Aldehyde Group of Dialdehyde Compound by Polymer Matrix.....	22
13. Examples of Redox Polymers.....	23
14. Synthesis of Poly(hydroquinone-esters).....	27
15. Friedel-Crafts Reaction of Chloromethylated Poly(styrene-divinylbenzene) with Redox Units.....	35
16. Friedel-Crafts Alkylation of Styrene-Divinylbenzene Copolymer with 2,5- and 3,4-Dimethoxybenzyl chloride.....	37
17. Synthesis and Polymerization of Vinylhydroquinone.....	42
18. Synthesis of Protected Vinylhydroquinone and Vinylcatechol.....	43

19.	Preparation of 2,5-Dimethoxy-3,4,6-trimethylstyrene.....	47
20.	Synthesis of Poly(3-vinylpyrazoloquinone).....	50
21.	Pyraniloxy as Protecting Group.....	50
22.	Synthesis of Poly(4'-vinyl-2,5-dihydroxy-1,1'-biphenyl)....	52
23.	Synthesis of Poly(3,4-dihydroxybenzyl methyl methacrylate).....	53
24.	Reaction of Poly 28 with BCl_3 -Dodecyl Mercaptan.....	133

ABSTRACT

5-Vinyl-1,3-benzodioxole, 28, 3,4-dimethoxystyrene, 29, 2,3-dimethoxystyrene, 30, 6-vinyl-1,4-benzodioxane, 31, and 4-vinyl-1,3-benzodioxole, 32 were synthesized and evaluated as poly(vinylcatechol) precursors. Four methods for preparing these monomers were explored: 1) dehydration of α -phenethyl alcohol derivatives, 2) decarboxylation of cinnamic acid derivatives, 3) Wittig methenation of benzaldehyde derivatives, and 4) Wittig reaction of benzyl ylide derivatives with formaldehyde. Dehydration of α -phenethyl alcohols was the best general procedure; the monomers could be isolated in the following yields: 28, 63%; 29, 45%; 30, 85%; 31, 65%; 32, 50%. The polymerizabilities of the five monomers were ascertained under free radical, anionic, and cationic conditions. Molecular weights as high as 95,000 in the case of poly(2,3-dimethoxystyrene) were achieved in the presence of free radical initiators. The kinetics of free radical polymerization of 2,3-dimethoxystyrene, 30, was studied dilatometrically and the overall rate of the reaction was found to be $R_p = 2.53 \times 10^{-2}$ mol/L min. Radical copolymerizations of monomers 30 and 31 with styrene and methyl methacrylate were examined. The reactivity ratios of monomer 30 (M_1) with comonomers (M_2) were $r_1 = 0.69$, $r_2 = 0.92$ and $r_1 = 0.92$, $r_2 = 0.23$ respectively. Q and e values of 30 were calculated to be $Q_1 = 1.89$, $e_1 = -1.48$ in the styrene system and $Q_1 = 1.91$, $e_1 = -0.83$ in the methyl methacrylate system. The copolymerization parameters of monomer 31 were $r_1 = 1.09$, $r_2 = 0.96$; $Q_1 = 1.33$, $e_1 = -1.00$ in the first system, and $r_1 = 0.45$, $r_2 = 1.05$; $Q_1 = 0.45$, $e_1 = -0.47$ for the

second system. Polystyrene grafts onto poly(vinylcatechol) precursors were also prepared. Poly(vinylcatechol) precursors were further characterized by DTA and TGA techniques; they were found to be thermally stable and decompose only at a temperature range of 360-550 °C.

Chloromethylation of poly 31 only with chloromethyl ethyl ether and subsequent quaternization were successful. Lithiation of poly 28, poly 30, and poly 31 was studied. Bromination of each poly(vinylcatechol) precursor was thoroughly examined; quantitative substitution was achieved and bromination locations were determined using a ^{13}C NMR technique. Phthalimidomethylation, followed by hydrazinolysis of poly 29, poly 30, poly 31, and poly 32 afforded aminomethylated polymers. Sulfonation of poly 29, poly 30, and poly 31 with chlorosulfonic acid was possible and could produce water soluble polymers.

Conditions for deblocking the protecting groups to liberate the catechol functions were established. Boron trichloride in the presence of dodecyl mercaptan was found to be the most effective cleaving reagent. Subsequent oxidation of poly(3- and 4-vinylcatechols) with ceric ammonium nitrate generated poly(benzoquinones).

Redox potentials of the oxidation of catechol and poly(3-vinylcatechol) were estimated by potentiometric titration employing 0.05 N ceric ammonium nitrate in 90% acetic acid as titrant. At 23 °C, the midpotentials were found to be 764 and 707 mV respectively. At 35 °C, while one midpoint potential, 290 mV, was observed for the polymeric catechol, two midpoint potentials, 432 and 870 mV were detected for the catechol.

INTRODUCTION

A. Polymer Reagents in Organic Synthesis

In a classical organic reaction, conventional laboratory techniques, such as extraction, precipitation, sublimation, and chromatography, are used to isolate the product from the reaction mixture. Frequently, purification of the desired product requires two or more of the above operations. Although the yield of an organic reaction may be improved by varying the conditions of the reaction, quantitative isolation of the final product in high purity demands an appreciable amount of time. To overcome some of the difficulty of separating reactants from products in conventional organic synthesis, polymers supporting reactants and transferring functional groups were introduced. Insoluble polymers simplify the isolation of products, because the resin-supported reagents can be removed by simple filtration. This facet of polymer chemistry has become an exciting field to explore since the brilliant success of Merrifield's solid state peptide synthesis in 1963.¹

Polymers as reagents exhibit several advantages over the low molecular weight counterparts, some of which are :

- 1) Polymer reagents are easily separable from low molecular weight compounds; with insoluble polymers, separation is achieved by simple filtration or centrifugation, and with soluble polymers, selective precipitation is employed.
- 2) The ease of separation encourages the chemist to use a large excess of either soluble or polymer reagent, and the enhanced concentrations of reactants increase the overall rate of reaction. Further, the use

of excess reagents may shift equilibria toward the completion of reaction, i.e., promote high yields.

- 3) The excess of reagent can be easily separated from the desired product and reused without further purification.
- 4) Side reactions can be minimized and the by-products are easily removed without any major difficulty.
- 5) The noxious properties of low molecular weight reagents, such as toxicity, volatility, and malodor, can be avoided by using polymeric supports.
- 6) Since the polymer can act as immobilizing agent, reactions which require high dilution in solution may be carried out at high concentration of reagents on polymer carriers.
- 7) The insoluble polymer support provides different steric and polar environments from solution analogues. This property was exploited in Dieckmann condensation² which proceeds selectively on the polymeric carriers. The steric properties of the polymer backbone and/or bulky substituents may be used to promote selective attack on one component of a substrate mixture.

The reactions occurring on polymer matrices, once claimed to be difficult to follow and not amenable to common analytical methods such as UV and NMR spectroscopy, are now easily monitored by UV, as reported recently by Patchornik et al³ and ¹³C NMR as reported lately by Ford et al.⁴ Although it is true that polymer reagents have solved some major problems encountered in conventional organic synthesis, the inherent disadvantages rarely restrict their application. The few limitations of the use of the polymer reagents are:

- 1) Anchoring to and sometimes removal from the polymer carrier are

additional steps in the experiment procedure. Sometimes the cleavage, which is necessary at the end of the process, is incomplete resulting in lower yields or some extreme conditions used in cleaving lead to decomposition of the product.

2) The yields of the product of the reaction using polymer reagents can be sometimes lower than those in solution. This may be due to steric hindrance generated by polymer matrix at the reaction site.

3) The mechanism of the reaction on the polymeric reagent sometimes proceeds differently from that in solution. This was clearly observed in the bromination of cumene using insoluble poly(N-bromo-succinimide).⁵

Polymer reagents can be either organic or inorganic. The organic polymer can be prepared either by fixing the reagent on a given reactive polymer via chemical modification or by polymerization of a monomer reagent. The former method has been widely used in order to meet the required physical properties of a polymer, such as mechanical strength, porosity, and rigidity of the matrix. Polymers should meet the following conditions in order to be suitable in organic reaction:

1) The support should possess various reactive sites or should be readily functionalized.

2) The polymer should be rigid and easy to handle.

3) The reaction site of the polymer should be readily exposed to reagents. The most widely used polymer supports are copolymers of styrene and divinylbenzene because they exhibit good chemical and mechanical behavior and are easily functionalized.

Polymers as carriers have been applied in several ways for specific objectives. Hence, polymer reagents can be categorized into

three main classes: polymer transfer reagents, polymer catalysts, and polymers as protecting groups.

I. Polymer Transfer Reagents: The polymer acts by its functional group to transform the low molecular weight substrate into a product. Scheme 1 illustrates the different steps of this process. The functional polymer support, $(P)-F$, reacts with substrate S to produce the product S-F. This final product is separated by a simple filtration of the polymer followed by evaporation of solvent and purification. Polymers as transfer agents were widely employed for various well-known reactions, such as reduction, oxidation, halogenation, acylation, ...etc.

Scheme 1: Polymer Transfer Agents

Some important organic reactions using polymer transfer agents are given in Table 1. As mentioned earlier, the features of this process are the ease of removal of the polymer at the end of the reaction and the use of a large excess of polymer reagents affording, in many cases, products in high yields. As stated earlier, a change in mechanism of a reaction can occur due mainly to microenvironmental effects originated from the polymer matrix. For example, Patchornik⁵

Table 1: Polymer Transfer Agents in OrganicSynthesis

<u>X</u>	<u>Reaction type</u>	<u>Reference</u>
-SnH ₂ -n-C ₄ H ₉	Reduction of halide Reduction of carbonyl	6
-P(Ø) ₂ CH ₂ R X ⁻	Wittig reaction; olefin synthesis from carbonyl compounds	7,8
$\begin{array}{c} \text{Me} \\ + \\ \text{S} \\ - \\ \text{Me} \end{array} \quad \text{Br}^-$	Epoxide formation from carbonyl compounds	9
-CH ₂ -N=C=N-CHMe ₂	Moffat oxidation; oxidation of alcohol to aldehyde or ketone	10
-CO ₃ H	Epoxidation of olefins Oxidation of penicilines to sulfoxides and sulfones	11, 12 13
$\begin{array}{c} \text{Cl} \\ \\ -(\text{CH}_2)_n - \text{P} - (\text{Ø})_2 \\ \\ \text{Cl} \end{array}$	Acid chloride and nitrile synthesis	14

reported that cumene, which mainly undergoes α -bromination with N-bromosuccinimide (NBS), when treated with poly-(N-bromosuccinimide), PNBS, as brominating agent gave three different brominated products as shown in Scheme 2. A plausible mechanism of the formation of the products 1, 2, and 3, consists of a set of bromination and dehydrobromination reactions as suggested in Scheme 3.

Daly and Kaufman¹⁵ reported a synthesis of copoly(styrene-3-vinyl-5-t-butyl-1,2-benzoquinone), a valuable redox polymer. This copolymer shows great effectiveness in the oxidation of primary amines to ketones, Scheme 4, which is similar to a low molecular weight reaction reported by Corey.¹⁶

Scheme 4: Oxidation of Primary Amines by
Poly(benzoquinone)

Scheme 2: Bromination of Cumene

Scheme 3: Mechanism of Bromination of Cumene

with PNBS

Chloromethylation has been by far the most versatile reaction in polymer modification because the chloromethyl group, a key intermediate, is suitable for both nucleophilic elaboration, such as quaternization, phosphination, and esterification, and electrophilic addition to activated aromatic reagents. Chloromethyl methyl ether (CME) and bis(chloromethyl) methyl ether (BCME) and their bromo analogues have been the most efficient halomethylating agents, yet they are highly carcinogenic compounds. Although new reagents such as 1-chloromethoxy-4-chlorobutane and 1,4-bis(chloromethoxy)-butane were developed,^{17,18} the novel bromomethylating polymer, 4, recently prepared,¹⁹ could be the most convenient reagent to effect this modification. Bromomethylation of 1,2-dimethoxybenzene (veratrole) with this polymeric bromomethylating agent in the presence of Lewis acid, SnCl_4 , was successful, (eq. 1).

Among the earliest examples of polymer reagents are no doubt the ion exchange resins. Although, their application in organic chemistry has been neglected for sometime, the last two decades are full of examples showing their advantages over the soluble analogues. Quaternary ammonium resins, anion exchangers, are considered potential substitutes for tetraalkylammonium salts, catalysts usually employed in the phase transfer reactions. In general, these tetraalkyl

ammonium salt polymers are prepared by quaternization of some commercially available chloromethylated polymers. Table 2 contains some of well-known organic reactions using these anion exchangers during the last 15 years. The yields of reactions range generally between 70 and 100%. Again, the ease of removal of the resin from the reaction mixture remains the best feature in these systems. Also, the excess of reagents enhances yields and rates of reactions. Finally, the anion exchangers are readily prepared from less costly resins.

II. Polymer Catalysts: The common homogeneous catalysts are linked to the polymer matrix to catalyze an organic reaction. Polymer catalysts resemble polymer transfer agents in regards to their participation in the reaction, yet, according to the definition of a catalyst, they must be recovered unchanged at the end of the reaction. The general steps of this reaction are described in Scheme 5 where $\text{P}-\text{C}$ represents a catalyst bound to a polymer matrix P . A substrate S reacts with a reagent A in the presence of the polymer catalyst to afford the product D. After a simple filtration of the spent polymer, the final product D can be isolated by evaporation of the solvent followed by a purification technique. Generally, a polymer catalyst may have an enzyme, an inorganic or an organometallic compound on its active site. The most frequently used polymer reagents as catalysts are the ion exchange resins either in acidic form (H^+) or basic form (OH^-). They catalyze general acid or general base catalyzed reaction. One major advantage of the ion exchangers over the conventional acid and base is the absence of the corrosivity potential of the species in contact with a vessel or a reactor.

Table 2: Quaternary Ammonium Resins
in Organic Synthesis

<u>A⁻</u>	<u>Substrate</u>	<u>Product</u>	<u>Reference</u>
OCN ⁻	R-X	RNHCNHR	20
SCN ⁻	"	R-SCN	"
Br ₃ ⁻	$\text{R}_1\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{CH}_2\text{R}_2$	$\text{R}_1\text{COCHBrR}_2$	21
BrCl ₂ ⁻	>C=C<	$\begin{array}{c} \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{Br} \quad \text{Cl} \end{array}$	22
"	-C≡C-H	$\begin{array}{c} -\text{C} = \text{C}- \\ \quad \\ \text{Cl} \quad \text{Br} \end{array}$	"
NO ₂ ⁻	$\text{R}_1\text{R}_2\underset{\text{X}}{\text{C}}-\text{CO}_2\text{R}_3$	$\text{R}_1\text{R}_2\underset{\text{NO}_2}{\text{C}}-\text{CO}_2\text{R}_3$	23
$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ -\text{C}-\text{CH}-\text{C}- \end{array}$	R-X	$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ -\text{C}-\text{CHR}-\text{C}- \end{array}$	"
ArSO ₂ ⁻	"	ArSO ₂ -R	24
ArO ⁻	"	Ar-OR	23
F ⁻	"	R-F	25
"	RSO ₂ OR	R-F	"
"	$\begin{array}{c} \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{X} \end{array}$	>C=C<	26
"	RSO ₂ Cl	RSO ₂ F	27
RCOO ⁻	R'-X	RCO ₂ R'	28
HFe(CO) ₄ ⁻	R-X	RCHO	29
HCrO ₄ ⁻	R-CH ₂ X	RCHO	30
"	RR'CHOH	R-CO-R'	31
CN ⁻	Ar-CH ₂ X	Ar-CH ₂ CN	32

Scheme 5: Polymer Catalyst

a = Reaction of substrate S with reagent A

b = Filtration of polymer catalyst $\text{P}-\text{C}$

c = Evaporation of solvent and purification of product D

1. Polymer-bound transition metal complexes: Extensive studies have been conducted on polymer-bound catalysts bearing transition metal complexes. These systems successfully catalyzed hydrogenation,^{33,34} hydrosilylation,³⁵ and hydroformylation^{34,35} of olefins. Silica and polystyrenes were the most widely used supports carrying metal complex catalysts usually through phosphine groups. The polystyrene supports are easily prepared by chloromethylation of polystyrene crosslinked with divinylbenzene and subsequent treatment with lithium diphenylphosphide. Some polymer catalysts used in organic reactions are reported in Table 3. The polymer-bound catalyst containing rhodium, 5, a Wilkinson type complex, is a very useful catalyst in hydrogenation of olefins and shows more selectivity than normal catalyst; for example, it reduced cyclohexene at the same rate as with normal catalysts, but it reduced cyclododecene at 1/5 the normal rate.³³ The iridium-supported polymer, 6, revealed the same activity.³⁶ The decrease in activity of the rhodium and the iridium polymer catalysts is explained as due to the double linkage of the polymeric support to the metal of the complex. Hence, in order for

the polymer catalyst to be effective and to maintain its activity potential, the metal of interest should be linked to the polymer matrix by a single bond. As evidence for the double linkage, it was observed that at least two triphenylphosphine moieties were released from each metal incorporation during the preparation of polymer catalyst as outlined in eq. 2.

A similar type of chelation was formed when polymer-bound cobalt catalyst was synthesized.³⁷ The bis(polymeric) binding, in this case, occurs only when the polymer catalyst, 7, is subjected to heat as shown in eq. 3. Furthermore, investigations revealed that the formation of this bis(polymeric) binding could be substantially reduced by using 20% divinylbenzene instead of 2% crosslinking. Therefore, the catalytic activity of the polymer catalyst is enhanced. Accordingly the flexibility of copoly(styrene-2% divinylbenzene) results in dimerization. The rigidity of the polymer

plays an important role in the activity of the resin catalyst. For example, polymer-bound titanocene, 8, prepared using 20% divinylbenzene, was 25 to 100 times as active as its non solid phase analogue.^{38,39}

In the study of palladium catalyzed vinylic substitution on a variety of aryl halides, Heck⁴⁰ reported that nitrogen containing ligands were not effective in stabilizing the catalyst; palladium metal precipitates upon addition of aryl halides. Daly and Sun⁴¹ recently succeeded in binding palladium on poly(4-vinyl-pyridine) crosslinked with 10 or 15% divinylbenzene. This polymer-bound catalyst promoted effectively the vinylation of aryl halides.

In 1982, Allock⁴² reported that polyphosphazenes are well suited for use as carriers of organometallic catalysts. Among the polymeric phosphazene catalysts so far prepared are 9, 10, and 11. However, their application as effective catalysts in organic reactions was not mentioned.

Table 3: Polymer-bound Catalysts,

C	Reaction type	Reference
$-\text{SO}_3\text{H}$	Acid-catalyzed reaction	43
$-\text{CH}_2\text{N}^+(\text{Me})_3\text{OH}^-$	Base-catalyzed reaction	"
$-\text{AlCl}_3$	Lewis acid-catalyzed reaction	44, 45
$-\text{PRhClPPh}_2$	Hydrogenation, hydrosilylation 35, 38, 46 and Hydroformylation of olefins. Polymerization	
$-\text{RhCl}_3$		
$-\text{PtCl}_2$		
$-\text{PdCl}_2$

Rose Bengal	Photooxidation via singlet oxidation production	47

2. Immobilized enzymes: The synthesis of a polymer catalyst with the specificity and the activity of a naturally occurring catalyst, i.e., enzymes, has not been accomplished and would be of great value. Eventually, reactive and insoluble resin carriers with enzymes attached by covalent bonding were prepared.^{48,49} The enzyme thus immobilized retains its biological activity. A variety of such immobilized enzymes on polymers are employed in industrial processes. Again, the main feature of the use of immobilized enzymes is their easy separation from solution. Since they can be recycled and reused, many enzymatic reactions that were prohibitively expensive have now become of economic interest. The preparation of a reactive carrier can be achieved by incorporating a functional group into synthetically preformed polymer or natural polymer, such as cellulose or sephadex. For example, a cyano functional group can be attached to sephadex by reaction with cyanogen bromide, then the activated natural polymer is treated with enzyme as described in Scheme 6.⁵⁰

Scheme 6: Attachment of Enzymes on Sephadex

Poly(aminostyrene), a synthetic polymer, may be activated by diazotization or by reaction with thiophosgene. Enzymes can then be anchored and immobilized as shown in Scheme 7 with retention of its activity.⁵⁰

Scheme 7: Attachment of Enzymes on Polystyrene

The applications of immobilized enzymes in the industry are numerous. For example, isomerization of glucose to fructose occurs in the presence of an immobilized enzyme. The industries of the U.S.A. manufacture annually about 2 millions tons of fructose with this process.⁵¹ The DL-forms of amino acids are produced in large quantities and, since the biological system requires only L-form, a separation technique is strongly needed. In 1972, the use of immobilized enzymes on polymers was successful in separating the L-amino acid acylase.⁵² Also, hydrolyzed lactose, a sweetener for milk products, was obtained by cleaving of lactose by immobilized lactase.

III. Polymers as Protecting Groups: Scheme 8 illustrates the steps involved when polymer is used as a protecting group in an organic reaction. A difunctional reagent A is anchored by one of its functionalities to the polymer support, and two or more chemical transformations would take place to form $(P)-A-B-C$, a polymeric product. The final product A-B-C is released from the polymer support by a selective cleavage of the $(P)-A$ bond. As noted, this

Scheme 8: Polymer as Protecting Group

methodology assures the protection of one functionality of a bifunctional substrate by careful attachment to a polymer backbone. The sequence of reactions on the polymer support originates from Merrifield's solid state peptide synthesis.¹ A typical peptide synthesis is described in Scheme 9. In this, the amino acid is attached to the functionalized polymer by its carboxylic acid group. The N-protected group is then removed selectively and the free amine obtained is coupled with a carboxyl group of a second amino acid moiety. Depending on how long the peptide is wanted to be, this sequence may be repeated as often as necessary. The desired peptide can be isolated by acid or base cleavage of the amide group covalently attached to the polymer backbone. Oligomers, such as oligonucleotides and oligosaccharides,^{53,54} were also prepared by this method, usually

Scheme 9: Merrifield's Solid State Peptide

Synthesis

in high yields.

In 1985, Patchornik et al³ reported a fascinating methodology of solid state peptide synthesis. The principle of this methodology is based on the transfer of the N-protected amino acid from one insoluble polymer (donor) such as o-nitrophenyl ester to an insoluble polymer-bound amino acid (acceptor) with the aid of a soluble mediator molecule. A picture of the experimental procedure is drawn in Scheme 10. In this procedure, the polymer I carries an N-protected amino acid bound as an active ester. Polymer II is a Merrifield-type polymer carrying a peptide, amino acid or free amino group. The polymer I reacts with the mediator (imidazole) to release the soluble acylimidazole. Polymer II then reacts with the freed acylimidazole to add another amino acid. The free imidazole then repeats the cycle until polymer II is saturated. The best feature of this methodology is that the reaction is monitored by UV absorption of the circulating solution when entering and leaving polymer II. The Boc protecting group is removed for the next coupling step. The yields of peptides synthesized by this method range between 70 and 100% depending upon the type of polymer II used. This methodology has been extended to the sulfonation and phosphorylation reactions when polymer-bound dimethylaminopyridinium was employed.

The anchoring and protecting processes on polymers have been widely exploited in organic synthesis. The polymer serves as selective protecting group for one functionality of a multifunctional compound. For instance, the selective reaction of one hydroxyl group

Scheme 10: Solid State Peptide Synthesis
with Mobile Mediator

of a dialcohol with acyl chloride attached to the polymer matrix is considered as one of the best applications of polymers in organic reactions. The unprotected hydroxyl functionality may be subject to a variety of chemical modifications such as that shown in Scheme 11. In this example, a large excess of dialcohol substrate can be used to prevent bifunctional binding to the polymer.

Scheme 11: Protection of Hydroxyl Group of
Dialcohol by Polymer Matrix

Frequently, one may desire to selectively modify a single functional group on a bifunctional compound of identical functionality, such as dialdehyde, but both groups would react simultaneously with the specific reagent. However, a selective chemistry could be achieved on one aldehyde functionality of a dialdehyde if the other is well protected. As an example, Grignard and Wittig reactions can be carried out on a dialdehyde substrate with one group protected by a polymer matrix as outlined in Scheme 12.⁵⁷

**Scheme 12: Protection of Aldehyde Group of
Dialdehyde by Polymer Matrix**

B. Redox Polymers

Polymer redox systems are known by the terms "oxidation - reduction polymers" and "electron-transfer polymers". The name "electron-exchange polymers" was also assigned to these resins in analogy to "ion-exchange polymers", but Sansoni⁵⁸ pointed out that a transfer is occurring instead of exchange, thus this name has been dropped. These redox polymers are high molecular weight substances that can transfer electrons in contact with reactive ions or molecules. Therefore, polymers of this sort can be oxidized or reduced with appropriate oxidizing and reducing agents, respectively. These resins are usually loaded with functional groups of the redox-type. A variety of redox functionalities has been of

great interest for polymer chemists. Among the most widely studied redox polymers are ferrocene, pyridinium, mercaptyl, and hydroquinone containing polymers. Oxidized and reduced forms of these polymers are compiled in Scheme 13. Ferrocene-containing polymers are valuable electroactive resins. The ferrocene unit can be anchored onto a variety of polymer matrices. For example, Allock⁵⁹ reported recently a synthesis of polyphosphazene bearing ferrocene or ruthenocene, having molecular weight as high as 2,000,000. Recently, in Daly's laboratory⁶⁰, the ferrocene moiety was introduced on styrene-methyl methacrylate copolymer; this polymer-bound ferrocene exhibits a potential electroactivity as confirmed by cyclic voltammetric measurements.

Scheme 13: Examples of Redox Polymers

(P) = Polymer Backbone

A careful examination of redox polymers containing dihydroxybenzene reveals their importance. These redox resins belong to the polymer reagents class discussed in part A of this introduction. The first transfer agent polymers reported in the literature were undoubtedly the redox polymers, namely the electron-transferring agents. Some of the early examples are poly(vinylhydroquinones) and the condensation products of hydroquinone and formaldehyde. The first application of these resins was the oxidation of iodide to iodine as shown in eq. 4.⁹⁵

I. Synthesis of Redox Polymers: Three routes could be conceived as ways of preparation of redox polymers. They are : 1) condensation polymerization of suitable monomers, 2) attachment of redox groups onto preformed polymers, and 3) polymerization of vinyl monomers having redox groups.

1. Condensation polymers: The earliest redox polymers were undoubtedly the synthetic polymers derived from formaldehyde and hydroquinone. The condensation of these two substances yielded phenoplasts. Resorcinol and its derivatives are among those which are stable to oxidation and used in commercial phenoplast formulation. Catechol (1,2-dihydroxybenzene) and hydroquinone (1,4-dihydroxybenzene) are of interest because they are capable of forming quinoid systems. The naphthaquinone and anthraquinone derivatives are also examples of this category of polyphenols. The quinoid unit of

catechol is unstable and most quinones are sensitive to light and oxidants. Condensation polymers may be classified into two categories: those which have the redox units as part of the backbone and those which have them as pendent from the matrix.

a. Redox units as part of backbone: Although formaldehyde-hydroquinone polymers were prepared in the beginning of this century, it was only in 1949 that a description of these resins as electron-transfer polymers was given.⁶¹ The condensation polymerization of hydroquinone and formaldehyde is a base- or acid- catalyzed reaction.

Different products can be formed in three different stages of the reaction. These materials produced are dependent upon the initial hydroquinone-formaldehyde ratio and the reaction conditions. In the first stage, A-stage, the products exist as mono-, di-, and trinuclear methylolphenols which are soluble in acetone, ethyl acetate, and dioxane. In the second step, B-stage, as the condensation reaction continues, the products became thermoplastic with reduced solubility. These B-stage polymers are termed "resoles". The resoles possess highly branched structures with methylene bridges linking the benzene rings. In the third stage, C-stage, condensation continues on heating the resole mixture to produce high molecular weight

crosslinked polymers.

A change of formaldehyde-hydroquinone ratio results in a change of chemical and physical properties of the polymer. For example, the redox capacity increases as the formaldehyde concentration increases. Formaldehyde can be substituted by other aldehydes, such as acetaldehyde, benzaldehyde, furfural, glyoxal, and paraformaldehyde. This last aldehyde with hexamethylenetriamine releases formaldehyde upon hydrolysis, as reported by Kopra and Welcher.⁶²

Poly(2,5-dimethoxy-*p*-xylene) was made by reaction of 2,5-dimethoxy-4-methylbenzyltrimethyl ammonium chloride with alkali as in eq. 6. The quaternary ammonium salt was obtained by treating 2,5-dimethoxy-4-methylbenzyl chloride with trimethylamine. Demethylation of the polymer with hydrobromic acid gave poly(2,5-dihydroxy-*p*-xylene).

The hydroquinone diesters, Scheme 14, are readily reduced in good yields to the hydroquinone diols with lithium aluminum hydride. The hydroquinone moiety is easily oxidized almost quantitatively by

stirring a tetrahydrofuran solution with silver oxide and anhydrous magnesium sulfate to give the corresponding quinone diols.⁶⁴ The reaction of these quinoid dialcohols with a diacyl chloride in THF in the presence of pyridine yields polymer with a quinone unit as redox group. These polymers are easily reduced to hydroquinone polyesters with sodium dithionite or hydrogen and palladium-charcoal at ordinary temperature.

Scheme 14: Synthesis of Poly(hydroquinone-esters)

Cassidy^{6b} reported the preparation of hydroquinone polycarbonates. 2,5-Bis(3'-hydroxypropyl)-1,4-benzoquinone reacting with phosgene in THF medium containing pyridine afforded a polymer which precipitated in pentane in quantitative yield, eq. 7. This

polymer is soluble in organic media, such as acetone, chloroform, THF, and DMF, and can be readily reduced to the hydroquinone form by one of the reducing agents mentioned above.

Cassidy⁶⁶ also reported the synthesis of hydroquinone polyurethane. 2,5-Bis(3'-hydroxyalkyl)-1,4-benzoquinone can react with diisocyanate at room temperature in the presence of triethylamine or dibutyltin diacetate as catalyst to give the corresponding quinoid polyurethane as yellow flakes, eq. 8. In this case, all the reagents must be anhydrous and highly pure. The polymer in oxidized form can be precipitated from THF in n-hexane. The reduction of quinoid polymer to the corresponding hydroquinoid form is achieved with no detection of a cleavage of the backbone.

Quinone polyamines may be made by condensation of a diamine with a quinone as shown in eq. 9. Among the diamines used in the condensation with benzoquinone are p-phenylenediamine, benzidine, and hexamethylenediamine. A 1:3 ratio of diamine-benzoquinone is required to produce, after reflux in ethanolic solution, poly(aminoquinone).⁶⁷

Suzuki and Tazuke⁶⁸ recently prepared 2,5-bis(dimethylaminomethyl)hydroquinone (HQMe), and 3,6-bis(dimethylaminomethyl)catechol (CAME) by reacting hydroquinone or catechol with aqueous dimethylamine and formaldehyde as illustrated in eq. 10. Dimethylaminomethyl hydroquinone and the catechol analogue are used as monomers in the formation of polyionenes as outlined in eq. 11. The redox properties of these polyionenes were examined. They can be oxidized with O_2 in 1.5% sodium carbonate solution. The precipitated brown powders showed an absorption band at 1630 cm^{-1} in the infrared, indicating that hydroquinone units (or catechol) of the polymers were oxidized to benzoquinone units.

Redox polyamides were developed by Iwakura⁶⁹ by condensing di-lactones with diamine compounds. For example, in eq. 12 the di-

lactone obtained by heating the corresponding diacid at 280 °C condensed with the diamine in dimethylacetamide (DMAc) upon warming the mixture for several hours. The hydroquinone polymer was obtained in 75% yield and could be oxidized to quinoid polymer with ceric ammonium nitrate in DMAc.

In general, hydroquinone-formaldehyde based polymers are slow to react. To enhance their chemical reactivity, Manecke⁷⁰ designed a synthesis of redox polymers with good redox capacity (6.4 meq/g) and high reactivity by combining hydroquinone, phenol, and formaldehyde. A polymer of type 12 was obtained.

In the previously discussed hydroquinone containing polymers, the hydroquinone or quinone units are joined by single methylene bridges. In 1985, Dallal and co-workers⁷¹ reported the synthesis of poly(bismethylenehydroquinone), 13, where the hydroquinone moieties are held together by two methylene bridges. This polymer was prepared by mixing trioxane and an excess of hydroquinone in sulfolane and

water in the presence of a catalytic amount of toluenesulfonic acid. The mixture was heated at 175 °C for one hour. This new redox polymer is air oxidized and chemically oxidized with bromine-potassium hydroxide. Both reduced and oxidized forms were characterized by a combination of FT-IR, elemental analysis, and ^{13}C solid state CP/MAS NMR.

b. Pendent redox groups from backbone: The redox units such as hydroquinone and catechol may be pendent from the polymer matrix. In that case, oxidation and reduction will not affect the chain of the resin. Poly(2,5-dihydroxyphenylalanine) and poly(3,4-dihydroxy - phenylalanine) (DOPA) were synthesized by attaching hydroquinone and catechol units, respectively, on polypeptide matrices.⁷² For instance, 3,4-diacetoxyphenylalanine hydrochloride was prepared by treatment of 3,4-dihydroxyphenylalanine with acetyl chloride, eq. 13. Reaction of 3,4-diacetoxyphenylalanine with phosgene afforded N-carboxyanhydride which polymerized by a trace of sodium hydroxide in dioxane. Acidification followed by cleavage of the acetyl groups yielded poly(3,4-dihydroxyphenylalanine).

A pendent redox unit from a polyurethane matrix was also made.⁷³ As shown in eq. 14, the quinoid diol derivative reacted with diisocyanate to yield the monomer, 14, which upon condensation with glycol gave the corresponding polyurethane in which quinone diol alternates with quinone glycol.

Izoret⁷⁴ successfully synthesized a redox polymer with an anthraquinone as redox unit pendent from a polyester matrix. Reaction of diethyl malonate with 2-formylanthraquinone under "malonic ester" synthetic conditions afforded the vinylanthraquinone derivative, eq. 15. This latter compound could be condensed with a diol using sulfuric acid as catalyst to give the poly(anthraquinone)

derivatives. 1,4-Dihydroxybutane, diethyleneglycol, and glycerol were among the dialcohols used in this type of condensation.

2. Attachment of redox units onto preformed polymers:

Electron-transfer polymer may be prepared by attachment of a redox unit onto premade polymer. This attachment can be made by chemical substitution, displacement, or other types of reactions with the functional groups already existing on the polymer matrix. For example, as early as 1957, Sansoni⁵⁸ prepared redox polymer by reacting hydroquinone with poly(styrene-diazonium salts), eq. 16. This functionalized polymer was made by nitration of polystyrene followed by reduction of the nitro group to an amino group and subsequent treatment with nitrous acid. As expected, the diazonium salts generated crosslinking between the polymer chains. He also placed a ferrocene moiety on a polystyrene backbone employing a similar reaction.

As reported by Kun,⁷⁵ hydroquinone-quinone redox polymers may be readily made using either quinone or hydroquinone in protected or

unprotected form in a Friedel-Crafts reaction with halomethylated styrene-divinylbenzene copolymer. As outlined in Scheme 15, Friedel-Crafts reaction of the chloromethylated poly(styrene-divinylbenzene) with hydroquinone, benzoquinone, 1,4-dimethoxybenzene, and 1,4-diacetoxybenzene in the presence of a Lewis acid such as SnCl_4 gave polymeric vinylbenzylhydroquinone after removal of the protecting groups. The poly(vinylbenzylhydroquinone) may be oxidized to poly(vinylbenzylbenzoquinone) which, in turn, may be reduced to the hydroquinone again.

Because of the low reactivity of the chloromethyl group, Russian investigators⁷⁶ developed a synthesis of bromomethylated copolymer by reacting the chloromethylated resin with lithium bromide in a mixture of boiling dioxane and acetone for 20 hours. They carried out the Friedel-Crafts reaction of bromomethylated copolymer with quinone, anthraquinone, naphtaquinone, pyrogallol, hydroquinone, resorcinol, pyrocatechol, and dialkylether of hydroquinone. Dioxane and dichloroethane proved to be good swelling media for the bromomethylated resins.

Scheme 15: Friedel-Crafts Reaction of Chloro-
methylated Poly(styrene-divinylbenzene)
with Redox Units

The hydrophilicity of these redox polymers can be improved by the incorporation of an ion-exchange group. By limiting the concentration of redox units added to the polymer matrix, a significant number of halomethyl groups is available for subsequent chemical treatment. For example, reaction of the remaining chloromethyl groups with trimethylamine, eq. 17, yielded hydrophilic redox polymers containing anion exchange groups. While maintaining a maximum number of redox units available, increased hydrophilicity of the resins may be

achieved by reacting the hydroquinone units of the resins with chlorosulfonic acid as illustrated in eq. 18. The sulfonated redox polymers could be employed as cation-exchange resins.⁷⁷

Kun⁷⁸ also reported the attachment of anthraquinone and its derivatives such as 2-methylantraquinone and 2-ethylantraquinone onto styrene-divinylbenzene copolymer via the Friedel-Crafts alkylation reaction described above. By the same procedure, Warshawsky⁷⁹ treated the chloromethylated copolymer cited above with catechol to produce polymeric catechol. This latter resin, however, was destined to make polymer crown ethers.

Generally, in such alkylation reactions, the remaining unreacted chloromethyl groups of the supporting resin can cause side reactions and effects. To avoid such unwanted reactions, Iwabuchi⁸⁰ introduced hydroquinone or catechol units on the same support by Friedel-Crafts

alkylation of styrene-divinylbenzene resin with 2,5- and 3,4-dimethoxybenzyl chloride, followed by demethylation with hydrobromic acid as given in Scheme 16. In this fashion, a high content of redox units on the resin could be achieved.

Scheme 16: Friedel-Crafts Alkylation of Styrene-Divinylbenzene Copolymer with 2,5- and 3,4-Dimethoxybenzyl Chloride.

In Daly's laboratory,⁸¹ 1,3-benzodioxole, a valuable redox group precursor, was introduced into a variety of polymer matrices. The polymeric supports were several condensation polymers, such as poly(2,6-dimethyl-1,4-phenylene oxide), poly(phenylene ether sulfone), and phenoxy resin. To achieve a high degree of incorporation of catechol synthons, piperonyl chloride was reacted with the above chosen carriers under the standard Friedel-Crafts alkylation conditions, eq. 19. The methylenedioxy group was subjected to cleavage to produce polymeric catechols.

Manecke⁸² converted poly(styrene sulfonic acid) crosslinked with 10% divinylbenzene to poly(styrene-4-sulfonyl chloride) which is designed as starting material for different polymers containing *p*-benzoquinone for example, reaction of poly(styrene-4-sulfonyl chloride) with 2-aminohydroquinone-4-benzoate and subsequent debenzoylation followed by oxidation of the hydroquinone group yielded the redox polymer, 15. Another carrier can be obtained by reacting one amino group of a diamine compound, such as ethylenediamine and hexamethylenediamine, with sulfonyl chloride functionality of the polymer and the other with benzoquinone to give a polymer of type 16. Poly(vinyl alcohol) crosslinked with 1% terephthalaldehyde was also employed as benzoquinone carrier. These benzoquinone-carriers, reported by Manecke, exhibited great efficiency in immobilizing enzymes, e.g., chymotrypsin.

Kamogawa⁸³ reported the attachment of the hydroquinone moiety onto a polyacrylamide matrix. The homopolymer or copolymer of acrylamide can be methylolated with an equivalent of formalin or paraformaldehyde under basic conditions, eq. 20. Treatment of methylolated polyacrylamide with hydroquinone under acidic conditions affords the redox polyacrylamide.

As stated earlier, the anthraquinone group can be introduced onto a variety of polymer matrices. For instance, the reaction of 2-aminoanthraquinone with chloromethylated polystyrene crosslinked with divinylbenzene gave the hydrophilic redox polymer 17. Izoret⁸⁴ reported the incorporation of anthraquinone on the polymer backbone via an acetal linkage. He treated 2-formylanthraquinone with poly(vinyl alcohol) to produce polymer 18 which is highly stable under

17 18

alkali conditions. He also described a synthesis of anthraquinone polymer by reacting poly(vinyl alcohol) with 2-chloromethylantraquinone to give 19 where the redox unit is attached via an ether linkage. The same author prepared polymer 20 by treating poly(acrylic acid) with 2-hydroxymethylantraquinone.

19 20

3. Vinyl polymers: Despite the difficulties in the preparation and the overall low yields, synthesis of specific monomers for specific redox polymers has the advantages that the composition and

structure of the resulting polymers are known with increased certainty and they are readily characterized by analytical techniques. These synthetic difficulties are encountered when one has to apply acid-base or redox reactions to the preparation of materials themselves highly sensitive to acids, bases, or radicals.

It was anticipated that unprotected phenolic groups would be powerful inhibitors of free radical reactions; therefore, it was imperative to mask the phenolic functionality by means of a protecting group which can be easily removed under mild conditions. Cassidy⁸⁵ succeeded in preparing vinylhydroquinone in a multi-step synthesis. As outlined in Scheme 17, coumarin can be converted to o-coumaric acid with potassium persulfate to give 2,5-dihydroxycinnamic acid which can be decarboxylated at 200 °C to afford vinylhydroquinone. The polymerization of this monomer in the absence of a catalyst proceeded at 125 °C to produce a low molecular weight polymer indicating the inhibiting ability of the free hydroxy group of the ring.

Iwabuchi^{86,87,88,135} found that tributylborane (TBB) was capable of initiating copolymerization of some unprotected vinylhydroquinone derivatives with some common comonomers; copolymerization in the presence of TBB of 2-vinyl-1,4-hydroquinone and 2-methyl-5-vinyl-1,4-hydroquinone, respectively with methyl methacrylate, styrene, acrylonitrile, acrylamide, and 4-vinylpyridine was successful in each case. It was therefore concluded that vinylhydroquinone behaves like styrene in the copolymerization reaction initiated by TBB. However, the homopolymerization of unprotected vinylhydroquinone with the same catalyst failed to produce polymer under identical conditions.

Scheme 17: Synthesis and Polymerization of Vinyl-
hydroquinone

An interesting exception was the polymerization of 4-vinyl-2-methoxyphenol (4-vinylguaiacol); this monomer yielded a low conversion (12.5%) of moderately high molecular weight product after a polymerization time of 200 hours.⁸⁹

Esters, ethers, and acetals have been chosen as blocking groups by many investigators in this field. For example, Cassidy⁹⁰ selected bis(methoxymethyl) ether as protecting group in the synthesis of poly(vinylhydroquinone) and poly(3-vinylcatechol). Both catechol and hydroquinone were treated with sodium metal in methyl alcohol to produce the monosodium salt of hydroquinone or catechol, the chloromethyl methyl ether was added to react with the mixture to give the hydroquinone or catechol bis(methoxymethyl) ether as outlined in Scheme 18. When this latter compound was metalated by reaction with butyllithium and subsequently treated with ethylene oxide,

β -hydroxyethyl-hydroquinone bis(methoxymethyl) ether (or catechol analogue) was obtained in quantitative yield. Dehydration of this alcohol over potassium hydroxide afforded vinylhydroquinone bis(methoxymethyl) ether (or catechol analogue) in high yield. Polymerization of these monomers followed by hydrolysis in methanolic hydrochloric acid produced poly(vinylhydroquinone) and poly(vinylcatechol) respectively.

Scheme 18: Synthesis of Protected Vinylhydro-
quinone and Vinylcatechol

The main disadvantage of the use of bis(methoxymethyl) ether is that it releases free formaldehyde upon hydrolysis of the polymer. The formaldehyde can produce crosslinking in the presence of acid and hydroquinone. The use of its analogue, bis(ethoxyethyl) ether,

however, generates acetaldehyde which is less reactive than formaldehyde.⁹¹ But with either blocking group, crosslinking may occur during the deblocking process; the extent differs only with the carbonyl condensation.

Iwabuchi⁹² prepared 2-methyl-5-vinyl-o,o'-bis(1'-ethoxyethyl) hydroquinone in 14% yield from 2-methylhydroquinone using the method of Cassidy. He observed that when the corresponding alcohol was heated at higher temperature, e.g., 240 °C, the protecting groups were removed without the dehydration of the alcohol. Further, when the blocked alcohol was heated over acidic alumina at 200-220 °C, the major product was a cyclic ether, a coumarin derivative.

A very clean method to produce a protected hydroquinone monomer is the reaction of 1,4-dimethoxybenzene with butyllithium followed by reaction with ethylene oxide to give the β -hydroxyethyl-1,4-dimethoxybenzene, eq. 21a. Dehydration of the alcohol by heating it over fused potassium hydroxide provided 2,5-dimethoxystyrene.⁹³ Acetaldehyde can be substituted for ethylene oxide giving an α -hydroxy ethyl analogue, eq. 21b, which, upon acid-catalyzed dehydration, yields the vinyl monomer. The polymerization of this monomer in the presence of benzyl peroxide proceeded without complication.⁹⁴ Although the application of esters as blocking groups proved to be limited because they react with organometallic reagents, 2-vinyl-1,4-hydroquinone diacetate monomers were prepared.⁹⁵ The synthesis involved the reaction of vinylhydroquinone with acetic anhydride or benzoyl chloride as illustrated in eq. 22.

High polymers were readily obtained. The ester groups were afterwards removed via saponification of the polymer to yield poly(vinylhydroquinone).

It was noted that hydroquinone polymer oxidizes irreversibly. The intermediate semiquinone radical appears to add 1,4 to an unsubstituted ring of a quinone system. Therefore, polysubstitution

of the aromatic ring with appropriate groups, i.e., methyl, would stabilize the hydroquinone-quinone system. Cassidy and Kun⁹⁶ reported the synthesis of poly(1-vinyl-3,6-dimethyl-2,5-hydroquinone) and poly(1-vinyl-3,4,6-trimethyl-2,5-hydroquinone) employing the decarboxylation of the corresponding cinnamic acid. The corresponding diacetates of these two polymers were made by Manecke.⁹⁷ 2,5-Dimethoxy-3,4,6-trimethylstyrene was prepared by three routes^{96,98} as outlined in Scheme 19. The first path involved bromination of 1,4-dimethoxy-2,3,5-trimethylbenzene followed by formation of a Grignard intermediate which gave β -hydroxyethylbenzene derivative upon treatment with ethylene oxide. Dehydration of this alcohol over potassium hydroxide afforded the trisubstituted vinyl monomer. The second route consisted of acetaldehyde reaction with either the Grignard intermediate or the lithiated dimethoxybenzene to produce the corresponding α -hydroxyethylbenzene derivative. The lithiation step took place with butyllithium via a bromine lithium exchange. Vinyl monomer was obtained by dehydration of the resulting alcohol in the presence of an acid. The third technique involved the formation of the phosphonium chloride salt from 2,5-dimethoxy-3,4,6-trimethylbenzyl chloride and triphenylphosphine, eq. 23. Attack on the phosphonium chloride by butyllithium generated the corresponding ylide, which upon treatment with aqueous formaldehyde gave the vinyl monomer.

Scheme 19: Preparation of 2,5-Dimethoxy-3,4,6-trimethylstyrene

eq. 23

Manecke and co-workers⁹⁹ reported the preparation of 3-vinylpyrazoloquinone and its derivatives. Their polymers showed high stability and resistance to degradation reactions. For example, 3-vinylpyrazoloquinone can be prepared by 1,3-dipolar cycloaddition of diazopropen-2 to the disubstituted quinone as given in Scheme 20. It is interesting to notice that the N-pyrazoloquinones cannot undergo polymerization by radical initiators unless an epoxy group is introduced into the quinone side. The epoxy group may be removed at the end of the reaction with potassium iodide in acetic acid.

The hydroquinone-quinone redox systems can be stabilized also by annellation of the quinone with aromatic rings. Thus, poly(vinylnaphthaquinone) and poly(vinylanthraquinone) derivatives were prepared.¹⁰⁰ 2,5-Dimethyl-5-vinylnaphthaquinone, 21, and both vinylanthraquinone isomers, 22 and 23, were made by dehydration of the hydroxyethylnaphthaquinone and anthraquinone analogue. The vinylnaphthaquinone polymerized only when an epoxy group was introduced into the quinone unit as required for the polymerization of 3-vinylpyrazoloquinone. However, the 2-vinylanthraquinone could be cleanly homopolymerized and copolymerized with styrene and divinylbenzene, while the 1-vinylanthraquinone did not polymerize readily.

Pyranyloxyl groups also proved to be effective as blocking groups. Spinner and co-workers¹⁰¹ designed a synthesis of poly(2,5-dihydroxy-4'-vinyl diphenyl sulfone) from the corresponding monomer when the hydroxyl functionalities of the hydroquinone units were protected by pyraniloxy groups. Reaction of *p*-(β-bromoethyl) benzene sulfonic acid, prepared from β-bromoethylbenzene, with benzoquinone led to the corresponding hydroquinone sulfone as shown in Scheme 21. Treatment of this sulfone with 2,3-dihydropyran gave the protected hydroquinone sulfone. Dehydrobromination with alcoholic potassium hydroxide yielded the corresponding vinyl monomer. The same investigators¹⁰² reported the preparation of poly(2,5-dihydroxy-4-methyl-4'-vinyl diphenyl sulfone) employing a similar procedure.

Kamogawa¹³⁴ attached hydroquinone to N-hydroxyethyl methyl acrylamide prepared by alkaline methylolation of acrylamide with formaldehyde at room temperature as shown in eq. 24. The attached hydroquinone monomer was readily polymerized to afford redox resin.

Scheme 20: Synthesis of Poly(3-vinylpyrazoloquinone)

Scheme 21: Pyranoxyl as Protecting Group

Recently, Mehta¹⁰⁴ prepared poly(4'-vinyl-2,5-dihydroxy-1,1'-biphenyl), poly(4'-vinyl-2,3-dihydroxy-1,1'-biphenyl), and poly(4'-

vinyl-3,4-dihydroxy-1,1'-biphenyl) by polymerizing the corresponding monomers obtained via Wittig reaction. For example, bromination of 4'-methyl-2,5-dimethoxy-1,1'-biphenyl with N-bromosuccinimide in the presence of benzoyl peroxide gave 4'-bromomethyl-2,5-dimethoxy-1,1'-biphenyl as illustrated in Scheme 22. The treatment of this bromomethyl compound with triphenylphosphine yielded 4'-(triphenylphosphonium)methyl-2,5-dimethoxy-1,1'-biphenyl bromide. The mixture of this phosphonium bromide salt and 50% aqueous sodium hydroxide and 37% aqueous formaldehyde provided 4'-vinyl-2,5-dimethoxy-1,1'-biphenyl which polymerized cleanly in the presence of AIBN. Demethylation was induced by boron tribromide.

Iwabuchi and co-workers^{105,106} described the copolymerization of some naturally occurring vinylcatechol precursors with some common comonomers. The copolymerization reaction of 4-propenylpyrocatechol derivatives, such as eugenol, 24, isoeugenol, 25, isosafrole, 26, and safrole, 27, with acrylonitrile, maleic anhydride, and methyl methacrylate, were investigated employing TBB as initiator. It was found that only homopolymerization occurred when they were reacted with methyl methacrylate under the same conditions. More recently, the same investigators¹⁰⁷ developed a synthesis of a vinyl monomer containing 1,3-benzodioxole and methyl methacrylate units. As described in Scheme 23, 3,4-methylenedioxybenzyl methacrylate was prepared from 3,4-methylenedioxybenzyl alcohol and methacryloyl chloride. The monomer was radically polymerized in the presence of TBB. Treatment of the resulting polymer with phosphorus pentachloride gave the corresponding carbonate which upon hydrolysis yielded the poly(3,4-dihydroxybenzylmethacrylate).

Scheme 22: Synthesis of Poly(4'-vinyl-2,5-dihydroxy-1,1'-biphenyl)

24

25

26

27

Scheme 23: Synthesis of Poly(3,4-dihydroxybenzyl-
methacrylate)

II. Properties of Redox polymers

1. Condensation polymers: Among the condensation polymers studied, the ones derived from formaldehyde-phenol were given the most attention. These crosslinked resins with phenol or resorcinol moieties condensed with a variety of redox units including hydroquinone or quinone exhibit a wide range of properties. Table 4 compiles the properties of some polycondensates of phenol-formaldehyde with various redox units. Some of these resins were quite stable; others degraded and decomposed in contact with strong oxidants.

As stated earlier, the change in concentration of one component of a mixture results in change of physical and chemical properties of the resin. In fact, the redox capacity (the amount of redox equivalent per gram of redox resin) of the resin increases with increase in ratio of formaldehyde. The phenol-formaldehyde-hydroquinone polymers generally show decreased chemical stability as the phenol content is lowered; however, the content of formaldehyde seems to have slight effect on its chemical stability. Kruglikova and Pashkov^{108,109} prepared the sulfonic acid derivatives of pyrocatechol and hydroquinone by polycondensation with formaldehyde and phenol. They found that the chemical stability and the swelling properties of such polymers increased with the ratio of phenol, but their redox capacities decreased.

Resins containing anthraquinone were found to react more slowly with redox agents than those having hydroquinone units. Rendering the resin hydrophilic by replacement of phenol with phenolsulfonic acid failed to increase the redox activity.

Table 4: Properties of Some Polycondensates of

Phenol-Formaldehyde with Redox Units *

<u>Redox unit</u>	<u>Formula</u>	<u>Redox cap.</u> <u>(meq/g)</u>	<u>E_m (V)</u> <u>(pH=7)</u>
Alizarin		0.5	-
Anthrarufin		1.1-2.1	-
Chrysazin		1.5-2.5	-
Hydroquinone		7	0.22
2-Hydroxy-anthraquinone		1.1	0.19
Juglone		4.5	0.12
Quinalizarin		1.4-2.5	-
Purpurin		0.7	-

*
References 128, 129, and 130

Redox polyamides⁶⁹ (eq. 12) in reduced form were white to light brown powder flakes, soluble in DMAc, DMF, and formic acid. The oxidized polymers were yellow solids, soluble in the same solvents. Unfortunately, the redox properties of these polyamide resins were not studied.

Hydroquinone polycarbonates⁶⁵ (eq. 7) had molecular weights ranging between 380 and 20,000. While the reduced forms existed as colorless waxes or oils, the oxidized forms were yellow or brownish-yellow solids. The viscosities of the reduced resins were found to be higher than those of the oxidized forms. The midpoint potentials were generally around 0.64V.

Hydroquinone polyurethanes⁶⁶ (eq. 8) were generally soluble in THF and DMF. The reduced polymers were white powders; the oxidized ones were bright yellow solids. The viscosities of the reduced forms were larger than those of oxidized forms. The redox potentials were 0.25-0.29V.

2. Vinyl polymers: In general, polymers in which hydroxyl functionalities are masked by protecting groups such as benzoyl, methyl, bis(methoxymethyl), and bis(ethoxyethyl), are readily soluble in halogenated solvents, benzene, and toluene. They can be precipitated from these solvents into methanol or ethanol as white powders. On the other hand, ^tThe free OH-polymers once produced are no longer soluble in the above-mentioned solvents, but are soluble in methanol, dioxane, THF, and DMF. The free hydroquinone polymers are not very soluble in glacial acetic acid, but if little water is added they dissolve readily, suggesting that intermolecular interactions of the polar groups may crosslink the chain but the weak association is

readily replaced by interaction with water molecules.

These polymers are white in color when initially isolated. As opposed to their precursors, they become unstable to air and turn pink especially when moisture is present. The fully oxidized polymers are yellow and exhibit lower solubility than the reduced resins, but they can be dissolved in THF, DMF, and dioxane. The partially oxidized polymers show also decreased solubility in organic solvents.

These polymers can be made water-soluble if a sulfonic acid group is introduced. For example, Cassidy¹¹⁰ reported the sulfonation of poly(vinylhydroquinone dibenzoate) with concentrated sulfuric acid. The resulting sulfonated polymer, with the ester group cleaved in situ, is quite soluble in water. Another method of producing water-soluble resins is to copolymerize a redox monomer with hydrophilic comonomer such as acrylic acid, ester, and amide. For example, N-4-vinylbenzylnicotinamide homopolymer is insoluble in water; water-soluble copolymer could be obtained, however, by copolymerization with methylacrylic acid or with acrylamide.⁹⁴

Crosslinked polymers show no solubility in organic solvents but they can be swollen in some media. For example, the copolymer of vinylhydroquinone dibenzoate with divinylbenzene was obtained as hard, white, opaque beads that swelled in toluene and benzene. Upon saponification, these beads swelled in t-butyl alcohol and became transparent.⁹⁵ A terpolymer of vinylhydroquinone, α -methylstyrene, and 5% divinylbenzene behaved in the same way as the copolymer. The sulfonation of this resin yielded a product in the form of beads which were highly swollen in water, and could be readily oxidized and then reduced. Degradation of the polymer was detected after prolonged

contact with strong oxidizing agents such as ceric sulfate or bromine water. The sulfonated polymer behaved as redox resin and cation exchange resin as well. The redox capacity was evaluated as 5.7 meq/g, and the cation-exchange capacity was found to be 3.9 meq/g.¹¹¹

III. Applications: The best application of redox polymers is their use as insoluble and recyclable oxidizing and reducing agents in chemical reactions. In this case, the feature of their use is the easy separation from the substrate solution by simple filtration, thereby eliminating the purification work-up and possible contaminants. This was observed in the oxidation of primary amines to ketones by tert-butyl-o-benzoquinone redox resins as mentioned earlier¹⁵ (eq. 4). Moreover, Manecke¹¹⁸ oxidized numerous organic compounds by passing them through a resin bed composed of hydroquinone-phenol-formaldehyde condensation resin, or by mixing the resin with the substrate solutions. In this way, Haas and Schuler¹¹⁹ were able to dehydrogenate tetralin to yield naphthalene. Also, Cassidy¹²⁰ described the oxidation of hydrazobenzene to azobenzene employing the same technique. Manecke^{121,122} further reported the oxidation of cysteine to cystine and ascorbic acid to dehydroascorbic acid.

Redox polymers in their reduced forms were used for the reduction of ions and for depositing metals from solutions. For example, Manecke¹¹⁷ employed poly(vinylhydroquinone) resin to deposit several metals from their ion solutions by a batch process. In this manner, silver was deposited from AgNO₃ solution, copper from Cu²⁺-sulfuric acid solution, tellurium from tellurite solution, and selenium from sulfuric acid-selenate solution. The deposited metals could be

dissolved without affecting the redox resins. Iwabuchi⁸⁰ studied the adsorption of metallic ions onto resins having hydroquinone and catechol moieties. In this investigation, resins with catechol units adsorbed nearly 10 times more mercuric ions (Hg^{2+}) than other metallic ions studied, i.e. copper (Cu^{2+}), aluminum (Al^{3+}), cobalt (Co^{3+}), and lead (Pb^{2+}). Under the same conditions as the catechol experiments, adsorption of metallic ions by resins with hydroquinone group failed in all cases.

Removal of oxygen from water is desirable because the corrosion of iron and steel in contact with water is thought in part to be related to the dissolved oxygen in water. Manecke¹²² reported that condensation polymers of hydroquinone-phenol-formaldehyde removed oxygen from water very efficiently without the addition of salts or other contaminants. The course of this removal of oxygen apparently involved the oxidation of the reduced form of the resin with oxygen to quinone while the resulting hydrogen peroxide reacted with another hydroquinone group to give quinone and water. The deoxygenation by this method was found to be more efficient and faster than the conventional technique using nitrogen. The resin showed great potency in converting dissolved oxygen to hydrogen peroxide in the presence of stabilizers; the yield was between 80 to 100%. It was also suggested that the above redox resins may be used as antioxidants because of their great reactivity with oxygen.

Oxidation-reduction polymers containing hydroquinone-quinone systems may be used to maintain a given redox potential in biological systems and to maintain the reducing conditions.¹²³ Reduced cytochrome c was prepared using redox polymers;¹²⁴ the activity of

this enzyme was retained after the treatment with the polymer. The advantages of this method over the conventional way of reducing cytochrome c (with dithionite and hydrogenation using a platinum or palladium catalyst) are freedom from ionic contaminants and no need for a metal catalyst. Another biochemical application is the dehydrogenation of NADH to NAD^+ by the use of the quinone form of the condensed redox polymer.^{118,125}

Other applications of redox polymers include photographic and electrical uses. It was found that hydroquinone redox polymers could be employed as non-diffusing reducing agents to photographic color emulsions.¹²⁶ Redox polymers were also applied in depolarization mass for primary and secondary cells.¹²⁷ Batteries using redox polymers are claimed to eliminate possible deterioration due to the corrosion of the lead or iron accumulators caused by liquid electrolytes.

C. Objectives

The foregoing survey of the literature drove us to highly esteem the value of redox polymers. Our work focused on evaluating poly(vinylcatechols) because redox polymers with pendent catechol groups would exhibit : a) low redox potentials, b) high reactivity towards electrophilic substitution, and c) coplanar bidentate complexing properties. The possibility of undesirable side reactions stemming from condensation of unreacted chloromethyl groups after attachment of hydroquinone or catechol moieties onto preformed chloromethylated polymer, or electrophilic addition to the active aromatic ring of the catechol precursors, are distinct disadvantages to preparation of polymeric catechols by polymer modification. The

side reactions introduce crosslinks which will render a soluble polymer substrate insoluble, or reduce the accessibility of active sites on a crosslinked matrix. Although these resins exhibited interesting redox and chelating properties, they were difficult to characterize due to the extent of their insolubilities. Thus polymeric catechols with high content of catechol redox units, and which could be easily amenable to spectroscopic characterization techniques are very desirable. Synthesis of poly(vinylcatechols), readily characterized polymers, proved to be the preferred route in providing a large content of catechol groups on the polymer chains. Even though vinylhydroquinone polymers have been synthesized and showed some valuable redox properties, poly(vinylcatechols) give promise of possessing better redox properties and by far more efficiency in adsorption of metallic ions. The objective of this research was to synthesize monomeric catechol precursors, ascertain their polymerizability, investigate the reactivity of poly(vinylcatechol) precursors, and finally generate poly(vinylcatechol) and characterize its activity.

RESULTS AND DISCUSSION

As described in the introduction, polymeric catechols cannot be readily synthesized in a single step. The phenolic functionalities are anticipated to be powerful inhibitors of free radical polymerization of vinyl monomers. Therefore, the phenolic functions must be masked. The methylenedioxy group, a formal linkage, was the first choice as a blocking group because we anticipated its facile acid cleavage to liberate the free catechol moieties. Hence, 5-vinyl-1,3-benzodioxole, 28, was prepared and polymerized to afford poly(5-vinyl-1,3-benzodioxole) with no major difficulty; however, rather extreme conditions (BCl_3 in CH_3OH) were required to liberate the catechol function. As an additional aspect of our study, this polymer was subjected to chemical reactions in order to evaluate its reactivity. Chloromethylation, a key intermediate process for subsequent nucleophilic modifications, was explored; the result was always an insoluble blue resin which defied characterization. Similar results were observed when imidoalkylation was attempted. We related these results to the formation of an unusually stable complex between the methylenedioxy group and a Lewis acid. The unexpected stability of benzodioxoles prompted us to reevaluate methoxy substituents as blocking groups. Also, we expected that a 1,4-benzodioxane functional group would be easier to hydrolyze than a 1,3-benzodioxole group. Accordingly, the synthesis of monomeric vinylcatechol precursors, 29-32, was designed and their polymerizability was investigated.

A. Monomer Synthesis

We explored four different routes for the synthesis of monomeric vinylcatechol precursors, i.e.:

- 1) Dehydration of the corresponding α -phenylethyl alcohols,
- 2) Wittig methenation of the benzaldehyde derivatives,
- 3) Decarboxylation of the cinnamic acid derivatives, and
- 4) Wittig reaction of substituted benzyl ylides with formaldehyde.

With the exception of 2,3-methylenedioxybenzaldehyde, a key intermediate of monomer 32 the benzaldehyde derivatives employed in the first two methods were purchased. Therefore, a synthesis of this intermediate was undertaken. A number of workers have reported methylenation of catechol derivatives. Bonthron and Cornforth¹³⁷ were able to methylenate catechol using dibromomethane in dipolar aprotic solvent such as DMSO in the presence of solid sodium hydroxide. Bashall and Collins¹³⁸ conducted the methylenation reaction of catechol derivatives in the absence of a dipolar aprotic solvent by employing a phase transfer catalyst and a strong base. In our work, two methods were evaluated for the preparation of 2,3-methylenedioxybenzaldehyde as shown in equation 27. The better procedure involved reaction of 2,3-dihydroxybenzaldehyde with diiodomethane and potassium carbonate in the presence of cupric oxide; the benzaldehyde derivative could be isolated in 60% yield. Reaction of the dihydroxybenzaldehyde with dichloromethane and a large amount of cesium fluoride as described by Miller¹³⁹ yielded only 23% of the desired product. The driving force of the methylenation of the catechol in this reaction is thought to be the formation of a hydrogen bond between the fluoride anion and the aromatic molecule. The

chemical shift of the methylenedioxy protons of 2,3-methylenedioxybenzaldehyde is downfield (6.2-6.3 δ) from that observed in the spectrum of piperonal (5.82 δ). 2,3-Dimethoxybenzaldehyde could be also prepared in 77% by treatment of 2,3-dihydroxybenzaldehyde with iodomethane according to equation 27 (eq. 27a).

α -Phenylethyl alcohol derivatives were obtained in quantitative yields (73-90%) via Grignard reactions as shown in equation 28. The commercially available methylmagnesium bromide in ether was found more efficient than methylmagnesium iodide produced in situ in terms of yields isolated. As long as the Grignard reagent existed in ether solution, cleavage of the blocking groups could not be detected; solid Grignard reagents when freed from ether form amorphous solids and acquire the property of cleaving ethers.¹⁴⁰ Although the reactions were all carried out in anhydrous ether, the Grignard reaction of 1,4-benzodioxane-6-carboxyaldehyde using anhydrous THF failed to produce the corresponding alcohol. The Grignard procedures were carried out with stirring by a magnetic stirring bar because when a mechanical stirrer was used in the Grignard procedure, the product obtained was the polymer instead of the alcohol. The α -phenylethyl alcohols were characterized by ^1H NMR (Table 8) and were used without further purification; the chemical shift of the hydroxyl function

(HOCHCH_3) varied between 2.5 and 4.05 δ and the peaks were generally broad.

Monomers:

28, $R_1 = \text{H}$, $R_2 = R_3 = -\text{OCH}_2\text{O}-$; 29, $R_1 = \text{H}$, $R_2 = R_3 = -\text{OCH}_3$; 30, $R_3 = \text{H}$, $R_1 = R_2 = -\text{OCH}_3$; 31, $R_1 = \text{H}$, $R_2 = R_3 = -\text{OCH}_2\text{CH}_2\text{O}-$; 32, $R_3 = \text{H}$, $R_1 = R_2 = -\text{OCH}_2\text{O}-$.

The dehydration occurred at moderate temperatures (180-200 °C) over potassium bisulfate in the presence of an inhibitor, cuprous chloride, and the vinyl monomers were distilled under reduced pressure. The inhibitor was not completely effective as the thermal polymerization decreased the isolated yields of the vinyl monomers 28, 29, 31, and 32 substantially. Attempted dehydration over potassium hydroxide led to isolation of the pure distilled alcohols. On the other hand, the dehydration of α -phenylethyl alcohols in the presence of a trace of acid and at higher temperatures afforded an insoluble black tar in the distilling flask. Cationic polymerization of the initially formed vinyl monomer accompanied by attack of the growing

carbonium ion and/or of a protonated benzyl alcohol unit on the active aromatic ring of the prepolymer generated, will result on a crosslinked resin. Isolated yields and properties of the monomers are given in Table 6 and their properties are summarized in Table 7.

2,3-Dimethoxystyrene, 30, was more difficult to polymerize thermally; it could be distilled several times under reduced pressure without producing a residue even when the inhibitor was omitted. It was first believed that an ortho methoxy substituent either inhibits the formation of the 2+4 cycloaddition adduct, which is postulated to be the key intermediate in the thermal polymerization of styrene,¹⁴¹ or the regioselectivity of the process allows the formation of bridgehead methoxy adducts only. To estimate the extent of the ortho-methoxy effect, o-methoxystyrene was prepared in high yield (90%) according to equation 28. Thermal polymerization of 30 and o-methoxystyrene was observed only when distillation of the monomers at 200-220 °C under atmospheric pressure was attempted. These results demonstrate the retarding effect of an ortho-methoxy group on the thermal polymerization of styrene monomers.

None of the alternative synthetic approaches produced the desired monomers in yields comparable to those obtained from the dehydration process. Monomer 28 was the only one synthesized via decarboxylation of the cinnamic acid derivative in the presence of hydroquinone (eq. 29). Neutralization of the quinoline component with aqueous H₂SO₄ and subsequent work-up afforded the monomer 28. The miniscule yield (8.3%) recovered precluded further evaluation of this method.

The Wittig reaction (eq. 30), using the ylide derived from methyltriphenylphosphonium bromide was moderately successful. The same benzaldehyde precursors required for the Grignard procedure could be converted to monomers upon treatment with phosphonium ylides produced by attack of methyltriphenylphosphonium bromide by butyllithium. However, the yields were generally half those obtained from the Grignard procedure and an organometallic reagent was still required. An enormous quantity of phosphine oxide, a by-product, was isolated by filtration. Attempts to conduct the Wittig reaction in benzene-alkaline mixtures as described by Tagaki et al.¹⁴² failed in each case; the starting material remained intact and can be recovered almost quantitatively. The use of methylene chloride as alternative solvent and tetrabutylammonium chloride as a phase transfer catalyst did not alter the reaction. Probably this may be due to the decomposition of the phosphonium salt.

A multistep monomer synthesis, which does not require organometallic reagents, involves initial conversion of benzyl alcohols to benzyl chlorides, formation of benzylphosphonium salts, and finally treatment of benzyl ylides with formaldehyde (eq. 31).¹⁴³ Reaction of

appropriately substituted benzyl alcohols with thionyl chloride or with concentrated hydrochloric acid in the presence of a catalytic amount of sulfuric acid, produced the corresponding benzyl chlorides in moderate yields (60-90%). Physical properties, yields, and mass spectra of the benzyl chlorides are summarized in Table 9. They were all purified by vacuum distillation before use. However, after prolonged standing at room temperature, the benzyl chlorides solidified to blue black crystals which were easily dissolved in halogenated solvents; benzylation may occur between the benzyl chloride molecules due to the great activity of the aromatic ring, which is expected since the alkoxy groups are powerful electron donating substituents. Quaternization of triphenylphosphine with the benzyl chlorides was carried out in chloroform; the corresponding phosphonium salts were isolated in quantitative yields (97-100%) as white solids by precipitation in ether. Their melting points ranged between 215 and 240 °C. Yields, physical properties and mass spectral

data are compiled in Table 9. However, the final step, generation of the phosphonium ylides and concomitant reaction with formalin in 50% aqueous sodium hydroxide afforded the vinyl monomers in moderate yields after purification by passage through silica gel.

B. Polymerization Reactions of Monomers

1. Homopolymerization: Vinylcatechol monomer precursors were all polymerized via free radical, anionic, and cationic polymerization reactions. The isolated polymers were characterized by ^1H NMR, ^{13}C NMR, IR, and elemental analysis (Table 10). The extent of conversions, the viscosity values, and the molecular weights were determined and are compiled in Table 11.

1. Free radical reaction, bulk polymerization: Bulk or mass polymerization is the simplest polymerization process and the polymer can be isolated with a minimum of contamination because of the absence of other additives. It involves addition of a small amount of initiator to the pure monomer and heating to a temperature where the initiator breaks down to give free radicals. However, several inherent disadvantages may limit its applicability. First, thermal control of the reaction may be difficult due to the high exothermicity

of vinyl polymerization. The viscosity of the system increases rapidly, and at high conversion, the kinetics of bulk polymerization become complicated by chain transfer to polymer and by a gel effect.

Polymerization of each of the pure monomers was conducted in bulk in the presence of azobisisobutyronitrile (AIBN) at 70 °C. The highly viscous polymer produced dissolved in organic media with great difficulty. However, moderate to high conversions to polymer were achieved within one hour. All of the polymers were soluble in halogenated solvents except carbon tetrachloride, and in benzene. Poly 31 swells in toluene to a high degree; the rest of the polymers dissolved cleanly. The intrinsic viscosities were measured in toluene and calculated according to the following relationship; benzene was the solvent for poly 31.

$$[\eta] = \lim_{C \rightarrow 0} \eta_{sp}/C$$

$$\eta_{sp} = \frac{t - t_0}{t_0}$$

C = concentration in g/mL

t = efflux time of a pure polymer

t₀ = efflux time of a pure solvent

The instrinsic viscosities ranged from 0.15 dL/g for poly(5-vinyl-1,3-benzodioxole) to 0.32 dL/g for poly(2,3-dimethoxystyrene). Molecular weights were estimated using Mark-Houwink constants for poly(p-methoxystyrene)¹⁴⁴ according to the following relationship, and were moderate.

$$[\eta] = K M^0$$

The maximum viscosity average molecular weight attained was 95,000 using monomer 30. Apparently the blocking groups act as chain transfer agents in early termination of the growing chains.

2. Dilatometric studies of the homopolymerization of monomer

30: The kinetics of the free radical polymerization of 30 were evaluated dilatometrically and the result was compared to the overall rate of polymerization of styrene under the same conditions. The initial and overall rates of polymerization (R_p' and R_p) were obtained by using the following relationships respectively:

$$R_p' = -\Delta M/[M] = \Delta V/VK ; R_p = R_p' [M]$$

where $\Delta V/V$ is the rate of the volume change, V is the total volume of the system, $[M]$ is the monomer concentration, and K is the contraction constant. K , a characteristic quantity for a given monomer, was evaluated by gravimetric determination of overall conversion to be 0.0998. The plot (Fig. 1) of contraction during the polymerization of the monomer provided the calculation of $\Delta V/\Delta t$ from the slope. The overall rate, R_p , was found to be equal to 2.53×10^{-2} mol/L min. The corresponding rate for styrene under identical conditions was observed to be 2.56×10^{-2} mol/L min. The overall rate of polymerization of monomer 28 was also estimated dilatometrically and was found to be

Figure 1: A plot of contraction in the dilatometer during the polymerization of 2,3-dimethoxystyrene

comparable to that of styrene.⁸¹ Thus, the methoxy and methylenedioxy substituents do not impact upon the free radical polymerization of the monomers. A more profound impact would be expected on the cationic polymerization because of the anticipated stabilization of the growing carbonium ion by the substituents.

3. Cationic polymerization: The cationic polymerization of dimethoxystyrenes has been extensively studied by Marechal.¹⁴⁵ He reported that moderately high molecular weight polymers could be obtained from 29 in the presence of Lewis acids such as boron trifluoride etherate, titanium tetrachloride, stannic chloride, and aluminum chloride. Trichloroacetic acid could be used as an inifer (coinitiator). We observed that treatments of solutions of monomers 28, 31, and 32 in dichloromethane with anhydrous stannic chloride at room temperature produced an intense purple color accompanied by an exotherm. Low molecular weight poly 28, poly 31, and poly 32 were isolated in 76, 94, and 18% yield, respectively, within 20 minutes (Table 11). A thorough washing of the isolated polymers could not discharge the slight pink color of the resin due to the presence of tin salts. When the temperature was lowered to -50 °C, moderately high molecular weight poly 29 was obtained in 46% yield, a corresponding increase in molecular weights was not observed with monomers 28, 31, and 32. These results are more consistent with those recently reported on the polymerization of 3-methoxy-4-benzyloxystyrene,¹⁴⁶ where intramolecular termination by cyclization limits the molecular weights achieved. An extensive study on cationic polymerization of ortho- and para-methoxystyrene with boron trifluoride etherate was reported by Imanishi et al.¹⁴⁷ Effects of solvents,

electrostatic and steric effect of the substituent on the monomer transfer reaction were investigated. The low molecular weights in cationic polymerization of the alkoxystyrenes in general are due mainly to the formation of the substituted phenylindane moiety, 33, as end group.

Attempts to polymerize monomer 30 cationically failed; a red complex formed but no polymer could be isolated. Extending the polymerization time, lowering the temperature, and using trichloroacetic acid as an inifer failed to induce polymerization. A complex between monomer 30 and stannic chloride could be formed. This would initiate the polymerization of styrene and monomer 28. Stable complexes of this type have been reported;¹⁴⁵ 3,4,5-trimethoxystyrene could not be polymerized in the presence of TiCl_4 due to Lewis acid-Lewis base complex formation. Low reactivity of o-methoxypropenylbenzene and o-methoxystyrene toward cationic polymerization in the presence of titanium chloride was reported by Lester et al.,¹⁴⁸ and attributed to a steric interaction between the carbonium ion and the o-methoxyl group. However, we found that o-methoxystyrene polymerized in the presence of stannic chloride without any major complication.

Figure 2: 100 MHz ^1H NMR spectra of partially deblocked poly(3,4-dimethoxystyrene): A, solvent $\text{DMSO-d}_6/\text{CDCl}_3$; B, solvent CD_3OD .

4. Anionic polymerization: A survey of the anionic polymerizability of the monomers was conducted in anhydrous benzene at room temperature using butyllithium as the initiator. The color of the solution first changed to yellow and then bright red with the progress of the polymerization accompanied with an exotherm; the red color is an indication of the presence of monomer anion. This color persisted for long periods of time and disappeared on quenching with methanol and the mixture became viscous. In general, low conversions to low molecular weight polymers were observed suggesting high vacuum techniques will be required to obtain useful polymers. Attempts to polymerize the monomers 28, 30, and 31 anionically at temperature as low as $-50\text{ }^{\circ}\text{C}$ produced polymers only in very low conversions. No evidence for ring metalation or cleavage¹⁴⁹ of the blocking groups was detected with monomers 28, 30, 31, and 32. However, cleavage of one of the methoxy groups occurred during the anionic polymerization of 3,4-dimethoxystyrene, 29. A polymer soluble in methanol and dimethylsulfoxide was obtained. Proton NMR in $\text{DMSO-d}_6\text{-CDCl}_3$ (Fig. 2a) revealed the remaining methoxy substituent at $3.5\text{--}3.8\delta$ and a sharp peak at 8δ assigned to a hydroxyl group. The latter peak disappeared when CD_3OD was used as solvent due to deuterium-hydrogen exchange (Fig. 2b). The FT-IR spectrum exhibited a broad stretch at $3450\text{--}3430\text{ cm}^{-1}$ and the absorption bands of the methoxy group at $1050\text{--}1260\text{ cm}^{-1}$. Attempts to polymerize 29 in the presence of sodium naphthalide afforded a polymer with the same properties. Sodium naphthalide used in the latter attempt was obtained by stirring sodium metal and sublimed naphthalene in anhydrous THF at room temperature for 2 hours.

Selective methoxy cleavage by an anion radical derived from the reaction of pyridine and alkali metals has been reported (eq. 44).¹⁵⁰ p-Methoxystyrene was synthesized to check if poly(p-hydroxystyrene) was formed when the monomer was subjected to the same anionic polymerization conditions used with 3,4-dimethoxystyrene; however, polymerization under the above conditions gave pure poly(p-methoxystyrene). Therefore, a single para-methoxy substituent did not promote the electron transfer cleavage.

II. Copolymerization Reaction of Monomers 30 and 31:

Copolymerizations of 30 and 31 with the comonomers styrene and methyl methacrylate were carried out to ascertain their polymerizabilities. These can be ascertained by the values of their reactivity ratios, r_1 and r_2 , calculated from the copolymerization feed ratios and the corresponding copolymer composition. In addition, the polymerizability of a monomer can be correlated to the Q-e scheme introduced by Alfrey and Price in 1947.¹⁵¹ The value of Q predicts the resonance stabilization of a monomer and the monomer radical and that of e defines the polarity of the monomer and of its radical. Values of Q and e have been assigned to the monomers based on their r values and the arbitrarily chosen reference values of $Q = 1$ and $e = -0.80$ for styrene. Values for methyl methacrylate of $Q = 0.74$ and $e = 0.40$ were used in our study.

Mayo-Lewis¹⁵² and Alfrey-Goldfinger¹⁵³ independently described a method of calculation of r_1 and r_2 . Equation 32 relates the copolymer composition to the reactivity ratios, in which $[M_1]/[M_2]$ is the monomer ratio in the feed. A simpler method involves carrying out the copolymerization to low conversions (<10%) and using the approximate form of the equation 32, where $d[M_1]/d[M_2]$ is equal to m_1/m_2 which is the mole fraction of the monomers in the copolymer.

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1]/[M_2] + 1)}{[M_2](r_2 + [M_1]/[M_2])} = \left(\frac{m_1}{m_2}\right) \quad \text{eq. 32}$$

In this study, the ratios $[M_1]/[M_2]$ and m_1/m_2 were estimated from the feed and elemental analysis or ^1H NMR respectively. If these ratios are replaced by F and f as described by Fineman and Ross,¹⁵⁴ the above equation can be rearranged to:

$$F/f (f-1) = r_1(F^2/f) - r_2$$

A plot of $F/f (f-1)$ as ordinate and F^2/f as abscissa is a straight line whose slope is r_1 and intercept is minus r_2 . The method of intersections was also adopted in this study. In principle, this involves the plotting of r_2 versus r_1 for different values of $F/f (f-1)$ and F^2/f ; theoretically, all the straight lines must intersect and the coordinates of the point of intersection are r_1 and r_2 . Practically, these lines do not intersect, thus the barycenter of the triangle formed between at least three lines is considered as the

point of choice; r_1 and r_2 are the coordinates of the barycenter in this case. As regards to Q-e scheme, their values can be calculated from r_1 and r_2 values employing the following relationships:

$$e_2 = e_1 \pm (-\ln r_1 r_2)^{1/2}$$

$$Q_2 = Q_1 / r_1 \exp[-e_1(e_1 - e_2)]$$

a. Copolymerization of 2,3-dimethoxystyrene: The reactivity ratios of 2,3-dimethoxystyrene (M_1) and styrene (M_2) were estimated using the method of intersections. The copolymerization reactions were carried out in bulk in the presence of AIBN. Conversions lower than 10% were achieved. The parameters of the copolymerization are summarized in Tables 12 and 13. From figure 3, r_1 and r_2 were evaluated to be 0.69 and 0.92, respectively, and the product $r_1 r_2$, a measure of the alternating tendency in copolymerization, was found to be 0.64 (Table 16). The Q_1 and e_1 values of monomer were calculated to be 1.89 and -1.48.

On the other hand, the reactivity ratios of monomer 30 (M_1) and methyl methacrylate (M_2) were evaluated from the method of intersections (Fig. 4) and the Fineman-Ross method (Fig. 5). Both methods gave reliable and precise values. The mean values of r_1 and r_2 were found to be 0.92 and 0.23, respectively; Q_1 and e_1 were estimated as 1.91 and -0.83.

Since the reactivity ratios were all found to be less than unity (Table 16), all radicals show a tendency to alternate ($r_1 r_2 < 1$), i.e., add to the other monomer. The alternation tendency is strongest

Figure 3: Method of intersection plot for 2,3-dimethoxy-styrene (M_1) - styrene (M_2) copolymerization.

Figure 4: Method of intersection plot for 2,3-dimethoxystyrene (M_1) -methyl methacrylate (M_2) copolymerization.

Figure 5: Fineman-Ross plot for 2,3-dimethoxystyrene (M_1)
 - methyl methacrylate (M_2) copolymerization.

Table 17: Copolymerization Parameters of Some
Substituted Styrene Monomers

Comonomers 1:2	r_1	r_2	Q_1	e_1	Reference
2,3-dimethoxystyrene:styrene	0.69	0.92	1.89	-1.48	Present work
" :MMA	0.92	0.23	1.91	-0.84	Present work
2,5-dimethoxystyrene:styrene	1.13	0.77	1.76	-1.17	155
" :MMA	0.72	0.25	1.76	-0.91	"
2,6-dimethoxystyrene:styrene	0.55	0.98	1.91	-1.59	156
" :MMA	0.74	0.14	2.6	-1.10	"
3,4-dimethoxystyrene:MMA	0.15	0.35	0.92	-1.20	89
3,4-methylenedioxystyrene:styrene	1.02	0.60	2.9	-1.50	81
" :MMA	1.10	0.45	-	-	"
" : "	0.45	0.40	1.10	-0.91	89
6-vinyl-1,4-benzodioxane:styrene	1.09	0.91	1.34	-1.00	Present work
" :MMA	0.45	1.05	0.50	-0.47	Present work

Figure 6: Plot of the mole fraction of 2,3-dimethoxystyrene (M_1) in the feed versus the mole fraction in the copolymer: $\bullet$, styrene (M_2); $+$, methyl methacrylate (M_2).

with methyl methacrylate radical, apparently due to the large difference in its electron affinity compared with that of 2,3-The alternation tendency is much less pronounced in the styrene system.

A comparison of Q and e values of some methoxy substituted styrene monomers is illustrated in Table 17. The value of Q_1 in the styrene system is similar to that of 2,5-dimethoxystyrene ($Q = 1.76$) and to that of 2,6-dimethoxystyrene ($Q = 1.91$). The large value of Q_1 (1.89) indicates that the vinyl group of this monomer is considerably stabilized by resonance. This is supported further by the large value of Q_1 (1.91) in the methyl methacrylate system. It indicates also that the vinyl group is able to remain coplanar with the phenyl ring. The e_1 values in both systems are more negative than that of styrene (-0.80). The large negative value in the styrene system indicates that the vinyl group of this monomer is more electron rich due to the presence of the electron donating methoxy substituents in positions ortho and meta to the vinyl group. Figure 6 plots the mole fraction of the monomer in the feed versus the mole fraction in the copolymer.

b. Copolymerization of 6-vinyl-1,4-benzodioxane: The copolymerization of monomer 31 with styrene and with methyl methacrylate proceeded similarly to that of monomer 30. The results are compiled in Tables 14 and 15. The reactivity ratios were determined from the method of intersections and the method of Fineman and Ross (Fig. 7,8,9,10). Their mean values were found to be $r_1 = 1.09$ and $r_2 = 0.96$ in the styrene system. The value of $r_1 r_2$ (1.04) is closer to unity which indicates that the copolymerization proceeded ideally or randomly; the two propagating species show no preference

Figure 7: Method of intersection plot for 6-vinyl-1,4-benzodioxane (M_1) -styrene (M_2) copolymerization.

Figure 8: Fineman-Ross plot for 6-vinyl-1,4-benzodioxane
 (M₁) - styrene (M₂) copolymerization.

Figure 9: Method of intersection plot for 6-vinyl-1,4-benzodioxane (M_1) - methyl methacrylate (M_2) copolymerization.

Figure 10: Fineman-Ross plot for 6-vinyl-1,4-benzodioxane
 (M_1)-methyl methacrylate (M_2) copolymerization.

for adding one or the other of the two monomers. In the methyl methacrylate system, the $r_1 r_2$ value was found equal to 0.47 which predicts the tendency of the copolymerization to alternate. From the table of comparison (Table 17), monomers 31 and 28 show almost the same reactivity. However, their Q and e values differ somewhat. The value of Q_1 of monomer 31 in the styrene system reflects also a high degree of stabilization of monomer by resonance. On the other hand, the e_1 value (-1.00) was found more negative than that of styrene (-0.80) suggesting that benzodioxane functionality increases the electronegativity of the vinyl group. In the copolymerization with methyl methacrylate, both stabilization and electronegativity of the vinyl group were somewhat reduced based on the small values of Q_1 and e_1 (0.45 and -0.47). This was also observed in the case of 3,4-methylenedioxystyrene as shown in Table 17. The mole fraction of monomer 31 in the feed is plotted against the mole fraction in the copolymer in figure 11.

III. Graft Copolymer on Poly(vinylcatechol) Precursors: Graft copolymers are ordinarily prepared using the phenomenon of chain transfer with polymer molecules in free radical polymerization. However, Overberger¹⁵⁷ observed that various aromatic hydrocarbons act as molecular terminating agents in the ionic polymerization of styrene. A novel means of making graft copolymers involves an ionic chain transfer. Ikeda et al.¹⁹² reported the graft copolymerization of 1,3-dioxolane onto poly(p-methoxystyrene). In this study, cationic ring opening polymerization of 1,3-dioxolane was effected by acetyl salts (AcX ; $\text{X} = \text{SbF}_6^-$, BF_4^- , ClO_4^-) in the presence of poly(p-methoxystyrene); homopolymer and graft copolymer were

Figure 11: Plot of the mole fraction of 6-vinyl-1,4-benzodioxane (M_1) in the feed versus the mole fraction in the copolymer: +, styrene (M_2); o, methyl methacrylate (M_2).

obtained. As to the formation of the graft copolymer, it is believed that the propagating carboxonium ion of 1,3-dioxolane attacks the aromatic rings of poly(p-methoxystyrene). However, the extraction of homopolymer of 1,3-dioxolane with methanol is questionable because this homopolymer is insoluble in methanol. Hence, cationic polymerization of styrene in the presence of poly(vinylcatechol) precursors synthesized as described above, was investigated. Our main interest in carrying out this experiment was to demonstrate the potential reactivity of polymeric catechols having electron donating substituents. Stannic chloride initiated polymerization of styrene in the presence of poly(2,3-dimethoxystyrene) affording a homopolymer and the graft copolymer which were easily separated. The homopolymer was precipitated by pouring the reaction supernatant into methanol, isolated in 35% yield, and was characterized by ^1H NMR as mainly polystyrene. The insoluble red resin, the graft copolymer, was thoroughly washed to eliminate the tin salts before its characterization. The FT-IR spectrum (Fig. 12) revealed the absorption bands of poly 30 with an extra band at 698 cm^{-1} attributable to polystyrene. Cationic polymerizations in the presence of poly 28 and of poly 31 were also conducted and resulted also in homopolymer polystyrene and a graft copolymer; in each case, an additional band in the IR appeared at $680\text{--}700\text{ cm}^{-1}$. These results strongly indicate that the transfer reaction occurred by a Friedel-Crafts alkylation of the phenyl ring. A growing polystyryl carbonium ion has a tendency to attack the activated aromatic groups of the polymeric catechol precursor. The general reaction may be represented as follows (eq. 33):

Figure 12: FT-IR spectrum of 2,3-dimethoxystyrene-styrene graft copolymer

These graft copolymers, once subjected to cleavage, may contain a large number of catechol units. Thus, their oxidized forms should exhibit higher capacities and may be preferred over the reported crosslinked redox resins such as styrene-divinylbenzene-3-vinyl-5-t-butyl-1,2-benzoquinone terpolymer in polymer reagent applications; the yields of the oxidation of primary amines to ketones with the oxidized forms of these grafted polymeric catechols would be enhanced owing to the high concentration of the polymeric reagent.

C. Thermal Stability of Poly(vinylcatechol) Precursors

The thermal stability of poly(vinylcatechol) precursors was examined by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) techniques. The weight changes of polymers were followed under nitrogen at a constant heating rate of 20 °C/min. The weight losses at the corresponding decomposition temperatures derived from the thermograms (Fig. 13) are summarized in Table 18. From this, it can be noted that for poly 28 and poly 30 a weight loss of 5% arose in the temperature range of 350-380 °C. For poly 29 and poly 31, 10% weight loss was detected at temperatures of 100 and 150 °C. A weight

Figure 13: Thermal gravimetry analysis (TGA) curves of the polymers: 20 °C/min;
Al₂O₃ as a support; under N₂ atmosphere.

Table 18: TGA Results

<u>Poly 28</u>		<u>Poly 29</u>		<u>Poly 30</u>		<u>Poly 31</u>		<u>Poly 32</u>	
<u>* W (%)</u>	<u>T (°C)</u>	<u>W (%)</u>	<u>T (°C)</u>	<u>W (%)</u>	<u>T (°C)</u>	<u>W (%)</u>	<u>T (°C)</u>	<u>W (%)</u>	<u>T (°C)</u>
5	380	10	150	5	350	10	100	30	230
50	450	13	380	94	430	20	390	38	400
100	>800	80	450	100	550	90	450	100	450
		100	>550			100	550		

* W = Weight loss

loss of 50% of poly 32 was observed at temperature of 380 °C. With the exception of poly 28, all polymers drastically decomposed over a temperature range of 450–550 °C. Total decomposition of poly 28 occurred at temperature higher than 800 °C. In general, the thermograms show for all polymers two steps of degradation, suggesting a change in the decomposition mechanism. This change in degradation mechanism seems to be most pronounced for poly 28.

Results of DTA are compiled in Table 19 from the curves in figure 14. The glass transition temperature, which is the temperature at which the amorphous regions of polymers take on the characteristic properties of a glass state, i.e., brittleness, stiffness, and rigidity, can be derived from a DTA curve. It ranges between 100 °C for poly 29 and 125 °C for poly 31; that of polystyrene is well known as 100 °C.

Table 19: DTA Results

Polymer	T _g (°C)	Decomposition temperature, °C
poly 28	125	415; exothermal
poly 29	100	400; endothermal
poly 30	115	375; endothermal
poly 31	125	420; endothermal
poly 32	105	395; endothermal

Figure 14: Differential thermal analysis (DTA) curves of the polymers: 20 $^\circ\text{C min}$; Al_2O_3 as a reference; under N_2 atmosphere.

In the DTA curve of poly 28, an endothermal peak followed by a sharp exothermal peak was observed between 380 and 415 °C. This sharp exothermal peak may correspond to the pronounced change in the decomposition mechanism as revealed by the corresponding TGA curve. However, the DTA of its isomer, poly 32, exhibited a double endothermal peak followed by a small exothermal one between 380 and 415 °C. For the rest of the polymers, the DTA curves revealed an endothermal peak in conjunction with a negligible exothermal peak.

From these analyses, it is clear that the poly(vinylcatechol) precursors are thermally stable resins and decompose only in the temperature range of 360-550 °C. Also, the thermal stability order of these polymers can be conclusively drawn as follows: Poly 31 > Poly 32 > Poly 28 > Poly 30 > Poly 29 (the sign > means more stable). It appears, therefore, that a cyclic ether substituent as in poly 28, poly 31, and poly 32, enhances the thermal stability better than methoxy groups.

D. Chemical Modification of Poly(vinylcatechol) Precursors

Functionalized polymers have found various applications as supports in solid phase synthesis, reagents, and protecting groups in organic synthesis as reviewed in section A of the introduction. However, the functionalization reactions are usually more difficult to control and to evaluate owing to the insolubility of the resins, which makes the reaction heterogeneous and often prevents characterization of the products by the usual methods of analysis. Crosslinked polystyrene has been the resin of choice because of its commercial availability in various forms. A number of functionalization reactions

such as chloromethylation, halogenation, acylation, lithiation, chlorosulfonation, nitration, and a few others were carried out on this resin. Chemical modification of such functionalized resins is suitable to introduce other functionalities.

Two reasons led us to evaluate the functionalization of the poly(vinylcatechol) precursors and to ascertain the limitations of their chemical reactivities. The first is their susceptibility toward electrophilic substitution owing to the presence of electron donating groups as blocking groups. Haas¹⁵⁸ observed that when the phenyl rings of polystyrene have been substituted in the para position with a methoxy group, the ring reactivity is increased one hundred times. This reactivity of the aromatic ring was confirmed by the successful graft copolymerization reaction discussed earlier. The other reason stemmed from the ease of their characterization by proton and carbon-13 NMR spectroscopy.

I. Chloromethylation Reaction: Probably the most versatile reaction on polystyrene resins is chloromethylation, because the chloromethylated resins are readily chemically modified due to the high reactivity of the chloromethyl groups. We anticipated at the beginning of this research that poly(5-vinyl-1,3-benzodioxole) could be chloromethylated with no major complication. However, this assumption did not hold true. Attempts to chloromethylate this polymer employing a variety of chloromethylating agents in the presence of stannic chloride immediately produced insoluble deep blue resins. Chloromethylating agents used in this study were 1,4-bis(chloromethoxy)butane prepared according to the procedure described by Olah¹⁵⁹ and the commercially available chloromethyl methyl ether

and chloromethyl ethyl ether. Extending the reaction conditions by employing an excess of chloromethylating agent, raising the temperature, using different halogenated solvents, and varying the reaction time could not bring the reaction to a success. Polymer was isolated unchanged when the reaction temperature was maintained below 0 °C, suggesting that chloromethylation will take place only at higher temperatures. Similar results were obtained when poly 29, poly 30, and poly 32 were subjected to chloromethylation. In all cases, the chloromethylation undoubtedly occurred under the reaction conditions but the crosslinking took place rapidly as the active aromatic ring attacks the chloromethyl group in a Friedel-Crafts alkylation as illustrated in equation 34. Not all the chloromethyl groups reacted because elemental analysis of the products revealed the presence of chlorine. For example, the chloromethylation of poly 30 resulted in 59% of unreacted chloromethyl groups based on elemental analysis.

A stable polymer complex of poly 28 with stannic chloride is formed by reacting a polymer solution with this Lewis acid in the absence of the chloromethylating agent. Consequently, the crosslinking also will ensue. Such complexation was also observed during the chloromethylation of poly(oxy-2,6-dimethyl-1,4-phenyl-1,4-phenylene) and occurred between the Lewis acid and the oxygen of the

phenoxy group.¹⁷ With this polymer, the chloromethylation in the presence of titanium tetrachloride, zinc chloride, aluminum chloride, or arsenic chloride ended up with the formation of stable polymer complexes and no substitution occurred.

The chloromethylation of unprotected poly 30 with chloromethyl ethyl ether in the presence of stannic chloride was carried out in a heterogeneous system. A purple color of the mixture was observed and was persistent till the end of the reaction. The extent of substitution was found to be 19% according to elemental analysis. This low substitution may be due to the great capability of the catechol moiety to coordinate with stannic chloride.

The chloromethylation of poly 31 was successful when the reaction mixture was quenched with methanol after stirring for less than 5 minutes. Within this time, intermolecular alkylation and the complexation seemed to be prevented. This result demonstrates the high rate of the reaction on this polymer. The resulting polymer was soluble in organic media. Proton NMR spectrum showed a broad peak at 4-5 δ assigned to chloromethyl group overlapping with $-\text{OCH}_2\text{CH}_2\text{O}-$. Elemental analysis indicated 73% substitution. The chloromethylation reaction of the rest of the polymers was again attempted under identical conditions and was a failure in all cases.

II. Quaternization of Chloromethylated Poly 31:

Chloromethylated poly 31 was quaternized with triethylamine in methanol. About 47% of the active chloromethyl functions could be quaternized at room temperature within 3 days. Apparently, the polymer backbone did not impose any substantial steric barrier to the attack by triethylamine. Although the isolation of the quaternized

polymer presented some difficulty, it was readily soluble in methanol. Proton NMR in CD_3OD showed clearly a benzylamine linkage at 4.8 δ and ethylamino group at 3.2 and 1.4 δ as quartet and triplet. In addition, the presence of nitrogen was confirmed by elemental analysis. A crosslinked quaternized poly 31 would be conceived as a cation exchange resin.

III. Synthesis and Chloromethylation of Model Compounds: With the hope to understand the chloromethylation reaction, model compounds were prepared and subjected to chloromethylation under similar conditions. 5-Methyl-1,3-benzodioxole and 5-ethyl-1,3-benzodioxole were chosen as model compounds for poly(5-vinyl-1,3-benzodioxole). The Clemmensen reduction of piperonal in the presence of amalgamated zinc afforded the former model compound in 32% yield after refluxing for 24 hours. Proton NMR revealed the methyl group at 2.2 δ as a singlet peak; no aldehyde group could be detected. 5-Acetyl-1,3-benzodioxole, a precursor for the second model, was prepared by acylation of 1,3-benzodioxole with acetic anhydride in the presence of trifluoroacetic acid. The recrystallized product from ethanol was characterized by the combination of proton NMR, IR (>C=O , 1640 cm^{-1}), and mass spectra. The Clemmensen reduction of this carbonyl compound under conditions similar to the above gave 5-ethyl-1,3-benzodioxole in 44% yield. Its identification was confirmed by the usual analytical techniques.

The chloromethylation of 5-methyl-1,3-benzodioxole was conducted in chloroform employing chloromethyl ethyl ether in the presence of stannic chloride; the mixture was refluxed for 3 hours at 65 °C. The product was isolated as sticky material which could be readily

dissolved in halogenated solvents and precipitated by pouring the solutions into methanol. Besides the peaks of 5-methyl-1,3-benzodioxole, ^1H NMR spectrum exhibited an additional peak at 3.8 δ attributable to the benzylic linkage (Ar- CH_2 -Ar). Chloromethylation reaction of the second model was carried out under the same conditions; the isolated product was similar to the one above. The peak at 3.8 δ is strong indication of benzylic linkage which confirms the intermolecular alkylation proposed in equation 34.

IV. Lithiation Reaction: Metalation of polystyrene resins has been a key for the introduction of useful functional groups. Fairly recently, Kaneko et al.¹⁶⁰ immobilized tris(bipyridyl) ruthenium (II) complex $[\text{Ru}(\text{bpy})_3]$ onto a polystyrene resin via lithiation; this product showed remarkable photocatalytic reactivity. Braun¹⁶¹ lithiated some soluble halogenated polystyrenes with an excess of butyllithium. However, Chalk¹⁶² developed a method that involves the direct lithiation of polystyrene solution with a 1:1 complex of butyllithium and TMEDA at 60 °C. Evans¹⁶³ studied this reaction further and showed that both meta and para lithiation occurred in 2:1 ratio.

Lithiation of poly 28, poly 30, and poly 31 was conducted in benzene in the presence of n-butyllithium and TMEDA, and the mixture was brought to reflux at 65 °C for 8 hours. To test the reactivity of the polystyryllithium derivative, trimethylchlorosilane was added to yield trimethylsilylated polymer. High degrees of substitution on the polymers could not be achieved. The use of sec-butyllithium, a more basic reagent, did not improve the extent of substitution as illustrated in Table 20. The maximum substitution which could be

obtained was only 58% for poly 30 using butyllithium; lower degrees of substitution were observed when sec-butyllithium was employed.

Appearance of a sharp peak near TMS and downfield in the ^1H NMR and ^{13}C NMR spectra indicates the presence of the trimethylsilyl function. The ^{13}C NMR spectrum of the silylated poly 28 is provided in figure 15. From this spectrum, it is clear that the trimethylsilyl group in the polymer did not alter the chemical shifts of the carbons; therefore, the position of this group could not be deduced from this spectrum. Since the chemical shift of the trimethylsilyl group is downfield from that of TMS, substitution on the aromatic ring is indicated; thus lithiation occurred on the aromatic ring. Benzyl trimethylsilane absorbs near TMS but upfield. Furthermore, the typical red color of the benzylic anion was not observed; hence, metalation took place entirely on the benzene ring (eq. 35).

V. Bromination Reaction: Halogenation of polymers has been always desirable. Bromine atoms introduced onto the aromatic ring of poly(phenylene oxides) have effects on the flammability and the thermal properties of the polymer. However, the synthesis of brominated poly(phenylene oxide) was not a direct bromination of the polymer, but it rather involved a condensation polymerization of dibromophenols in the presence of sodium hydroxide.¹⁶⁴ Direct

Figure 15: 200 MHz ^{13}C NMR spectrum of silylated poly(5-vinyl-1,3-benzodioxole).

bromination has been reported by White;^{164a} aryl bromination is achieved simply by exposure of a polymer solution to bromine. On the other hand, Heitz and Michels¹⁶⁵ brominated the insoluble polystyrene resin with bromine in the presence of ferric chloride as catalyst. The reaction has, however, been reported to give unreproducible results¹⁶⁶ and often yielded a colored resin. A second method was described by Camps et al.¹⁶⁷ in which the resin reacted with a stoichiometric amount of thallic acetate followed by bromination. The major drawbacks of this procedure are the use of a large quantity of the costly thallic acetate and the need of extensive washing required to remove the thallium salts generated by the reaction. Frechet¹⁶⁸ employed other catalysts in different solvents such as zinc chloride in THF and stannic chloride in CCl₄. He found that bromination of polystyrene in acetic acid in conjunction with a catalyst afforded good result; the mixture became gradually homogeneous as the polymer dissolved. He also observed that an extensive cleavage of the polymer chains occurred as evidenced by the low viscosity measured.

The bromination of poly(vinylcatechol) precursors was thoroughly examined. We found that bromination of these polymers proceeded rapidly even in the absence of a catalyst. Also, a high degree of functionalization could be always achieved and the results were quite reproducible. Furthermore, the brominated polymers were easily soluble, which facilitated their characterization.

Two approaches were evaluated: a direct bromination and a bromination via lithiation reaction according to equation 36. The direct bromination reaction (eq. 36a) involves a dropwise addition of bromine solution to the polymer medium while stirring. The brominated

resins were isolated without complication and most of them were almost colorless. In general, high yields to high substitutions were achieved for all polymers as reported in Table 21. Monobromination

was detected when a stoichiometric quantity of bromine was used. However, when excess bromine was employed, polybromination may occur for some polymers. For instance, bromination of poly 31 and poly 32 with 25 to 50% excess of bromine yielded a mixture of mono- and dibromo- polymers. The use of dioxane to complex with bromine could not control the monobromination. Similar results were obtained when monomeric catechol reacted with a bromine-dioxane complex prepared according to the method of Yanovskaya et al.¹⁶⁹ On the other hand, 1,3-benzodioxole, a catechol precursor, was readily brominated using a stoichiometric amount of bromine. In this case, one bromine atom per molecule was detected by ¹H NMR, and GC/MS. The bromine atom was attached selectively to the aromatic ring at position 5 (meta to methylenedioxy group). This selectivity may be due to electronic factors and steric requirements of the complex formed between the

Figure 16: 200 MHz ^{13}C NMR spectrum of poly(5-vinyl-1,3-benzodioxole).

Figure 17: 200 MHz ^{13}C NMR spectrum of brominated poly(5-vinyl-1,3-benzodioxole).

bromine molecule and the oxygen of the methylenedioxy unit, and not to those of bromine-dioxane as reported.⁸¹

In the second procedure (eq. 36b), the polymer was allowed to react with butyllithium in the presence of TMEDA to produce the lithiated resin, followed by addition of bromine solution. In this approach, not only was the isolation of the brominated polymers difficult, but also the extent of functionalization was minute. The same content of bromine was found when the bromination was attempted in the presence of TMEDA only (no butyllithium). In both cases, a water soluble residue was isolated as side product. This is believed to be either a salt formed upon reaction of TMEDA with the hydrogen bromide by-product of aryl substitution or a stable complex between TMEDA and bromine; the former is likely to occur due to its solubility in water whereas the latter would be rather soluble in organic media. In either event, the required amount of bromine was reduced which accounts for the low degree of bromination. Lithiation in the absence of TMEDA followed by bromination resulted in a highly functionalized polymer. The water soluble side product previously obtained was not detected. In this last attempt, lithiation probably did not occur as TMEDA is required for the metalation of aromatic ring; bromine attacks the ring directly. Therefore, the direct bromination remains the more reliable and more consistent method.

The electron withdrawing character of the bromine substituent could not effectively limit further substitution. Hence, bromine seemed to exhibit an electron donating behavior once incorporated on the aromatic ring. The low redox potential found for the mono-brominated unprotected poly 30 supports the electron donating nature

of the bromine; the bromine atom was anticipated to prevent the early oxidation of polycatechol by raising its redox potential. However, the oxidation potential of the brominated catechol was found lower than that of the catechol.

At this point, the determination of the position of the bromine atom on the ring was imperative. We found that carbon-13 NMR was a useful analytical technique to achieve this objective. The corresponding spectra of the non-brominated and the brominated polymers were taken in CDCl_3 with or without TMS. The assignments of chemical shifts were deduced from the combination of the spectra of polystyrene and low molecular weight catechol precursors such as meta-substituted 1,3-benzodioxole and 3,4-dimethoxytoluene. It is interesting to point out that all polymer lines show some broadening. This could be ascribed to restricted rotation within the polymer chains or to the size of the polymer molecule which restricts microscopic molecular motion even when the polymer is dissolved in a solvent.

In comparing the spectra of non-brominated and brominated poly 28 (Fig. 16 and 17), it can be deduced that the chemical shifts of the carbons C9 and C4, which were equivalent and absorbed at 121 ppm in poly 28, were shifted upfield to 113 and 115 ppm respectively in the brominated resin; the rest of the carbons absorbed at the same chemical shifts. This alteration in chemical shifts is due to the presence of the bromine atom on the ring. Therefore, bromine atom is distributed between C9 and C4 when the ring is monobrominated. Surprisingly, a bromine atom was not found on C8 which is a meta position to the methylenedioxy group as is C4. This could be due to a

steric effect displayed by the methylenedioxy group. Since this steric factor apparently manifested itself on C8 and not on C4, the spatial geometry of the methylenedioxy unit in the polymer could be then deduced. The influence of bromine on the carbon spectra is difficult to predict. In principle, the electronegativity of the substituent works to deshield a given carbon, thus this substituted carbon will absorb downfield. However, cases have been observed where the electronegativity effect of the bromine does not impart a significant deshielding influence and the brominated carbons absorbed upfield suggesting that these carbons are shielded. This shielding can be attributed to a heavy halogen effect,¹⁷⁰ which is observed in many aromatic compounds such as monobrominated biphenyl, brominated toluene, and others. In every case, the change at the substituted carbon is on the order of 5 to 8 ppm upfield.

The bromination of poly 29, poly(3,4-dimethoxystyrene), occurred mainly on carbon C10 as evidenced by ^{13}C NMR (Fig. 18 and 19). It is apparent that the carbon C10, which absorbed at 121 ppm in poly 29, now absorbs upfield at 115 ppm. Although the absorption of C4 is not well resolved, it absorbs at the same chemical shift as in the non-brominated poly 29 indicating that no bromine is attached on this carbon. Since this position was easily brominated in poly 28, the lack of substitution could be ascribed to steric hindrance imposed by the adjacent methoxy group. The steric bulk of the other methoxy group did not allow the carbon C9 to be brominated. The upfield absorption of C10 can be attributed to the heavy halogen effect observed earlier.

Figure 18: 200 MHz ^{13}C NMR spectrum of poly(3,4-dimethoxystyrene).

Figure 19: 200 MHz ^{13}C NMR spectrum of brominated poly(3,4-dimethoxystyrene).

The presence of the bromine in poly(2,3-dimethoxystyrene), poly 30, affected the absorption intensities of the backbone carbons as noted in the spectra (Fig. 20 and 21). The restriction of the motion of the 2-methoxy being adjacent to the backbone of the polymer is apparent by the broad peak at 61 ppm. From the spectra, it appears clearly that carbons C8 and C9 were brominated. Both electronegativity and heavy halogen effects were manifested in this case; the carbon C8 absorbed downfield due to the former factor and the carbon C9 absorbed upfield due to the second factor.

As observed with poly 30, the presence of the bromine also affected the absorption peaks of the backbone of poly 32 (Fig. 22 and 23). Also, the same effects of the bromine on the absorptions of the carbons of the ring were noted. While the carbon C7 absorbed downfield and the peak intensity was reduced sharply, the carbon C8 absorbed upfield with the same peak intensity. The electronegativity and the heavy halogen effects of bromine were imposed on carbons C7 and C8, respectively.

Although the elemental analysis confirms a bromine content consistent with monosubstitution of poly 31, the orientation of the bromine substituent could not be ascertained by nmr spectroscopy. The presence of the bromine atom seemed to have an impact on the intensities of the peaks of all carbons of the polymer; the peaks are broad and shorter. Although the ^{13}C NMR spectrum of the non-brominated poly 31 (Fig. 29) can be resolved, that of the brominated polymer (Fig. 30) posed some difficulty in assigning the brominated positions. The chemical shifts of the possibly brominated carbons C4, C9, and C10 are not altered. However, a slight upfield displacement

Figure 20: 200 MHz ^{13}C NMR spectrum of poly(2,3-dimethoxystyrene).

Figure 21: 200 MHz ^{13}C NMR spectrum of brominated poly(2,3-dimethoxystyrene).

Figure 22: 200 MHz ^{13}C NMR spectrum of poly(2,3-methylenedioxybenzylstyrene).

Figure 23: 200 MHz ^{13}C NMR spectrum of brominated poly(2,3-methylenedioxybenzylstyrene).

Figure 29: 200 MHz ^{13}C NMR spectrum of poly(6-vinyl-1,4-benzodioxane).

Figure 30: 200 MHz ^{13}C NMR spectrum of brominated poly(6-vinyl-1,4-benzodioxane).

of the chemical shift of C3 can be noted, but this position is unlikely to be brominated.

VI. Cyanogenation Reaction: We anticipated that cyanogenated polymers could be obtained by chemical modification of the brominated resins previously synthesized. If the cyanogenation reactions were successful, aminomethylated polymers could have been generated by reduction of the cyano groups. Although the cyanogenation of bromobenzene derivatives is well documented, application of this procedure to brominated polymers proved to be difficult. The brominated poly(5-vinyl-1,3-benzodioxole) was allowed to react with copper cyanide under extreme conditions, i.e., in DMF at reflux (215 °C) for four hours. The polymer isolated was colored due to the presence of copper salts despite extensive washing. The low nitrogen content and the absence of the characteristic cyano absorption band in the IR are strong indications that substitution of the bromine is limited. This could be attributed to the impact imposed by the electron donating nature of the alkoxy substituents. The failure of the cyanogenation reaction of poly 28, poly 29, and poly 30 precluded its further evaluation on poly 31 and poly 32.

VII. Aminomethylation Reaction: The problems inherent to chloromethylation of poly(vinylcatechol) precursors, i.e., propensity toward crosslinking, potential carcinogenicity of chloromethyl alkyl ethers as chloromethylating agents, and the failure of the cyanogenation reaction prompted us to direct our attention to a more direct means of introducing the aminomethyl substituent. While the amidoalkylation of monomeric compounds via N-methylene substituted amides and imides has been known for many years and reviewed by

Zaugg,¹⁷¹ only a few experiments on α -amidoalkylation of aromatic polymers have been reported.^{172,173} In these studies, N-methylol-, or N-chloromethylphthalimide, and N-methylolacetamide were used as alkylating agents. Merrifield^{174,175} reported a direct amidoalkylation of polystyrene resins which, upon hydrazinolysis, yielded aminomethylated resins, key intermediates for further chemical modifications. Daly¹⁷⁶ reported the amidomethylation of poly(oxo-2,6-dimethyl-1,4-phenylene); this resin was readily characterized owing to its solubility in organic solvents.

The treatment of poly 28 in dichloromethane with N-methylolphthalimide in trifluoroacetic acid in the presence of trifluoromethanesulfonic acid (eq. 37) gave deep red-wine color followed by a formation of blue precipitate after 3 to 4 hours of reaction. Due to its insolubility, this product could not be readily characterized. On the other hand, unreacted starting material was recovered upon terminating the reaction before the blue product separated. Crosslinking seemed to occur as soon as the amidoalkylation started. The phthalimidomethylation of poly 32, an isomer of poly 28, afforded an insoluble brown resin. The infrared spectrum (Table 24) revealed absorbances attributable to the carbonyls of a phthalimido group, 1770 and 1720 cm^{-1} , and to the C-N bond, 1180 cm^{-1} . A 73% substitution was consistent with elemental analysis. Subsequent hydrazinolysis of the amidomethylated polymer in ethanol afforded insoluble aminomethylated resin as evidenced by IR; no carbonyl absorption was detected, and a broad band at 3370 cm^{-1} indicated primary amine in conjunction with absorption band at 1180 cm^{-1} confirming the benzylic linkage.

The phthalimidomethylation of poly 29, poly 30 and poly 31 proceeded very cleanly (eq. 37); in all cases, a very viscous material separated from the mixture after 16 hours of stirring at room temperature. The products were readily reprecipitated from DCM into methanol to give white powders. The extent of substitution estimated from chemical analysis was excellent (>72%). The amidomethyl group failed to deactivate the aromatic ring; multiple substitution was obtained when excess of N-methylolphthalimide was employed. Monosubstitution may be controlled by employing a stoichiometric amount of the amidoalkylating reagent. In each case, the carbonyl groups of the phthalimido function were detected at 1773 and 1717 cm^{-1} in the FT-IR spectra. The FT-IR spectrum of the amidomethylated poly 30 is illustrated in figure 24 as an example. In the proton NMR, the benzylic protons appeared as a broad band at 4.5-5.45 δ and the aromatic protons of the phthalimido ring were evident also as a broad peak at 7.50 δ .

Hydrazinolysis of the amidomethylated polymers was carried out in the presence of hydrazine in ethanol at 50-60 °C. After 14 hours of reflux, the phthaloylhydrazide, a by-product which precipitated, was

Figure 24: FT-IR spectrum of the phthalimidomethylated poly(2,3-dimethoxystyrene).

removed by filtration. The viscous filtrate was diluted with chloroform. Evaporation of the solvent produced a clear film, which could not be redissolved in organic solvents. However, the FT-IR spectrum revealed a broad band at 3350 cm^{-1} assigned to the primary amine, and the carbonyl absorptions disappeared. The insolubility may be due to extensive intermolecular hydrogen-bonding between the hydrogens of the amino group and the oxygens of the protecting groups. An attempt to break up this bonding by refluxing the polymer in methanolic hydrochloric acid system failed. All the aminomethylated polymers reacted with ninhydrin solution positively indicating the presence of a primary amine function.

An alternative method of amidomethylation was explored by employing N-bromomethylphthalimide as a substrate for nucleophilic attack. In this method, the polymer was treated initially with alkyllithium followed by an S_N2 reaction of the lithiated polymer with N-bromomethylphthalimide (eq. 38). Addition of the amidoalkylating agent to the mixture was accompanied by a red color which turned yellow at the end of the reaction. The product of this reaction was unexpectedly insoluble in common solvents. The degree of substitution was moderate (40%) which is consistent with the extent of lithiation of poly(vinylcatechol) precursors previously discussed. Nonetheless, absorption bands at 1750 and 1690 cm^{-1} attributable to carbonyl functions are strong indication of the success of the reaction. In addition, this result confirms that the lithiation evidently took place.

Quaternization of aminomethylated poly 30 was performed by treatment with excess iodomethane (eq. 39). The brown color of the starting material changed to red after 4 days indicating that a reaction occurred. Less than 10% of methanol-soluble quaternized resin was isolated. The presence of iodine in quantitative amount in the insoluble residue was confirmed by elemental analysis.

In an attempt to introduce ethylamino group onto the aromatic ring, poly 30 was treated with N-(2-hydroxyethyl)phthalimide under conditions similar to amidomethylation. The polymer isolated contained nitrogen; however, both ^1H NMR and IR failed to confirm the presence of an ethylphthalimido group.

VIII. Sulfonation Reaction: Sulfonated styrene-divinylbenzene copolymers have been used as ion exchange resins in water treatment, in the recovery of metals from aqueous solutions, in chromatography, in catalysis, and in the pharmaceutical industry. Very recently, Ogawa and Marvel¹⁷⁷ reported the sulfonation of poly(aromatic ether ketones) and poly(aromatic ether keto-sulfone). However, their

applications are restricted owing to poor solubility. In this work, polymers were sulfonated with liquid sulfur trioxide in the presence of trialkyl phosphate. This complex sulfonating agent was also used by Noshay and Robeson¹⁷⁸ suggesting that this mild sulfonation should have minimized or even eliminated possible side reactions. In addition, McGrath et al.¹⁷⁹ and Daly et al.¹⁰³ employed this sulfonating agent to sulfonate poly(arylene ether sulfone); the sulfonated resin could be cast into membranes which exhibited limited permselectivity.

Poly 29, poly 30, and poly 31 were treated with a stoichiometric amount of chlorosulfonic acid; excess chlorosulfonic acid was avoided to prevent the formation of chlorosulfonated polymers and degradation or crosslinking of the polymers. Immediate phase separation occurred when the reactants were mixed, but the precipitated gel was readily soluble in water. The aqueous mixture was made alkaline before addition of tetraalkylammonium chloride. The quaternary ammonium salt was intended to serve as an analytical probe as described by McGrath.¹⁷⁹ The quaternized sulfonated polymers could be isolated only from DMF-water system into acetone. The white products obtained were less water soluble than the sulfonated polymers; the sulfonated polymers were highly moisture sensitive. The measured intrinsic viscosity (0.41 dL/g) of the quaternized sulfonated poly 29 indicates that the sulfonation occurred without degradation of the polymer. The quaternization was not quantitative based on the small content of nitrogen revealed by elemental analysis despite a prolonged time of the reaction; however, a high content of sulfur was detected. The quaternization reaction, therefore, is limited.

A relatively higher content of nitrogen was found in quaternized sulfonated poly 29. The symmetric $O=S=O$ stretching of the sulfonate group was visible at 1000 cm^{-1} whereas the asymmetric stretching, expected at $1100\text{--}1170\text{ cm}^{-1}$, was poorly resolved due to the overlap with the absorption bands of the methoxy groups.

The proton NMR spectrum of the quaternized sulfonated poly 29 concentrated in D_2O revealed a sharp peak at 3.4 δ assigned to the hydrogens of the tetramethyl group; while the absorption peaks of the methoxy groups and the benzene ring were slightly visible, that of the backbone was totally buried.

IX. Sulfomethylation Reaction: The use of sulfonated polystyrene resins is restricted because of their low thermal stability; above 150°C the aromatic sulfonic acid functions are increasingly hydrolyzed.¹⁸⁰ Therefore, alkylsulfonated polymers were synthesized and were expected to exhibit higher thermal stability.¹⁸¹ In this synthesis, a direct sulfoalkylation could be achieved only with

sultones. Sulfomethylation and sulfoethylation of polycatechol precursors were reported by Patel;¹⁸² these sulfoalkylated poly(catechols) were shown to exhibit a marked ability to control the viscosity, the gel strength, and the filtrate loss of aqueous oilfield drilling fluids.

Using conditions described by Patel, an alkaline suspension of poly 28 was treated with formaldehyde sodium bisulfite addition compound and the mixture was refluxed for 4 hours at 60 °C. The unreacted polymer was recovered quantitatively by filtration and the solute in the aqueous filtrate could be easily precipitated by pouring into methanol. Application of the sulfomethylation reaction with the rest of the polymers afforded the same results. Hence, the sulfomethylation of these polymers did not succeed under these conditions.

E. Removal of Blocking Groups

Hydroiodic and hydrobromic acids have been the reagents of choice when cleavage of ethers was needed. These Bronsted acids in acetic acid were able to cleave the methoxy group of a low molecular weight compound when heated under reflux;¹⁸³ however, with hydroiodic acid, the escape of methyl iodide, a carcinogenic substance, is unavoidable. Bronsted acids have been also used by Cassidy⁹⁴ and Iwabuchi⁸⁰ to remove the protecting groups to generate poly(hydroquinone) and poly(catechol). Hydrochloric acid has been found to cleave only some special types of ethers such as benzyl, t-butyl, allyl, trityl, and benzhydryl ethers.¹⁸³ Trifluoroacetic acid has been used to cleave selectively benzyl ethers without affecting

methyl ethers or esters.

Among the Lewis acids employed to cleave ethers are aluminum halides. Boron trichloride has been extensively used as a reagent for the cleavage of a wide variety of ethers like alkyl aryl ethers, mixed aliphatic ethers, cyclic ethers, and methoxy derivatives of carbohydrates. It can also cleave acetals and certain type of esters. Gerrard and Lapport¹⁸⁴ suggested that the cleavage of the C-O bond proceeded by an S_N1 mechanism in boron trichloride systems. With this Lewis acid, methylenedioxy was claimed to be cleaved selectively in the presence of methoxy groups.¹⁸⁵ In contrast, boron tribromide can cleave methoxy functions under conditions which do not affect the methylenedioxy groups. The reactivity difference between methoxy and methylenedioxy substituents is large enough to allow selective cleavage of the former in the presence of the methylenedioxy group. Recently, boron tribromide has become the preferred reagent because the cleavage of ether can be effected under mild conditions, and the need for strongly acidic or basic reaction can be avoided. While the preceding reagents cleave the C-O bond by an S_N1 or S_N2 pathway, with phosphorus pentachloride the methylenedioxy group undergoes chlorination followed by carbonylation as illustrated in Scheme 23; the C-O bond is not cleaved directly.

Cleavage of the formal group to liberate the catechol moiety has been evaluated thoroughly. Although it is possible to cleave a ketal blocking group, i.e., a 2,2-dimethyl-1,3-benzodioxole with p-toluenesulfonic acid and butyl mercaptan,¹⁵ the formal linkage proved to be much more stable. Treatment of poly 28 and poly 32 in acetic acid with 48% hydrobromic acid at 115 °C yielded blue insoluble resins

which defied characterization. Only boron trichloride was effective in cleaving the methylenedioxy group. When poly 28 was treated with boron trichloride in the presence of dodecyl mercaptan in dichloromethane, a phase separation occurred shortly, but the polymer could be redissolved by adding enough methyl alcohol. An insoluble, almost white polymer with a strong OH stretch in the IR spectrum was isolated. This resin could be swollen in DMSO, 90% acetic acid, and the extent of swellability increases as the acidity of the medium increases. The reaction is believed to proceed via nucleophilic attack of dodecyl mercaptan on the more electron deficient carbon of the oxonium species initially formed by complexation of BCl_3 , a Lewis acid, to oxygen as shown in Scheme 24.

Scheme 24: Reaction of Poly 28 with BCl_3 -Dodecyl Mercaptan

Cleavage of the methoxy blocking groups in poly 29, poly(3,4-dimethoxystyrene), could be effected with 48% hydrobromic acid under the conditions described above. The poly(4-vinylcatechol) was soluble

in methanol initially, but exposure to air rapidly induced darkening to a deep purple and the resin became insoluble in all solvents. This insolubility could be due to crosslinking occurring by nucleophilic attack of a catechol unit on a quinoid moiety formed by autooxidation of catechol units. The quinoid units act as an electrophilic species relative to catechol moieties, and dimerization takes place as shown in equation 41.

The purple intermediate resin may contain stable semiquinone radicals as evidenced by ESR spectroscopy.¹⁸⁶ On the other hand, poly 30 and poly 31 were not cleaved by 48% HBr; although partial dissolution in the strong acid appears to occur, no evidence for hydroxy absorption can be detected in the infrared spectra of the resins recovered by pouring the acid mixture into methanol. In contrast, boron trichloride in dichloromethane cleaved the methoxy group of poly 30 quantitatively and the poly(3-vinylcatechol), 34, was isolated without difficulty (eq. 42).

Figure 25: FT-IR spectra of poly(2,3-dimethoxystyrene), curve A, and poly(3-vinylcatechol), curve B.

Figure 26: 200 MHz ^1H NMR spectra of poly(3-vinylcatechol): A, in DMSO-d_6 ; B, in $\text{DMSO-d}_6/\text{D}_2\text{O}$.

Poly(3-vinylcatechol), 34, exhibits high stability to air; the purple color indicative of oxidation began to appear after several months of exposure to air but the resin remained soluble in methanol, suggesting that the above mentioned dimerization process did not occur. In the FT-IR spectra shown in figure 25, a pronounced hydroxyl group absorption at $3500\text{--}3200\text{ cm}^{-1}$ is apparent and the methoxy group absorptions at 1030 and 1260 cm^{-1} have disappeared. The proton NMR spectra taken in DMSO-d_6 are poorly resolved, but the broad band at 4.5δ undergoes deuterium exchange when D_2O is added indicating that this band should be assigned to OH (Fig. 26). A survey of the literature did not reveal a spectroscopic characterization of any poly(catechol) synthesized to date because the resins failed to dissolve in any solvent. Therefore, poly(3-vinylcatechol) exhibits unique properties and is easy to work with due to its solubility.

As mentioned, poly 31 was prepared because we anticipated that the 1,4-benzodioxane functional group would be easier to hydrolyze than the 1,3-benzodioxole group. The action of boron trichloride on poly 31 in the presence of dodecyl mercaptan produced an immediate phase separation. The isolated polymer was readily soluble in halogenated solvents and could be precipitated in methanol like the starting material, which indicates that no cleavage has occurred. This rapid phase separation was also observed with poly 28 as described above. This could be due to coordination of the Lewis acid (BCl_3) to the oxygen of the methylenedioxy and ethylenedioxy groups. However, the nucleophilic attack of dodecyl mercaptan proposed in Scheme 24 failed to occur. Boron tribromide and its dimethylsulfide complexes, hydrobromic acid, p-toluenesulfonic acid, and dilute

Figure 31: ^1H NMR of poly(6-vinyl-1,4-benzodioxane).

Figure 32: ^1H NMR of poly(6-vinyl-1,4-benzodioxane) after treatment with 57% HI.

sulfuric acid failed to cleave the ethylenedioxy blocking group; the properties of the poly 31 recovered from the various acid treatments were unchanged.

Treatment of poly 31 with 57% hydroiodic acid yielded polymer which could be isolated by pouring the acid solution into ice-water. Initially, this would suggest that the ethylenedioxy group had been cleaved, and poly(4-vinylcatechol) then would be insoluble in halogenated solvents, but the isolated polymer was soluble in these solvents. In addition, the precipitation of the polymer from chloroform solution into various solvents such as methanol, ethanol, acetone, ether, and hexane failed to occur. Hence, the properties of poly 31 were altered somewhat by reacting with aqueous HI. The structure of poly 31 may be modified as suggested by proton NMR data; in this spectrum (Fig. 32), while the ethylenedioxy hydrogens absorbed at the same chemical shift, the absorption bands of the benzene hydrogens appeared as one broad peak instead of two broad peaks as in poly 31 (Fig. 31). The spectrum suggests that a substitution of the benzene ring took place. However, an iodine substitution was ruled out because the iodine content was negligible according to the elemental analysis. Henceforth, it is clear that poly 31 is not a practical poly(vinylcatechol) precursor.

F. Oxidation of Poly(vinylcatechols) to Corresponding

Poly(benzoquinones)

Earlier in our laboratory, the oxidation of pendent catechol units in terpolymers was performed using oxidizing agents such as ceric ammonium nitrate and chlorine.¹⁸⁷ However, the oxidations were

reported partially successful. Therefore, hydrogen peroxide and potassium nitrosodisulfonate, a Fremy's radical, were employed as alternative oxidants in subsequent work.⁸¹ However, characterization of the oxidized polymers posed some difficulty due to the relatively small loadings of catechol moieties.

In this study, cerium(IV) ammonium nitrate was the oxidant of choice. The oxidation of poly(3- and 4-vinylcatechol) was performed in the presence of a large quantity of ceric salt in THF (eq. 43); the heterogeneous mixture turned brownish after 48 hours at room temperature. The characterization of the oxidized products by many spectroscopic techniques was precluded by the total insolubility of the resins in all solvents. Consequently, we had to rely on the data obtained from the infrared spectra. For instance, the resins with

benzoquinone functions exhibited typical carbonyl absorptions at 1750 and 1650 cm^{-1} , and the reaction seemed to be complete based on the large intensity of the bands. For both poly(vinylcatechols), an increase in weight was detected after the oxidation reaction, suggesting that a degree of coordination of catechol units with cerous ion occurred.

G. Potentiometric Titration of Poly(3-vinylcatechol)

For the characterization of the redox polymers, the redox capacities and the redox potentials are the definitive properties. The redox capacities depend on the decomposition of the polymer and are measured in meq/g resin. The measurement of their redox potentials estimates their applicability as oxidant-reductant reagents. The potentiometric titration of redox systems is considered to be the most convenient technique to determine their potentials. The equation below (eq. 25) describes the redox process hydroquinone (H) - quinone (Q):

The Nernst equation for this redox system is shown in equation 26 where E_h represents the potential of the system against the hydrogen electrode measured in volts; E_m is the potential at 50% oxidation.

$$E_h = E_m + \frac{RT}{2F} \ln \frac{[Q]}{[H]} \qquad \text{eq. 26}$$

In a potentiometric titration of a redox substance in solution, two electrodes are needed. A reference electrode which with its ambient solution constitute a half-cell. In most cases, the calomel or silver-silver chloride serve as reference electrodes rather than

the hydrogen electrode. The indicator electrode is usually made of an inert metal such as platinum or gold. It forms a half-cell with the solution of the redox substance. The two coupled half-cells comprise the electrochemical cell. For each addition of titrant, the observed potential is allowed to reach a value constant with time. This is assumed to represent an equilibrium state. In ordinary potentiometry with simple redox substances, the indicator electrode responds very rapidly to the addition of the titrant. However, the response of the electrode is rather slow with solutions of redox polymers.¹¹⁰

In dealing with the measurement of the potentials, several factors seem always to be the sources of difficulties in measuring the redox properties of polymers. A major factor is the presence of oxygen. Titration of atmospheric oxygen with titanium chloride is always possible. Solubility and wettability of the resins contribute to the complications. Solubility problems may arise with linear polymers; wettability may affect the properties of crosslinked polymers. A third source of difficulty is the slowness of reaching the equilibrium value with redox polymers due to redistribution of the oxidized sites. When the redox polymer is titrated, the reaction with the titrant is usually fast in respect to the redox functionality of the polymer.¹¹¹ However, it might take minutes to hours for potentiometric equilibrium to be reached. The reason is that equilibrium is reached only after an interchange process in which the oxidized groups are distributed to equilibrium along the chains, and thus the process is slow.

Potentiometric titration curves of the redox resins generally show higher midpoint potentials, E_m , than the corresponding monomer

units. The slopes of the curves show a steeper increase and sometimes the curves are unsymmetrical. This behavior can be explained in terms of influence of inductive effect, the complexation, and the steric effect on the potentials of neighboring hydroquinone-quinone systems.^{112,117} Some examples of redox polymers with redox potentials are listed in Table 5.

A variety of oxidants and reductants were employed in oxidation-reduction reactions of the redox resins.⁷⁷ Bromine, iodine, cerium(IV), iron(III), and hydrogen peroxide are considered the most efficient oxidants. Reduction of the oxidized form may proceed with titanium(III), potassium iodide, sodium sulfite, sodium bisulfite, and sodium dithionite. The above-cited oxidants are useful titrants in potentiometric titration of soluble polymers.

If the redox properties of a polymer are to be determined electrochemically, it would be desirable to work in aqueous media. Although poly(2,3-dimethoxystyrene) and the rest of the polymers could be dissolved in glacial acetic acid after prolonged time, poly(3-vinylcatechol), 34, proved to resist solubility in this solvent. However, like poly(vinylhydroquinone) it could be readily dissolved in 90 or 95% aqueous acetic acid. Therefore, 90% acetic acid was the solvent of choice in measuring the redox potential of 34 under inert atmosphere. Moreover, ceric ammonium nitrate in 90% acetic acid (0.05N) was selectively employed as titrant among the oxidants mentioned above. Even though bromine water in acetic acid has been the most versatile oxidant, its possible reaction with catechol units by electrophilic substitution prevented its use in our study. The greatest variations in midpoint were found with changes with solvent

Table 5: Examples of Redox Polymers and Their Redox Potentials

<u>Polymer support</u>	<u>Redox unit</u>	<u>E_m (V)</u>	<u>Ref.</u>
Poly(N-hydroxymethylacrylamide)	hydroquinone	0.64 ^a	134
Poly(vinylhydroquinone)	"	0.45 ^b	91
Cellulose	"	0.695	132
Poly(vinylalcohol)	"	0.706	133
Vinylhydroquinone-maleic anhydride copolymer	"	0.752 ^c	135
Poly(4-vinylcatechol)	catechol	0.673 ^c	89
Styrene-divinylbenzene copolymer	anthraquinone	0.15 ^d	78
"	1-aminoanthra- quinone	0.52	131

^a Ceric sulfate (0.0922 N), H₂SO₄ (0.5 N), 25 °C; ^b Bromine (0.1 N), AcOH (90%), 29.7 °C

^c Ceric ammonium nitrate (0.05 N), AcOH (90%), 25 °C; ^d Estimation based upon Clark's values for the corresponding quinones.¹³⁶

systems as would be expected with the resultant changes in the liquid junction potentials. In our work, the pH change of the polymer solution (pH= 0.27 at 23 °C) during the titration process was very small; at the end of the titration, the pH change was in the order of 0.5 suggesting that the ceric solution added tended to render the system a buffer. Cassidy⁶¹ also observed a little change in pH during the titration of poly(vinylhydroquinone). On the other hand, noticeable differences were observed when we measured the redox potentials of catechol and poly(3-vinylcatechol) at two different temperatures, 23 (room temperature) and 35 °C.

At 23 °C, the establishment of a stable potential during the titration of the catechol was observed within a few minutes. The color of the system changed from yellow to deep brown at 50% oxidation, and turned yellow at the end point. This yellow color is indicative of fully oxidized quinone system.

With polymer systems, measurement of the potential was within 5 to 10 mV, and the establishment of a constant potential was always slow. This slowness has been a common observation to several investigators when dealing with the potentiometric titration of redox polymers at room temperature. Cassidy¹¹⁰ related this behavior to an intramolecular redistribution of the semiquinone intermediates. However, the coloration change during the titration was similar to that of the catechol system. The pink-orange color, observed with poly(vinylhydroquinone) upon addition of a titrant, was not detected with our polymer; Cassidy⁶¹ reported that the colorless solution became pink-orange with the first drop of oxidant and the pinkness became intense when approaching the midpoint. He attributed the pink

color to semiquinone radical formation. This color was observed with hydrolyzed poly 28, poly 29, and poly 30 upon exposure to air, but the insolubility of the first two polymers indicates that the semiquinone radical formation is accompanied by dimerization. The titration curves of the monomeric catechol and the poly(3-vinylcatechol) at 23 °C are shown in figure 27. The midpoint potential of the catechol was found to be 764 mV. That of the polymer was determined to be 707 mV; the midpotential of the partially hydrolyzed poly[2-(o-methyl)-4-vinylcatechol)] was reported to be 724 mV under the same conditions.⁸⁹ Even though the shapes of these curves are typical redox titration curves, the experimental data of both redox systems do not fit the Nernst equation (eq. 26), and this departure is even more pronounced in the polymer case. For this latter, the data would not match the Nernst equation due to the possible failure to meet one or more of the eight conditions postulated by Clark.¹³⁶

Potentiometric titration curves of redox resins were reported to show higher midpoint potentials, E_m , than the monomer units. For example, Nakabayashi et al.⁷³ reported that the midpoint potentials of hydroquinone polymers were higher than those of monomeric hydroquinone derivatives. Iwabuchi¹³⁵ also observed that the midpoint potential of 1:1 vinylhydroquinone-maleic anhydride copolymer was about 30 mV higher than those of hydroquinone and vinylhydroquinone. The relatively high potentials of the redox polymers is believed to be associated with "polymeric effect" factors; the oxidized form of the redox resin tends to adhere to the indicator electrode, therefore the potential will raise. In our study, we observed that the midpoint potential of the poly(3-vinylcatechol) was lower than that of the

Figure 27: Potentiometric titration curves at 23 °C:
o, catechol; Δ, poly(3-vinylcatechol).

monomeric catechol suggesting a "reverse polymeric effect". This effect could be generated from the non-adsorption of the oxidized product on the electrode due to its slow precipitation. However, a polymeric effect factor still manifested itself on the rate of establishment of a constant potential value as discussed earlier.

To determine the effect of temperature on the midpoint potentials of our systems, potentiometric titrations were conducted at elevated temperature, 35 °C. Not only the midpoint potentials varied, but also the shapes of the curves and the course of the titrations changed. Surprisingly, the establishment of a stable potential in the titration of the catechol was very slow this time, while that of the polymer was rapid before reaching the equivalence point. Moreover, the potentials of the redox polymer after the endpoint started to drift and were more or less stable only after about one hour. The titration curves of the catechol and the polymer at 35 °C are shown in figure 28. The titration curve of the catechol system exhibits two equivalence points indicative of intermediate semiquinone radical formation. Consequently, two midpoint potentials corresponding to two oxidation reactions could be deduced and they are 432 and 870 mV. The other unique feature of this titration at this temperature lies in the coloration change of the system; the catechol solution had been colorless upon addition of ceric ammonium nitrate solution till the second endpoint where a yellow color began to appear.

The titration of poly(3-vinylcatechol) at 35 °C showed some similarity to that at 23 °C in terms of color change. However, the shape of the first half of the curve was unusually flat. The flatness of this portion of the curve and the low potentials measured suggest

that initial complexation of the cerous ion by a catechol group becomes more readily reversible; stable complex would tend to raise the potential, because it requires more work to dissociate the complex group.

Two phenomena are likely to occur simultaneously during the titration of poly(3-vinylcatechol):

- 1) An oxidation reaction which tends to raise the potentials, thus an upward curve would be expected and
- 2) A precipitation of poly(o-benzoquinone), oxidized poly(3-vinylcatechol), which tends to reduce the potentials, hence a downward curve would result. This precipitation would imply the formation of nucleating micelles which will withdraw the oxidized units from the participation in the equilibrium. Consequently, the sum of these two curves would result in a flattened curve. Indeed, this flatness is observed for both experimental conditions, i.e., 23 and 35 °C. Moreover, a downward drift in potentials is visible at the end of the titration in both cases and this could be the result of only the precipitation phenomenon; no oxidation reaction is taking place at this stage. The drifting potentials at this level of titration were also observed by Cassidy⁶¹ during the titration of poly(vinylhydroquinone). However, at the end of the titration of catechol in both conditions, the curves show a plateau. This would be expected because the o-benzoquinone, oxidized catechol, remained soluble in the acidic medium, thus the precipitation phenomenon is not observed; therefore, a constant potential is detected afterwards. Also, it can be noted that only oxidation occurred in the first stage of titration of catechol for both conditions; this is illustrated by

Figure 28: Potentiometric titration curves at 35 °C:
o, catechol; Δ, poly(3-vinylcatechol).

the upward shapes of the first portions of titration curves of catechol (Fig. 27 and 28).

On the other hand, the lower potentials measured at 35 °C for both systems could be related to the energy supplied to the system. Hydrogen bonds, which exist between the catechol functionality and the carboxylic groups of acetic acid, must be broken in order to abstract electrons; hence, high potentials would be observed. However, these bonds could be broken by supplying energy to the system and lower potentials would be expected. In fact, lower potentials were measured at elevated temperature (35 °C), where hydrogen bonding is weaker.

Because poly(4-vinylcatechol) was insoluble due to the rapid dimerization discussed earlier, we were unable to evaluate its redox potentials by conventional procedure; for example, measurement of redox potentials in 90% acetic acid. We precluded a heterogeneous titration because a confusing measurement of the potential will ensue owing to the effective adsorption of polymer on the electrode; a higher potential will be measured. Manecke¹⁹³ and Iwabuchi⁸⁰ examined the redox potentials of some insoluble redox resins employing hydrazobenzene as a mediator. This soluble mediator may be added only in a small amount and should have a standard potential similar to the polymer in concern. Theoretically, the redox potentials of the mediator and the polymer would be equal when an equilibrium is established between them. In our study, we further precluded the use of hydrazobenzene as a mediator because we anticipated that a complex formation of type 35 may form between azobenzene and the catechol unit; macroreticular resin containing catechol system was reported to complex with azobenzene as evidenced by the coloration of the resin

upon the addition of this mediator.⁸⁰ In addition, other analytical alternative methods to determine the redox properties always require the experiment to proceed in a homogeneous system. Thus, the redox potential of poly(4-vinylcatechol) was not measured. Nonetheless, the midpoint potential would be anticipated to be closer to that of poly(3-vinylcatechol).

It is clear that the titrations of the catechol, a model compound, and poly(vinylcatechols) were somewhat similar. The closeness in their midpoint potentials, 764 and 707 mV respectively, indicates that the polymer-bound catechol should exhibit similar activity as a redox agent.

EXPERIMENTAL METHODS

A. General Information

Reagents All reagents used in the experiments were either commercial grade or were synthesized as described below. Reagent grade solvents were purified when necessary employing one of the methods described in "Purification of Laboratory Chemicals".¹⁹⁰

Sodium naphthalide A 250 mL flame dried three-necked round bottomed flask equipped with magnetic stirrer, was charged with 1.5 g (1.7 mmol) of 98% sublimed naphthalene, 50 mL of tetrahydrofuran refluxed over calcium hydride for 8 h before use, and 2 g of sodium metal cut into small pieces. The flask was sealed with rubber septa after purging the mixture with a stream of dry nitrogen. After 1 h of stirring at room temperature, the mixture turned dark green, an indication of the formation of sodium naphthalide initiator.

Styrene was purified by washing three times with equal aliquots of 10% sodium hydroxide to remove the aromatic inhibitor, hydroquinone, then washed with distilled water until litmus paper showed that all base has been neutralized. The monomer was then dried over anhydrous calcium chloride for 4 h and distilled under nitrogen at 20 mm and 43 °C.

Methyl methacrylate was extracted twice with equal portions of 10% sodium hydroxide, washed three times with distilled water until litmus paper indicates the absence of a base. The monomer was dried over calcium chloride and distilled under nitrogen at 60 mm and 33-35 °C.

Infrared spectra were recorded with a Perkin Elmer 621 (liquids) and IBM FT-IR (KBr pellets of polymers) spectrophotometers. Nuclear

magnetic resonance spectra were recorded with a Varian Associates HA60, a Bruker WP200 or an IBM NR100 spectrometer. Mass spectra were taken on a Hewlett 5985 GC/MS operating at 70 eV. Melting points were determined either with a Fisher-Johns or an Electrothermal Melting Point Apparatus.

Viscosity measurements were carried out with a 50M45 Cannon Ubbelohde Viscometer using toluene or benzene as solvent. Dilatometric studies were performed using a dilatometer constructed from a 10 mL test tube which was connected by a ground glass joint to a 30 mL length of 1 mm trubore capillary tubing calibrated in millimeters. Potentiometric titrations were conducted using a PH64 Research pH Meter; a platinum working electrode (a 20 mm x 2 mm platinum metal sealed to one end of a 10 mm glass tube; the conduction was provided by an iron wire immersed into a mercury layer in the tube) was coupled with a calomel reference electrode.

Elemental analyses were performed either by Galbraith Laboratories, Knoxville, Tennessee, or by MicAnal Organic Microanalysis, Tuscon, Arizona. Differential thermal analysis (DTA) curves were recorded with a DuPont 900 Thermal Analyzer and thermal gravimetry analysis (TGA) curves with a DuPont 951 Thermogravimetric Analyzer attached to the DTA unit.

B. Syntheses of Monomers

Four different approaches to the synthesis of monomeric catechol precursors were explored. The general techniques are described using 5-vinyl-1,3-benzodioxole, 28, as an example; the corresponding results from application of the methods to the remaining monomers are

Enumeration of Compounds

<u>R₁</u>	<u>R₂</u>	<u>R₃</u>	X			
			-HOCHCH ₃	-CH ₂ Cl	-CH ₂ P(=O)(Cl) ₃	-CH=CH ₂
H	-O-CH ₂ -O-		38	45	48	28
H	-OCH ₃	-OCH ₃	39	46	49	29
	-OCH ₃	-OCH ₃ H	40	47	50	30
H	-O-CH ₂ -CH ₂ -O-		41	-	-	31
	-O-CH ₂ -O-	H	42	-	-	32
	-OCH ₃	H H	43	-	-	36
H	H	-OCH ₃	44	-	-	37

Enumeration of Polymers

Y

R_1	R_2	R_3	Br	CN		$-\text{CH}_2\text{NH}_2$	$-\text{CH}_2\text{Cl}$	$-\text{Si}(\text{CH}_3)_3$	$-\text{SO}_3\text{NMe}_4$
H	$-\text{O}-\text{CH}_2-\text{O}-$		51	56	-	-	-	68	-
H	$-\text{OCH}_3$	$-\text{OCH}_3$	52	57	59	63	-	-	71
$-\text{OCH}_3$	$-\text{OCH}_3$	H	53	58	60	64	-	69	72
H	$-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-$		54	-	61	65	67	70	73
$-\text{O}-\text{CH}_2-\text{O}-$		H	55	-	62	66	-	-	75

summarized in Table 6.

Method A: Dehydration of 5-(1'-hydroxyethyl)-1,3-benzodioxole, 38:

a. Preparation of α -phenylethyl alcohol, 38: To a 1000 mL round bottomed flask fitted with a Claisen adapter, a reflux condenser, a nitrogen inlet-outlet, a dropping funnel, and a magnetic stirrer, and containing 7 g (0.29 mol) of flame dried magnesium turnings, a solution of 20 mL (0.32 mol) of iodomethane in 150 mL of anhydrous ether was added dropwise to prepare methylmagnesium iodide. As soon as the mixture began to reflux vigorously, an ice bath was provided to minimize the escape of ether and methyl iodide. When bubbling ceased and the mixture turned grey, a solution of 20 g (0.13 mol) of piperonal in 200 mL of ether was slowly dropped into the Grignard solution; a yellow precipitate started to form. After the piperonal solution was added, the mixture was refluxed for 0.5 h under nitrogen. The flask was cooled to room temperature, then was immersed into ice bath before either 100 mL of 10% hydrochloric acid or 100 mL of 5% ammonium chloride was added to decompose the Grignard complex and liberate the alcohol. The etherate layer was separated, washed with 5% sodium bicarbonate, and finally washed with water until pH neutral. After drying over anhydrous calcium chloride for 8 h, the ether was evaporated under reduced pressure to afford 19.15 g, 86.5%, of red oily alcohol, 38. Yields and ^1H NMR spectra of the different α -phenethyl alcohols prepared by this procedure are shown in Table 8.

b. Dehydration of 5-(1'-hydroxyethyl)-1,3-benzodioxole, 38: A 50 mL round bottomed flask containing 5 g of 38, 0.2 g of potassium bisulfate, and 0.2 g of cuprous chloride, and equipped with a vacuum distillation head, was immersed in an oil bath set at 180-190 °C. The

pressure was gradually reduced until distillation of 28 began. A colorless oil, 2.8 g, 63%, was collected at 95-96 °C/5 mm. Thin layer chromatography (hexane as eluent) showed one component, 5-vinyl-1,3-benzodioxole, 28, only. The other crude monomer distillates were each passed through a silica gel column (100-200 mesh, hexane as eluent) to yield the pure monomers. Isolated yields and spectral data, ^1H NMR and IR, for each of the monomers are reported in Table 7.

Method B: Decarboxylation of 3,4-methylenedioxycinnamic acid:

Copper powder, 1 g, was placed into a 250 mL three-necked round bottomed flask equipped with a vacuum head, a dropping funnel, and a thermometer. The flask was heated for 15 min at 225-230 °C. A solution of 5 g (0.026 mol) of 3,4-methylenedioxycinnamic acid (99% trans) and 0.1 g of hydroquinone in 70 mL of quinoline was added dropwise in a 15 min period. When gas evolution ceased, the content of the flask was distilled under reduced pressure at 110-130 °C. The brown yellow distillate was diluted with 50 mL of anhydrous ether, then poured into 100 g of crushed ice. The quinoline component was neutralized with 40 mL of 3 N sulfuric acid, the etherate layer separated, extracted with water, and dried over calcium chloride. Evaporation of the ether under reduced pressure and passage of the residue through a silica gel column (100-200 mesh, hexane as eluent) afforded 0.32 g, 8.3%, of monomer 28.

Method C: Wittig methenation of piperonal

A 500 mL three-necked round bottomed flask equipped with a mechanical stirrer, a dropping funnel, and a condenser with a nitrogen inlet-outlet, was charged with 18 g (0.05 mol) of 98% methyltriphenylphosphonium bromide suspended in 100 mL of anhydrous ether. Slow

addition of 20 mL of butyllithium (0.05 mol, 2.6 M in hexane) was accompanied by formation of a yellow orange colored solution; the salt dissolved completely. After stirring the ylide for 4 h at room temperature, a solution of 7.5 g (0.05 mol) of piperonal in 20 mL of ether was added over a 20 min period. A yellow white precipitate appeared almost immediately, the mixture was allowed to stir overnight at 40-45 °C. After cooling the flask to 25 °C, the slurry was diluted with 100 mL of ether and filtered, the ether filtrate was washed twice with water and dried over calcium chloride for 4 h. Evaporation of the ether under reduced pressure yielded 3.4 g of crude product. Passage of the crude monomer through a silica gel column (100-200 mesh, hexane as eluent) afforded 2.5 g, 33.8%, of pure monomer 28.

Method D: Wittig reaction of benzyl substituted ylides with formaldehyde

a. Preparation of 3,4-methylenedioxybenzyl chloride, 45:

1. With thionyl chloride, SOCl₂: Piperonal alcohol, 15 g (0.048 mol), was charged into a 250 mL round bottomed flask equipped with an efficient cooling system. Careful addition of 17.6 g (0.148 mol, 50% excess) of thionyl chloride was accompanied by vigorous evolution of hydrogen chloride and sulfur dioxide gases; a greenish color appeared. When gas evolution ceased, the flask was fitted with a condenser and the mixture was refluxed for 3 h at 60-70 °C. Evaporation of the excess thionyl chloride was effected by raising the pot temperature to 85-90 °C for 1 h. Distillation of the red residue under reduced pressure yielded 15 g, 89.2%, of colorless 3,4-methylenedioxybenzyl chloride, 45, bp 92-95 °C/2 mm. Yields and spectral data of the three benzyl chloride derivatives synthesized by

this technique are summarized in Table 9.

2. With hydrochloric acid, HCl: To a solution of 10 g (0.0657 mol) of piperonyl alcohol in 25-30 mL of methylene dichloride in a 250 mL round bottomed flask, 6 mL of concentrated hydrochloric acid and two drops of concentrated sulfuric acid were added. The flask was then equipped with a condenser and the mixture was refluxed for 3 h at 55 °C. After cooling the system to 25 °C, the greenish organic layer was extracted and washed with water, then with 5% sodium bicarbonate, and finally with water to pH neutral. After drying over anhydrous calcium chloride, the dichloromethane was evaporated under reduced pressure. Vacuum distillation gave 6 g, 53.64%, of colorless 3,4-methylenedioxybenzyl chloride, bp 92-95 °C/ 2 mm.

b. Preparation of 3,4-methylenedioxybenzyltriphenylphosphonium chloride, 48: A solution of 10 g (0.06 mol) and 15.5 g (0.059 mol) of 99% triphenylphosphine in 60-70 mL of chloroform was refluxed in a 250 mL round bottomed flask equipped with a condenser. After cooling the mixture to room temperature, the white chloride salt, 48, was precipitated in 600 mL of anhydrous ether, and dried in *vacuo* for 2 days at 40 °C to yield 25.3 g, 100%, of the desired product, mp 220-230 °C. Yields, melting points and mass spectra of the different benzylphosphonium chloride salts are compiled in Table 9.

c. Preparation of 5-vinyl-1,3-benzodioxole, 28: In a 250 mL Erlenmeyer flask equipped with magnetic stirrer, 15 g (0.035 mol) of phosphonium chloride salt, 48, was suspended in 150 mL of 37% formaldehyde and 20 mL of 50% sodium hydroxide was added dropwise. The exothermic reaction raised the temperature of the milky mixture to 44 °C. Stirring was continued for 5 h at the temperature of the

mixture before the monomer was extracted with two 50 mL portions of ether. The ether extract was dried over calcium chloride for 4 h. After evaporation of the solvent under reduced pressure, the residue was passed through a silica gel column (100-200 mesh, hexane as eluent) to afford 2 g, 38.9%, of pure monomer, 28.

C. Synthesis of 2,3-Methylenedioxybenzaldehyde

Method 1: McLean-Whelan's method:¹⁹¹ In a 2000 mL three-necked round bottomed flask fitted with a reflux condenser, a mechanical stirrer, and a glass stopper, a mixture of 25 g (181.25 mmol) of 2,3-dihydroxybenzaldehyde, 75 g (545 mmol) of potassium carbonate, 78.5 g (292.5 mmol) of diiodomethane, 2.6 g of cupric oxide and 215 mL of dimethylformamide was heated to 100-110 °C under nitrogen and stirred vigorously for 3.5 h. After allowing the mixture to cool to room temperature overnight, 1000 mL of water was added and the solution was extracted with two 750 mL aliquots of ether. The ether extract was washed sequentially with 5% hydrochloric acid and water, dried over calcium chloride, and the ether was evaporated to yield 28.9 g of red oil which crystallized upon refrigeration. Proton NMR revealed a mixture of 3,4-methylenedioxybenzaldehyde, 6.25 δ , s, 2H, $-\text{OCH}_2\text{O}-$, and diiodomethane, 4 δ , s, CH_2I_2 . After correcting for the diiodomethane content, 59% of the desired product was obtained, mp 27-30 °C, mass spectra: 149(100), 122(90.4), 135(68.2), 136(54.2), 150(1.9).

Method 2: Miller's method:¹³⁹ A mixture of 7.6 g (0.05 mol) of cesium fluoride and 1.66 g (0.012 mol) of 2,3-dihydroxybenzaldehyde was shaken in 32 mL of dimethylformamide for 20 min. The cesium fluoride was not completely dissolved in this system, even after

shaking for a long period of time. After addition of 0.935 g (0.011 mol) of dichloromethane, the mixture was refluxed for 2.5 h. The mixture became black and a precipitate appeared on the wall of the flask. After cooling the flask to room temperature, the 2,3-methylenedioxybenzaldehyde was extracted with 150 mL of ether, washed with water, 5% sodium bicarbonate and finally with water. After drying over anhydrous calcium chloride, the ether was evaporated under reduced pressure to afford 0.41 g, 22.72%, of a red substance which crystallized upon refrigeration. Proton NMR showed a singlet peak at 6.36 of the methylenedioxy group.

D. Polymerization Reactions of Monomers

1. Homopolymerization

a. Free radical polymerization: A solution of 1 g of monomer and 10 mg (0.062 mmol) of 2,2'-azobis-isobutyronitrile was subjected to two or three freeze-thaw cycles under nitrogen. The tube was sealed under vacuum and immersed into a 70 °C oil bath for 1 h, at which time the contents are quite viscous. The tube was cooled, opened, and the contents diluted with chloroform and precipitated in absolute methanol. The polymer was redissolved in chloroform and reprecipitated in methanol before it was dried **in vacuo** at 40 °C for 2 days. The results of the individual polymerizations are summarized in Table 11. Elemental analysis results are reported in Table 10. No evidence for residual vinyl group was detected in either the proton NMR or IR spectra of any of the polymers.

b. Anionic polymerization: To a solution of 1 g of freshly distilled monomer in dry benzene in a flame dried 100 mL three-necked

round bottomed flask equipped with two rubber septa and a nitrogen inlet-outlet was injected 1 mL of n-butyllithium (2.6 M in hexane). An exotherm was detected as the solution turned deep red. After 20 min at room temperature, 1 mL of absolute methanol was injected to terminate polymerization. Precipitation in methanol yielded a white powder which was recovered by filtration and dried in *vacuo* at 40 °C for 2 days. With the exception of that derived from monomer 29, the polymers recovered exhibited the same spectral characteristics as those obtained by free radical polymerization. The spectra of poly 29 revealed the presence of hydroxyl groups (8 δ , 3450-3430 cm⁻¹) indicating that the polymerization was accompanied by methoxy cleavage. When sodium naphthalide was used as an initiator in the polymerization of monomer 29, cleavage was observed also. The extent of conversion achieved and the viscosities of the polymers are compiled in Table 11.

Anionic polymerization of monomer 32 proceeded differently. Addition of n-butyllithium gave a persistent yellow color and no exotherm could be detected. After 40-50 min, 2 mL of absolute methanol was injected to discharge the yellow color. The solution turned purplish-blue upon exposure to air; it was poured immediately into methanol. The bluish precipitate was dissolved in dichloromethane and reprecipitated in methanol to yield a white powder; the spectral properties of the precipitate were consistent with the formation of low molecular weight poly 32.

Anionic polymerization of the monomers with n-butyllithium at temperature as low as -50 °C was also attempted but the polymers were isolated in very low conversions.

c. Cationic polymerization: Anhydrous stannic chloride, 0.5 mL, was added to a solution of 1 g of monomer in 30 mL of dichloromethane. A deep purple color accompanied by an exotherm was noted immediately. After 20 min at room temperature, 2 mL of methanol was injected to deactivate the catalyst and the polymer was precipitated in methanol. The precipitate was washed with water and methanol to remove the tin salts before drying the polymer in *vacuo* at 40 °C for 2 days. The results are summarized in Table 11. Cationic polymerization of monomer 29 was achieved at temperature -50 °C.

2. Dilatometric study of 2,3-dimethoxystyrene, 30:

The monomer 2,3-dimethoxystyrene was introduced into a dilatometer calibrated by mercury at 24 °C ($V_0 = 10.1383$, $\Delta V/\Delta H = 8.029 \times 10^{-3}$) containing 0.01 g (0.061 mmol) of recrystallized 2,2'-azobis-isobutyronitrile (AIBN) initiator. The capillary was inserted carefully to avoid trapping air bubbles. After firmly fastening the capillary to the test with springs, the joint was sealed with mercury. This complete system was then immersed carefully in a large constant temperature ($T = 70 \pm 0.05$ °C) water bath deep enough to cover the filled portion of the capillary. Initially the meniscus rose due to thermal expansion. Once some of the monomer was removed with a hypodermic syringe to keep the meniscus in the calibrated section of the capillary, the meniscus level was constant for a short time due to the inhibition by dissolved oxygen and then started to drop. The meniscus level was recorded every minute. After polymerization for 45 min (Fig. 1), the viscous solution in the bulb was cooled to room temperature and diluted in chloroform. Precipitation in absolute methanol, filtration, and drying in *vacuo* at

40 °C for 2 days yielded 1.96 g of poly(2,3-dimethoxystyrene). The initial rate of the bulk polymerization, R_p' , was calculated using the following relation:

$$R_p' = (\Delta V/\Delta t) \times (1/VK)$$

where K was estimated from the gravimetric conversion to be 0.0998. The initial and overall rates of polymerization, R_p' and R_p , were found to be $3.86 \times 10^{-3} \text{ min}^{-1}$ and $2.53 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$ respectively.

3. Copolymerization

a. Copolymerization of 2,3-dimethoxystyrene, 30

a-1. With styrene: Styrene (M_2) and 2,3-dimethoxystyrene (M_1) monomers were weighed in polymerization tubes containing 10 mg (0.061 mmol) of AIBN. The sum of the molar concentrations was maintained constant at 0.02 mol with variable feed ratio. The tubes were sealed **in vacuo** under nitrogen after degassing the dissolved oxygen in the solution by three to four alternate freeze-thaw cycles under nitrogen. The tubes were then immersed into a 70 °C oil bath until an increase in viscosity of the solution was noted. After cooling to room temperature, the viscous solutions were diluted in chloroform and precipitated in absolute methanol. The copolymers were dried **in vacuo** at room temperature for 3 days and weighed to calculate the extent of conversions. The composition of the copolymers were determined from elemental analysis. Results are shown in Table 12. Reactivity ratios r_1 and r_2 and Q-e copolymerization parameters are given in Table 16.

a-2. With methyl methacrylate: Copolymerization procedure was run in the same manner as with styrene, described above. Results are shown in Table 13. The r_1 , r_2 , Q , and e values are compiled in Table 16.

b. Copolymerization of 6-vinyl-1,4-benzodioxane, 31: The copolymerization procedure of monomer 30, described above, was applied for the copolymerization of monomer 31 with the same comonomers. However, the total molar composition of the monomer mixture was maintained at 0.01 mol. Results are reported in Tables 14 and 15. Reactivity ratios and Q - e parameters are found in Table 16.

4. Preparation of polystyrene grafts on poly 30: To a solution of 0.5 g of poly(2,3-dimethoxystyrene) in 30 mL of methylene chloride, 1.8 g of freshly distilled styrene was introduced. After stirring the mixture for 20 min, 0.5 to 1 mL of anhydrous stannic chloride was injected. The system was placed into an ice bath, the temperature was maintained between 0 and 20 °C, and allowed to stir for 1 h. The red precipitate was filtered and the solution was precipitated in absolute methanol giving a white powder once filtered. Both the insoluble red product and the soluble white powder were dried in *vacuo* at room temperature for three days to afford 0.40 and 0.81 g respectively; 35% of soluble fraction was isolated; polystyrene was the predominant component as evidenced by NMR. FT-IR spectrum of the insoluble product revealed the bands of poly 30 with an additional peak at 698 cm^{-1} which belongs to polystyrene as shown in figure 12.

Anal.: Found: C, 53.24; H, 5.15.

A similar procedure was used for the preparation of polystyrene grafts on poly(5-vinyl-1,3-benzodioxole) and on poly(6-vinyl-1,4-

benzodioxane). The soluble fractions, which were identified as predominantly polystyrene by NMR, were isolated in 53.6 and 77% yield respectively. With poly 28, a purplish blue color was noted instead of red. IR spectra of the insoluble grafted polymers revealed an additional peak at $680\text{--}700\text{ cm}^{-1}$ pertaining to polystyrene.

E. Chemical Modification of Poly(vinylcatechol) Precursors:

Electrophilic Approach

1. Bromination

Bromination of poly(5-vinyl-1,3-benzodioxole): To a solution of 1 g (6.75 mmol) of polymer in 60 mL of chloroform in a 250 mL round bottomed flask equipped with a magnetic stirrer and a dropping funnel, and coated to minimize exposure of the contents to light, a solution of 1.08 g (6.75 mmol) of bromine in 30 mL of chloroform was added dropwise; an evolution of hydrogen bromide gas was observed. Stirring was continued for 24 h at room temperature. The brown solution was precipitated in absolute methanol. The precipitate was redissolved in chloroform, reprecipitated in methanol, filtered and dried *in vacuo* at 40 °C for 2 days to afford 1.48 g of brominated poly 28. Elemental analysis, yields and extent of substitution upon bromination of all polymers are summarized in Table 21.

2. Cyanogenation

Cyanogenation of the brominated poly 28: Copper cyanide, 0.3 g (24% excess), was added to a solution of 1 g of polymer 51 in 80 mL of dimethylformamide in 250 mL round bottomed flask fitted with a reflux condenser. The mixture was heated for 4 h at 215 °C. After cooling the mixture to room temperature, the insoluble product was filtered

and the filtrate was precipitated in methanol. The precipitate was filtered and washed several times with water to remove the copper salts. The polymer was redissolved in dichloromethane, reprecipitated in methanol, and dried in *vacuo* at 40 °C for 2 days to yield 0.64 g. The cyanogenation reaction of the brominated poly(3,4-dimethoxystyrene), 52 and poly(2,3-dimethoxystyrene), 53 were also attempted by employing the same experimental procedure. The extent of substitution and elemental analysis for each derivative are given in Table 22.

3. Chloromethylation

Chloromethylation of poly(6-vinyl-1,4-benzodioxane), poly 31:

To a solution of 0.46 g (2.836 mmol) of poly 31 and 3 mL of chloromethyl ethyl ether (0.032 mol) in 30 mL of chloroform, 0.1 mL of anhydrous of stannic chloride was added. The mixture was allowed to stir for 5 min at room temperature. The catalyst was deactivated by injecting 2 mL of absolute methanol and the mixture was stirred for an additional 10 min. The product was precipitated from methanol, filtered and washed with methanol before drying in *vacuo* at 40 °C for 2 days to afford 0.39 g of 67 with 73.23% substitution based on elemental analysis. Proton NMR (CDCl_3) revealed a broad peak at 4-5 δ corresponding to an overlap of $-\text{OCH}_2\text{CH}_2\text{O}-$ with $-\text{CH}_2\text{Cl}$ group.

Anal. : Calcd. : C, 62.71; H, 5.26; Cl, 16.85.

Found : C, 63.89; H, 5.30; Cl, 12.34.

4. Quaternization of chloromethylated poly(6-vinyl-1,4-benzodioxane, 67): Chloromethylated polymer, 0.34 g, was suspended in 30 mL of absolute methanol and 5 mL of triethylamine was added to the slurry. The heterogeneous mixture was allowed to stir for three days at room temperature; the mixture became orange. The precipitate that

persisted during the reaction course was filtered and the filtrate was precipitated in hexane. The product was redissolved in absolute methanol, but an attempt to reprecipitate it in hexane failed. The solvents were evaporated under reduced pressure and the quaternized polymer was left as yellow orange solid. After drying *in vacuo* at room temperature for three days, the product weighed 0.24 g.

Elemental analysis indicated a 47.96% substitution. Proton NMR

(CD₃OD) : 4.8δ, Ar-CH₂-N≡, s; 3.2δ, ≡N-CH₂-CH₃, q; 1.4δ, ≡N-CH₂-CH₃, t.

Anal. : Found : C, 62.69; H, 6.77; N, 1.60; Cl, 4.56.

5. Lithiation

Lithiation of poly(2,3-dimethoxystyrene): To a solution of 0.5 g (3.04 mmol) of poly 30 in 50 mL of benzene in a 100 mL resin kettle fitted with a mechanical stirrer, a reflux condenser, a nitrogen inlet-outlet, and two rubber septa, 6 mL (15.6 mmol) of n-butyllithium (2.6 M in hexane) and 3 mL of N,N,N',N'-tetramethylethylenediamine (TMEDA) were injected. The mixture was refluxed and stirred under nitrogen at 65–70 °C for 8 h; a brown slurry was noted. The color turned yellow upon addition of 6 mL of trimethylchlorosilane after cooling the system to room temperature. Stirring was continued for 14 h at room temperature. The slurry was poured in methanol and the precipitate was redissolved in benzene, reprecipitated in methanol, filtered, washed with water and finally with methanol. After drying *in vacuo* for three days at room temperature, 0.49 g of silylated polymer, 69, was isolated. Characterization data and extent of substitution are summarized in Table 20.

The lithiation-silylation sequence was applied to poly 28 and

poly 31. Results are also shown in Table 20.

6. Phthalimidomethylation

Phthalimidomethylation of poly(2,3-dimethoxystyrene)

a. With N-methylolphthalimide and trifluoromethanesulfonic

acid: To a solution of 0.5 g (3.04 mmol) of polymer in 20 mL of dichloromethane placed in a 100 mL round bottomed flask, a mixture of 0.53 g (2.99 mmol) of N-methylolphthalimide, 1 g of trifluoromethanesulfonic acid in 40 mL of trifluoroacetic acid was added dropwise over 1 h period. The mixture started to turn yellow and cloudy. A purple color and a sticky material were noted after 16 h of stirring at room temperature. The solution was precipitated in absolute methanol. The purple precipitate was filtered, washed sequentially with water, 100 mL of ammonium hydroxide, water, and finally with methanol to afford a white polymer. Drying in *vacuo* at 40 °C for 2 days yielded 0.85 g of polymer 60.

The same experimental procedure was used for the phthalimidomethylation reaction of poly 29, poly 31 and poly 32 with the difference in color change throughout the course of the reaction; the addition of the N-methylolphthalimide solution was accompanied by appearance of purple color which turned greenish black after 8 h of stirring at room temperature. Polymer 62 was insoluble in common organic solvents. An increase in weight was obtained for all cases. Yields, extent of substitution, and characterization data are gathered in Tables 23 and 24.

b. With n-butyllithium and N-bromomethylphthalimide: The first step, lithiation, was carried out as described above using the same quantities of reagents. The second step consists of adding

dropwise a solution of 1 g of N-bromomethylphthalimide in 20 mL of benzene. The red persistent color of the mixture which appeared at the beginning of the addition turned yellow. The mixture was brought to reflux at 62 °C and stirred overnight. The precipitate from methanol was washed with water and methanol. The product dried in **vacuo** at room temperature for three days was insoluble in halogenated solvents. Elemental analysis indicated 40.20% substitution. IR (KBr pellet): 1750 and 1690 cm^{-1} (-CO-N-CO-).

Anal. : Calcd. : C, 70.57; H, 5.30; N, 4.33.

Found : C, 72.42; H, 6.66; N, 1.74.

7. Hydrazinolysis

Hydrazinolysis of polymer 60 : Hydrazine, 7 mL, was added to a suspension of 0.63 g of polymer 60 in 70 mL of absolute ethanol. The mixture was refluxed at 50-60 °C for 14 h. The solid by-product was filtered while the mixture was hot. The sticky material remaining after evaporation of ethanol under reduced pressure was dissolved in chloroform. The insoluble by-product, phthaloylhydrazide, was filtered. Attempt to precipitate the chloroform solution in methanol failed to produce any powder. A film was obtained after evaporation of chloroform. The film was dried in **vacuo** at 40 °C for 2 days to yield 0.43 g of brown material. A ninhydrin test on a slurry in water was positive; a purple blue color formed on the particles indicating the presence of amino groups. The strong absorptions in the FT-IR spectrum at 1774 and 1714 cm^{-1} disappeared and a broad band at 3450 cm^{-1} appeared, designating a primary amine. The hydrazinolysis reaction was applied to polymers 59, 61, and 62. Results and spectral data are given in Table 25.

8. Quaternization of the aminomethylated polymer, 64:

To a suspension of 0.2 g (1.04 mmol) of aminomethylated polymer in 60 mL of absolute methanol, 0.05 to 0.06 g of sodium carbonate and 1.47 g (10.4 mmol) of iodomethane were added. The mixture was stirred at room temperature for 2 days; the polymer was still suspended and no color change was noted. Another excess of iodomethane and 2 mL of concentrated hydrochloric acid were added to the mixture. Stirring for an additional 2 days afforded a red liquid along with a precipitate. The red solution was precipitated in water (it can also be precipitated in ether) and filtered. Drying in *vacuo* at room temperature for three days yielded 0.04 g of red brown polymer. This polymer was soluble in methanol. Proton NMR spectrum was not recorded due to the minuscule amount of sample available. The red insoluble product was dried and elemental analysis revealed the presence of iodine.

Anal. : Found : C, 42.82; H, 5.79; N, 3.06; I, 30.87.

9. Attempted phthalimidoethylation of poly 30: To a solution of 0.5 g of poly 30 in 20 mL of dichloromethane, a mixture of 0.6 g of 99% N-(2-hydroxyethyl)phthalimide, 40 mL of trifluoroacetic acid and 0.6 mL of trifluoromethanesulfonic acid, was added dropwise over a 0.5 h period. The brown solution was stirred at room temperature for 22 h at which time the color turned deeply brown. The solution was precipitated in methanol, washed with sodium hydroxide, water and finally with methanol. Drying in *vacuo* at room temperature for three days afforded 0.48 g of polymer. Elemental analysis indicated that nitrogen had been incorporated, but expected aromatic proton peak at 7.9-8.6 in ^1H NMR and the carbonyl absorptions at 1750 and 1690 cm^{-1} in

IR were absent.

Anal. : Calcd. : C, 71.20; H, 5.67; N, 4.15.

Found : C, 67.23; H, 6.51; N, 0.80.

10. Sulfonation

Sulfonation of poly 30: To a solution of 0.5 g of poly 30 in dichloromethane, was injected 0.2 mL of chlorosulfonic acid; a milky gel was formed rapidly. The mixture was then stirred for 0.5 h at room temperature. A clear solution was obtained upon addition of 30 mL of distilled water to the mixture; the gel dissolved cleanly in that system. To the acidic aqueous extract (pH $\approx$ 1), 50% sodium hydroxide was added dropwise until pH was basic, then 0.4 g of tetramethylammonium chloride was added at once and the mixture was stirred for 1 h at ambient temperature. After dilution with dimethylformamide, a white polymer was precipitated in acetone. The polymer was filtered and dried *in vacuo* for 2 days at room temperature to afford 0.5 g of polymer. Sulfonation of poly 29 and poly 31 were carried out similarly. Table 26 covers the elemental analysis and the extent of substitution.

11. Attempted sulfomethylation of poly 30: To a suspension of 0.5 g of poly 30 in 50 mL of water, aqueous sodium hydroxide (50%) was added dropwise while stirring until the pH was alkaline. After introduction of 0.93 g (54% excess) of the formaldehyde sodium bisulfite adduct, the slurry was heated at 63-65 °C for 4 days. The unreacted polymer was recovered by filtration and the aqueous filtrate was precipitated in methanol; attempt to precipitate it in acetone failed. Drying *in vacuo* at room temperature for three days afforded 0.82 g of water soluble product. Proton NMR (D_2O) spectrum was

inconclusive. Moreover, IR spectrum was entirely different from that of poly 30. The sulfomethylation reaction was also attempted with poly 28 and poly 31, and the same product was obtained as revealed by IR. The elemental analysis for the aqueous soluble fractions are respectively:

Anal. : Found : C, 1.91; H, 0.40; S, 21.94.

C, 2.24; H, 0.68; S, 16.79.

C, 0.89; H, 0.51; S, 21.80.

F. Synthesis of Model Compounds

1. Synthesis of 5-methyl-1,3-benzodioxole, Clemmensen

reduction of piperonal: A 1000 mL round bottomed flask immersed in an efficient cooling system, was charged with 20 g of mossy zinc, 12 g of mercuric chloride, 200 mL of water and 6 mL of concentrated hydrochloric acid. An exotherm was detected when shaking the mixture for 5 min. After decanting the liquid, 100 mL of benzene and 50 g of piperonal were carefully added to the amalgamated zinc remaining in the flask. The flask was immersed in a heating mantle and the mixture was vigorously refluxed for 24 h. After cooling the mixture to 25 °C and separating the benzene layer, the aqueous layer was extracted with two 75 mL aliquots of ether. The benzene and the etherate extracts were combined and dried over anhydrous calcium chloride for 24 h. The solvents were evaporated under reduced pressure. The residue was distilled to yield 14.4 g, 32%, of 5-methyl-1,3-benzodioxole, 85 °C/26 mm. Proton NMR (CDCl₃): 2.2δ, 3H, Ar-CH₃, s; 5.89δ, 2H, -OCH₂O-, s. IR (neat) shows no carbonyl group. Mass spectra: 135 (100), 136(76.5), 77(16.7), 78(16.4).

2. Acylation reaction of 1,3-benzodioxole: On mixing 15 g (0.123 mol) of 1,3-benzodioxole, 14.2 g (0.124 mol) of trifluoroacetic acid, and 27 g (0.265 mol) of acetic anhydride, a yellow color was produced. The mixture turned black upon heating for 2 h at 65-70 °C. Heating was continued for an additional 7 h. After cooling the mixture to 25 °C, it was poured into 100 mL of water. To neutralize the excess of acid, the organic portion was washed with 10% sodium bicarbonate and water. Unreacted 1,3-benzodioxole and acetic anhydride were removed by vacuum distillation, 90 °C/60 mm, and 10.4 g of red substance was obtained. This red residue solidified upon refrigeration. Recrystallization in hot ethanol afforded a shiny brown powder, mp 82-83 °C. Proton NMR (CDCl₃): 2.5δ, 3H, -CO-CH₃, s; 5.95δ, 2H, -O-CH₂-O-, s; 6.7-7.6δ, 3H, Ar-H, m. IR (KBr): 1640 cm⁻¹, -CO-CH₃. Mass spectra: 149(100), 121(52.5), 164(46.0).

3. Synthesis of 5-ethyl-1,3-benzodioxole, Clemmensen reduction of 5-acetyl-1,3-benzodioxole: The amalgamated zinc recovered from the reduction of piperonal was used. A similar procedure was also employed using 5 g of 3,4-methylenedioxyacetophenone and adjusting the amounts of reagents used. The distillation under reduced pressure of the residue yielded 2 g, 44%, of colorless 5-ethyl-1,3-benzodioxole, bp 82 °C/25 mm. Proton NMR (CDCl₃): 1.2δ, 2H, -CH₂-CH₃, q; 2.5δ, 3H, -CH₂-CH₃, t; 5.89δ, 2H, -O-CH₂-O-, s; 6.68δ, 3H, Ar-H, m. The carbonyl group band absorption was absent in the IR spectrum. Mass spectra: 135(100), 150(31), 77(8.6).

4. Chloromethylation attempt of 5-methyl-1,3-benzodioxole: A solution of 3.47 g (36.73 mmol) of chloromethyl ethyl ether and 0.43 mL (3.673 mmol) of anhydrous stannic chloride in 20 mL of chloroform

was added dropwise to a solution of 5 g (36.76 mmol) of 5-methyl-1,3-benzodioxole in 50 mL of chloroform. The red mixture obtained was stirred and refluxed at 65 °C for 3 h; an evolution of gas was noted. The mixture turned black. Evaporation of chloroform under reduced pressure afforded a sticky compound which was dissolved in the same solvent and precipitated in methanol. The brown black precipitate was filtered, washed with methanol, and dried *in vacuo* at 40 °C for 2 days to yield 1.5 g of chloroform soluble black powder. Proton NMR (CDCl₃): 6.8δ, Ar-H; 5.8δ, -OCH₂O-; 3.8δ, Ar-CH₂-; 2.3δ, Ar-CH₃.

Anal. : Found : C, 68.38; H, 5.08.

G. Removal of Blocking Groups

1. Deblocking of poly(3,4-dimethoxystyrene): A 150 mL three-necked round bottomed flask fitted with a magnetic stirrer, a stopper, a condenser, and a nitrogen inlet-outlet, was charged with 1.3 g of poly 29 and 35 mL of glacial acetic acid. The slurry was stirred at 30 °C for 2 days by which time the polymer was dissolved in acetic acid. 48% Hydrobromic acid, 20 mL, was added dropwise while stirring and refluxing at 70-80 °C under nitrogen. Refluxing was continued for 2 h at 120 °C. The purple red solution was cooled to 25 °C and poured in 500 mL of ice-water. The white precipitate obtained was filtered under nitrogen. This product was easily soluble in methanol when wet. When dried *in vacuo* at 40 °C for 2 days affording 0.8 g, the polymer turned purple and became insoluble in methanol.

2. Deblocking of poly(2,3-dimethoxystyrene): A solution of 0.5 g of poly(2,3-dimethoxystyrene) in 70 mL of dichloromethane was purged

with a stream of nitrogen before injecting 6 mL of 1 M boron trichloride in methylene chloride. Stirring was continued for 36 h at room temperature before hydrolysis of the intermediate borate complex was effected by adding 3 mL of absolute methanol. The reaction mixture was poured into 500 mL of ice-water to complete the hydrolysis of the excess boron trichloride. The white polymeric catechol was isolated, washed with dichloromethane, and dried *in vacuo* at room temperature to afford 0.38 g of poly(3-vinylcatechol). The proton NMR and IR spectra of this polymeric catechol are given in Fig. 26 and Fig. 25 respectively. Note the characteristic OH stretch centered at 3217 cm^{-1} and the absence of methoxy bands at 1030 and 1260 cm^{-1} in the infrared spectrum of poly(3-vinylcatechol).

Anal. : Found : C, 64.68; H, 5.66; Cl, 0.27.

3. Removal of formal group of poly 28:

a. With boron trichloride: Poly(4-vinylcatechol), 0.48 g, was obtained from 0.55 g of poly 28 employing the same experimental procedure for the synthesis of poly(3-vinylcatechol) described above. Poly(4-vinylcatechol) was readily soluble in methanol when initially isolated but became purple and insoluble when dried *in vacuo* at room temperature for three days indicating an autooxidation. IR (KBr) revealed a broad peak at $3500\text{--}3000\text{ cm}^{-1}$ and a disappearance of formal group bands at $2785\text{--}2765\text{ cm}^{-1}$.

b. With boron trichloride and dodecyl mercaptan: Dodecyl mercaptan, 0.8 mL, and boron trichloride (1 M in dichloromethane), 4 mL, were added sequentially to a solution of 0.26 g of poly(5-vinyl-1,3-benzodioxole) in 25 mL of dichloromethane stirred under nitrogen. A red color as well as a precipitate started to appear 10

min later. Addition of absolute methanol after 5 h of stirring at room temperature, dissolved cleanly the red yellow precipitate. The solution was poured into 300 mL of ice-water to precipitate the poly(4-vinylcatechol). This white polymer was isolated and dried in *vacuo* at room temperature to afford 0.24 g. A very light pink color of the polymer began to be noticed. This material was insoluble in methanol, swellable in dimethylsulfoxide and in 90% acetic acid. The extent of swellability increased upon addition of concentrated sulfuric acid.

4. Attempt of deblocking poly 31

a. With boron trichloride and dodecyl mercaptan: As soon as 6 mL of 1 M boron trichloride was injected to a solution of 0.33 g of poly 31 in 25 mL of dichloromethane and 1 mL of dodecyl mercaptan, a red color and a precipitate were noted immediately. The precipitate was redissolved in the system upon addition of 4 mL of absolute methanol. Attempt to precipitate the solution in ice-water failed but the product precipitated in methanol. The isolated polymer was soluble in the same common organic solvents as the starting polymer which indicated a failure to deblock the catechol functions.

b. With hydroiodic acid: Poly 31, 1 g, was dissolved in 50 mL of glacial acetic acid in a 250 mL three-necked round bottomed flask equipped with a condenser, a dropping funnel, a mechanical stirrer, a nitrogen inlet-outlet. The solution was stirred and heated until the pot temperature reached 120 °C, then a 10 mL of 57% hydroiodic acid was added slowly. The mixture was stirred for 2 h at 116 °C under nitrogen. After cooling the flask to 25 °C, the mixture was poured into 500 mL of ice-water and a cream colored precipitate

appeared. The isolated polymer, 0.91 g, was soluble in halogenated solvents. A chloroform solution failed to precipitate in methanol, ether, acetone, hexane, and ethanol. Proton NMR (CDCl_3) spectrum was identical to that of the polymer with the exception of the benzene ring chemical shift, being one broad peak instead of two broad peaks.

Anal. : Found : C, 69.25; H, 5.84; I < 0.5.

H. Oxidation of Poly(vinylcatechols) to Poly(vinylbenzoquinones)

In a 100 mL round bottomed flask equipped with a magnetic stirrer, 0.23 g of poly(3-vinylcatechol) was suspended in 50 mL of THF. To this mixture was added 4 g of ceric ammonium nitrate, and stirring was continued for 48 h at room temperature. The polymer was filtered, washed several times with water, and dried *in vacuo* to afford 0.27 g of orange yellow polymer. The product was insoluble in all solvents tried, but IR analysis revealed a considerable oxidation as evidenced by a strong C=O absorption at 1650 and 1750 cm^{-1} .

Oxidation of poly(4-vinylcatechol) was proceeded in the same manner as above and IR analysis showed the same absorptions.

I. Potentiometric Titration

Potentiometric titration of poly(3-vinylcatechol) with ceric ammonium nitrate: Poly(3-vinylcatechol), 0.02 g was dissolved in 150 mL of 90% acetic acid in 250 mL beaker fitted with a magnetic stirrer. The platinum and the calomel electrodes, connected properly to the PHM64 Research pH Meter, were immersed into the solution (pH = 0.28) and the reading was set to mV knob. Readings of potential were recorded in millivolts during the titration process with 0.05 N ceric

ammonium nitrate in 90% acetic acid. The temperature of the system was 23 °C (room temperature). The solution turned brown upon addition of the first drops of the cerium solution and this color became intense at 50% oxidation. The mixture became completely yellow at the end of titration.

Similarly, catechol was potentiometrically titrated with 0.05 N ceric ammonium nitrate at 23 °C. The results of the titrations at 23 °C are given in Table 27a,b. The potentiometric curves are illustrated in figure 27.

Redox titrations of catechol and the polymeric catechol were also conducted at an elevated temperature, 35 °C. Results are reported in Table 28a,b and the titration curves are shown in figure 28.

Table 6: Yields and Physical Properties
of Monomers

Monomer	Method	Yield (%)	bp (°C/mm)	mp (°C)
28	A	63	95-96/5	-
"	B	8	50.5-51/0.27 ⁸⁹	-
"	C	34		-
"	D	39		-
29	A	45	136-140/5	-
"	C	32	98-99/1.5 ⁸⁹	-
"	D	37		-
30	A	85	115-118/14	23
"	C	45	"	"
"	D	57	"	"
31	A	65	111/1	-
"	C	37	"	-
32	A	50	116/1	-
36	A	90	63-64/2-4	-
37	A	60	70/4	-

Table 7a: ^1H NMR and IR Data of Monomers

Monomer	^1H NMR (CDCl_3)	IR (NaCl)
	Chemical shift, ppm	Frequency, cm^{-1}
28	6.65-6.90, Ar-H, m; 5.82 O-CH ₂ -O, s; 6.60, -CH=CH ₂ , s; 5, cis, -CH=CH ₂ , d; 5.4, trans, -CH=CH ₂ .	3075, 3065, 3000, C-H (ring); 2875, 2765, C-H stretch (-CH ₂ -); 1620, 970, -CH=CH ₂ ; 1580, 1490, C=C ring stretch; 1250, 1215, 1100, 925, 720, C-O-C.
29	6.51-7.90, Ar-H, m; 4.9- 6.3, vinyl; 3.75, -OCH ₃ d.	3065, C-H ring stretch; 2980, 2940, 2910, -CH ₃ ; 1615 900, -CH=CH ₂ ; 1565, 1465, C=C ring stretch; 1030, 1260, C-O-C.
30	6.7-7.1, Ar-H, m; 5.1- 6.69, vinyl group; 3.75, -OCH ₃ , d.	Same as 29
31	6.5-6.8, Ar-H, m; 4.9-6.3, vinyl group; 4.1, -OCH ₂ CH ₂ O-, s.	3060, 3025, C-H ring stretch; 2960, 2910, 2826, -CH ₂ - , 1565, 1490, C=C ring stretch;
32	6.8-7.1, Ar-H, m; 5.4-	1610, 900, 980, -CH=CH ₂ ; 1300, 1280, 1259, 1240, 935, 720, C-O-C.
32	6.8-7.1, Ar-H, m; 5.4- 6.5, vinyl group; 6.1, O-CH ₂ -O, s.	Same as 28

Table 7a: Continued

Monomer	^1H NMR (CDCl_3)	IR (NaCl)
	Chemical shift, ppm	Frequency, cm^{-1}
36	7.2-7.5, Ar-H, m; 3.8, -OCH ₃ , s; 5.2-6.8, vinyl group.	3050, C-H ring stretch; 2980, 2940, 2875, -CH ₃ ; 1610, 990, 900, -CH=CH ₂ ; 1580, 1450, C=C ring stretch; 1280, 1020 C-O-C.
37	6.8-7.3, Ar-H, 2d; 3.8, -OCH ₃ , s; 5.2-6.6, vinyl group.	Same as 36

Table 7b: Mass Spectra Results of Monomers

Monomer	Mass spectra
	m/e (relative intensity)
28	147(100), 148(89), 89(32.5), 91(11.6)
29	164(100), 91(55.6), 77(55.3), 149(37.1), 78(36.6), 103(35.9), 121(20.5)
30	121(100), 91(88.8), 164(63.4), 77(58.2), 78(55.3), 149(44.3), 51(28.2).
31	162(100), 78(65.7), 106(46.9), 163(32.3)
32	148(100), 91(92.2), 89(76.1), 147(51.4), 63(48.10)
36	91(100), 119(47.4), 134(45.9), 65(25.5)
37	134(100), 91(76.3), 119(52.4), 65(38.8)

Table 8: Yields and ^1H NMR Results of sec-Phenylethyl Alcohol Derivatives

Alcohol	Yield	^1H NMR (CDCl_3); Chemical shift, ppm
38	86.50	6.65-6.8, Ar-H, m; 5.75, OCH_2O , s; 4.65, $-\text{CH}-\text{CH}_3$, q; 4.05, $-\text{OH}$, s; 1.32, $-\text{CH}-\text{CH}_3$, d.
39	73.20	6.60-6.90, Ar-H, m; 4.6, $-\text{CH}-\text{CH}_3$, q; 3.75, $-\text{OCH}_3$, d; 3.4, $-\text{OH}$, b s; 1.35, $-\text{CH}-\text{CH}_3$, d.
40	75.14	6.60-6.90, Ar-H, m; 4.9, $-\text{CH}-\text{CH}_3$, q; 3.72, $-\text{OCH}_3$, d; 3.00, $-\text{OH}$, b s; 1.32, $-\text{CH}-\text{CH}_3$, d.
41	83.20	6.7, Ar-H, s; 4.5, $-\text{CH}-\text{CH}_3$, q; 4.2, $-\text{OCH}_2\text{CH}_2\text{O}-$, s; 2.15, $-\text{OH}$, b s; 1.32, $-\text{CH}-\text{CH}_3$, d.
42	91.04	6.78-7.10, Ar-H, m; 6.00, $-\text{OCH}_2\text{O}-$, s; 5.00, $-\text{CH}-\text{CH}_3$, q; 3.10, $-\text{OH}$, b s; 1.4, $-\text{CH}-\text{CH}_3$, d.
43	63.44	6.8-7.2, Ar-H, m; 5.10, $-\text{CH}-\text{CH}_3$, q; 1.48, $-\text{CH}-\text{CH}_3$, d; 3.8, $-\text{OCH}_3$, s; 2.8, $-\text{OH}$, b s.
44	86.54	6.8-7.2, Ar-H, 2d; 4.2, $-\text{CH}-\text{CH}_3$, q; 3.7, $-\text{OCH}_3$, s; 2.5, $-\text{OH}$, b s; 1.30, $-\text{CH}-\text{CH}_3$, d.

Table 9: Yields, Physical Properties and Mass Spectra of Benzylchloride
and Benzyltriphenylphosphonium Chloride Derivatives.

<u>Compound</u>	<u>Yield, %</u>	<u>bp, °C/mm</u>	<u>mp, °C</u>	<u>Mass spectra (relative intensity)</u>
45	89	92-95/2	-	135(100), 170(26.3), 77(14.7)
46 ^a	66.68	134/3-4 ^b	48 ^d	151(100), 186(20.8), 152(9.9)
47	61	110-114/7 ^c	-	136(100), 151(93.2), 91(80.7), 186 (44.1), 65(44.3), 77(35.5), 108(28.4)
48	100	-	220-230	183(100), 135(85.7), 108(49.7), 77(46.6), 107(43.8), 262(41.6), 51(41.1), 152(32.4), 396(11.4)
49	97	-	230-235	183(100), 108(71.1), 262(70.7), 107 (40.8), 151(31.6), 152(24.9), 51 (24.3), 77(20.7), 137(19.7), 397(19.4), 412(11.7)
50	97	-	215-220	183(100), 108(71.1), 262(70.7), 107 (45.0), 51(33.0), 77(23.7), 152 (21.9)

a, became black upon exposure to air; b, lit. 110-113/1.25⁸⁰ and 152-156/10¹⁸⁸;
c, lit. 130-131/12¹⁸⁹; d, lit. 48-49¹⁸⁸ and 49-50⁸⁰.

Table 10: Elemental Analysis of Polymers

<u>Polymer</u>	<u>Calculated</u>		<u>Found</u>	
	<u>% C</u>	<u>% H</u>	<u>% C</u>	<u>% H</u>
poly 28	72.97	5.40	72.55	5.52
poly 29	73.14	7.37	72.72	7.18
poly 30	73.14	7.37	72.00	7.16
poly 31	74.05	6.21	74.03	6.03
poly 32	72.97	5.40	72.38	5.36
poly 36	80.57	7.51	79.24	7.44
poly 37	80.57	7.51	79.76	7.51

Table 26: Results of Sulfonation of Polymers

<u>Polymer</u>	<u>Elemental analysis</u>			
	<u>Found</u>			
	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% S</u>
71	27.11	4.89	1.16	3.30
72	12.75	1.60	<0.5	11.94
73	19.93	2.40	<0.5	15.27

Table 11: Summary of Polymerization Data

Polymer	Free radical			Anionic			Cationic		
	$[\eta]$ dL/g	Conv. %	M_v $\times 10^{-3}$	$[\eta]$ dL/g	Conv. %	M_v $\times 10^{-3}$	$[\eta]$ dL/g	Conv. %	M_v $\times 10^{-3}$
poly 28	0.15	48	32.1	0.02	23	1.8	0.03	76	3.2
poly 29	0.24	50	62.9	-	78	-	0.18	46	41.7
poly 30	0.32	78	94.9	0.12	14	23.4	-	-	-
poly 31	0.29	66	82.4	0.05	13	6.7	0.08	94	13.1
poly 32	0.24	52	62.9	-	8	-	0.02	18	1.8
poly 36	-	-	-	-	-	-	-	90	-
poly 37	-	-	-	-	20	-	-	-	-

Table 12: Copolymerization of 2,3-Dimethoxystyrene (M_1) with Styrene (M_2)

<u>Feed</u>		<u>Mole fraction in feed</u>			<u>Time^a</u>	<u>Mole fraction in copolymer^b</u>			<u>% conversion</u>
<u>$W_1(g)$</u>	<u>$W_2(g)$</u>	<u>M_1</u>	<u>M_2</u>	<u>$F=M_1/M_2$</u>		<u>m_1</u>	<u>m_2</u>	<u>$f=m_1/m_2$</u>	
3.00	0.180	0.915	0.087	10.58	10	0.720	0.235	3.060	18.86
2.00	0.814	0.609	0.391	1.56	20	0.628	0.368	1.706	7.74
1.00	1.450	0.304	0.695	0.437	35	0.244	0.724	0.337	10.61
0.50	1.766	0.152	0.847	0.179	35	0.188	0.804	0.234	6.17

^a Time in minutes; temperature, 70 °C; initiator (AIBN), 10 mg

^b Calculated from elemental analysis

Table 13: Copolymerization of 2,3-Dimethoxystyrene (M_1) with
Methyl Methacrylate (M_2)

<u>Feed</u>		<u>Mole fraction in feed</u>			<u>Time^a</u>	<u>Mole fraction in copolymer^b</u>			<u>% Conversion</u>
<u>$W_1(g)$</u>	<u>$W_2(g)$</u>	<u>M_1</u>	<u>M_2</u>	<u>$F=M_1/M_2$</u>		<u>m_1</u>	<u>m_2</u>	<u>$f=m_1/m_2$</u>	
3.00	0.178	0.914	0.087	10.54	7	0.810	0.093	8.700	3.25
2.00	0.783	0.609	0.390	1.558	4	0.659	0.321	2.037	0.34
1.00	1.400	0.304	0.699	0.453	8	0.481	0.519	0.925	5.83
0.50	1.700	0.152	0.849	0.179	10	0.297	0.719	0.413	2.70

^a
Time in minutes; temperature, 70 °C; initiator (AIBN), 10 mg

^b
From elemental analysis

Table 14: Copolymerization of 6-Vinyl-1,4-benzodioxane (M_1)
with Styrene (M_2)

<u>Feed</u>		<u>Mole fraction in feed</u>			<u>Time^a</u>	<u>Mole fraction in copolymer^b</u>			<u>% Conversion</u>
<u>$W_1(g)$</u>	<u>$W_2(g)$</u>	<u>M_1</u>	<u>M_2</u>	<u>$F=M_1/M_2$</u>		<u>m_1</u>	<u>m_2</u>	<u>$f=m_1/m_2$</u>	
1.00	0.40	0.617	0.384	1.600	10	0.66	0.35	1.89	8.57
0.75	0.56	0.463	0.538	0.860	10	0.55	0.55	1.00	6.10
0.50	0.72	0.308	0.690	0.446	10	0.25	0.76	0.33	5.73
0.25	0.88	0.154	0.350	0.181	10	0.20	0.80	0.25	4.42

^a
Time in minutes; temperature, 70 °C; initiator (AIBN), 10 mg

^b
From proton NMR

Table 15: Copolymerization of 6-Vinyl-1,4-benzodioxane (M_1)

with Methyl Methacrylate (M_2)

<u>Feed</u>		<u>Mole fraction in feed</u>			<u>Time ^a</u>	<u>Mole fraction in copolymer ^b</u>			<u>% Conversion</u>
<u>$W_1(g)$</u>	<u>$W_2(g)$</u>	<u>M_1</u>	<u>M_2</u>	<u>$F=M_1/M_2$</u>		<u>m_1</u>	<u>m_2</u>	<u>$f=m_1/m_2$</u>	
1.53	0.08	0.943	0.080	11.800	9	0.810	0.153	5.294	3.72
1.00	0.40	0.616	0.393	1.543	9	0.550	0.430	1.279	4.28
0.76	0.54	0.470	0.540	0.869	5	0.340	0.580	0.586	2.30
0.50	0.72	0.308	0.719	0.429	5	0.550	0.330	1.670	0.82

^a
Time in minutes; temperature, 70 °C; initiator (AIBN), 10 mg

^b
From elemental analysis

Table 16: Reactivity Ratios and Q-e Parameters of Copolymerization

<u>$M_1 = 2,3\text{-Dimethylstyrene}$</u>										
<u>M_2</u>	<u>Method of intersections</u>					<u>Method of Fineman-Ross</u>				
	r_1	r_2	$r_1 r_2$	Q_1	e_1	r_1	r_2	$r_1 r_2$	Q_1	e_1
Styrene	0.69	0.92	0.64	1.89	-1.48	-	-	-	-	-
MMA ^a	0.97	0.22	0.21	2.03	-0.84	0.87	0.25	0.21	1.79	-0.83
<u>$M_1 = 6\text{-Vinyl-1,4-benzodioxane}$</u>										
Styrene	1.05	0.98	1.03	1.24	-0.97	1.13	0.84	0.95	1.43	-1.03
MMA ^a	0.53	1.00	0.50	0.53	-0.44	0.40	1.10	0.44	0.47	-0.50

^a
MMA stands for methyl methacrylate

Table 20: Results of Lithiation-Silylation of Polymers

Polymer	Reagent	Substitution (%)	Elemental analysis					
			Calculated ^a			Found		
			% C	% H	% Si	% C	% H	% Si
poly 28	n-BuLi	22.84	65.41	7.32	12.74	68.66	6.13	2.91
"	sec-BuLi	45.60	"	"	"	67.15	7.36	5.81
poly 30	n-BuLi	57.49	66.05	8.53	11.88	66.20	7.81	6.83
"	sec-BuLi	15.50	"	"	"	71.99	7.64	1.84
poly 31	n-BuLi	42.23	66.63	7.74	11.98	67.81	6.09	5.06

^a
Based upon monosubstitution

Table 21: Results of Bromination of Polymers

Polymer	Yield (%)	Substitution (%)	Elemental analysis					
			Calculated ^b			Found		
			% C	% H	% Br	% C	% H	% Br
51	96.57	105	47.6	3.1	35.19	48.93	3.14	37.09
52	100	95	49.40	4.56	32.86	46.08	4.15	30.80
53	100	94	"	"	"	47.05	4.19	30.52
54	100	>100 ^a	49.82	3.76	33.14	44.80	3.14	42.87
55	>100	>100 ^a	47.6	3.10	35.19	39.33	2.25	46.59

^a
Excess of bromine was used

^b
Based upon monosubstitution

Table 22: Results of Cyanogenation of Brominated Polymers

<u>Polymer</u>	<u>Substitution (%)</u>	<u>Elemental analysis</u>						
		<u>Calculated^a</u>			<u>Found</u>			
		<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% Br</u>
56	5.48	69.36	4.07	8.08	47.35	3.14	0.30	29.56
57	33.64	69.81	5.86	7.40	46.35	4.41	2.49	28.46
58	27.00	69.81	5.86	7.40	47.81	4.52	1.93	29.78

^a
Based upon quantitative displacement of bromine atom

Table 23: Results of Phthalimidomethylation of Polymers

Polymer	Yield (%)	Substitution (%)	Elemental analysis					
			Calculated ^a			Found		
			% C	% H	% N	% C	% H	% N
59	84.30	72.43	70.6	5.3	4.33	69.12	5.41	3.81
60	86.32	79.28	"	"	"	67.23	5.23	4.17
61	100	76.56 ^b	69.48	3.94	6.57 ^b	69.42	4.49	5.03
62	70.72	72.40	70.36	4.26	4.55	63.68	4.48	4.05

^a
Based upon monosubstitution

^b
Based upon trisubstitution

Table 24: Characterization Data of Amidomethylated Polymers

Polymer	¹ H NMR (CDCl ₃)		FT-IR (KBr)	
	Chemical shift, ppm		Frequency, cm ⁻¹
	$\text{>N-CH}_2\text{-}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{-C} \end{array} \text{ - N - } \begin{array}{c} \text{O} \\ \parallel \\ \text{C-} \end{array}$	$\text{-CH}_2\text{-N<}$
59	7.53	4.52	1773, 1714	1188
60	7.52	4.53	1774, 1717	1188
61	7.65	3.2-5.45	1774, 1717	1188
62 ^a	-	-	1770, 1720	1180

^a
This polymer was insoluble

Table 25: Results of Hydrazinolysis Reactions

Polymer	Substitution (%)	Elemental analysis					
		Calculated ^a			Found		
		% C	% H	% N	% C	% H	% N
63	71.50	68.37	7.83	7.23	61.23	6.92	5.17
64	85.05	"	"	"	60.18	6.88	6.19
65	86.16	63.40	7.70	17.06 ^b	57.96	5.82	14.70
66	47.00	67.96	6.23	7.86	60.60	6.22	3.70

^a
Based upon monosubstitution

^b
Based upon trisubstitution

Table 27a: Results of Titration of Catechol at 23 °C

<u>V (mL)</u>	<u>E_h (mV)</u>	<u>V (mL)</u>	<u>E_h (mV)</u>
0.1	703	2.5	755
0.2	707	3.0	760
0.3	710	3.5	764
0.4	715	4.0	769
0.5	719	4.5	773
0.6	722	5.0	775
0.7	725	5.5	779
0.8	727	6.0	783
0.9	730	7.0	790
1.0	732	7.4	994
1.1	735	7.5	996
1.2	736	7.6	996
1.3	738	7.8	996
1.5	742	8.0	996
2.0	749	8.5	996

Table 27b: Results of Titration of Poly(3-vinyl-
catechol) at 23 °C

<u>V (mL)</u>	<u>E_h (mV)</u>	<u>V (mL)</u>	<u>E_h (mV)</u>
0.5	690	6.0	794
1.0	693	6.5	865
1.5	696	7.0	979
2.0	697	8.0	1194
2.5	699	8.5	1163
3.0	701	9.0	1154
3.5	707	9.5	1153
4.0	712	10.5	1150
4.5	719		
5.0	737		
5.5	759		

Table 28a: Results of Titration of Catechol at 35 °C

<u>V (mL)</u>	<u>E_h (mV)</u>	<u>Color</u>
0	-	clear
1.0	403	clear
1.5	420	"
2.0	432	"
2.5	464	"
3.0	479	"
3.5	496	"
4.0	859	"
4.5	865	"
5.0	869	"
5.5	871	"
6.0	1071	yellow
6.5	1071	"
7.0	1072	"
7.5	1073	"
8.0	1073	"
8.5	1073	"
9.0	1073	"
10.0	1073	"

Table 28b: Results of Titration of Poly(3-vinyl-
catechol) at 35 °C

<u>V (mL)</u>	<u>E_h (mV)</u>	<u>Color</u>	<u>V (mL)</u>	<u>E_h (mV)</u>	<u>Color</u>
0.5	289	sl.yellow	6.5	695	yellow
1.0	290	yellow	7.0	934	"
2.0	291	brown	7.5	923	"
2.5	292	"	8.0	923	"
3.0	294	"	9.0	924	"
3.5	296	"	10.0	930	"
4.0	1013	yellow	10.5	932	"
4.5	1003	"	11.0	937	"
5.0	994	"	13.0	939	"
5.5	980	"	15.0	939	"

REFERENCES

1. R.B.Merrifield, *J.Amer.Chem.Soc.*, **85**, 2149 (1963).
2. J.T.Crowley and H.Rapport, *J.Amer.Chem.Soc.*, **92**, 6363 (1970).
3. Y.Shai, K.A.Jacobson, and A.Patchornik, *J.Amer.Chem.Soc.*, **107**, 4249 (1983).
4. W.T.Ford, S.Mohanraj, and M.Periyasamy, *Brit.Polym.J.*, **16**, 179 (1984).
5. C.Yaroslavsky, A.Patchornik, and E.Katchalski, *Tetrahedron Lett.*, 3629 (1970).
6. N.M.Weinshenker, G.A.Crosby, and J.Y.Wong, *J.Org.Chem.*, **40**, 1966 (1975).
7. S.V.Mckinely and J.W.Rakskys, *J.Chem.Soc., Chem.Comm.*, 134 (1972).
8. W.Heitz and R.Michels, *Angew.Chem.Int.Ed.*, **11**, 298 (1972).
9. S.Tanimoto, J.Horikawa, and R.Uda, *Kogyo Kagaku Zasshi*, **70**, 1269 (1967).
10. N.M.Weinshenker, and C.M.Chen, *Tetrahedron Lett.*, 3281 (1972).
11. T.Tagaki, *J.Polym.Sci., B*, **5**, 1031 (1967).
12. C.R.Harrison and P.Hodge, *J.Chem.Soc., Chem.Comm.*, 1009 (1974).
13. C.R.Harrison and P.Hodge, *J.Chem.Soc., Perkin I*, 2254 (1976).
14. H.M.Relles and R.W.Schluez, *J.Amer.Chem.Soc.*, **96**, 6469 (1974).
15. W.H.Daly and D.C.Kaufman, *Polymer Preprints*, **14**, 1181 (1973).
16. E.J.Corey and K.Achiwa, *J.Amer.Chem.Soc.*, **91**, 1429 (1969).
17. W.H.Daly, S.Chotiwana, and R.Nielsen, *Polymer Preprints*, **14**, 835 (1979).

18. W.H.Daly and F.B.Kaufman, *Proc.28th IUPAC Macromol. Symp.*,
Amherst, (1982).
19. A.Warshawsky and Deshe, *J.Polym.Sci., Polym.Chem.Ed.*, **23**, 1843
(1985).
20. G.Cainelli, F.Manescalchi, and M.Panunzio, *Synthesis*, 141
(1979).
21. S.Cacchi, L.Cagliotti, and E.Cernio, *Synthesis*, 64 (1979).
22. A.Bongini, G.Cainelli, M.Contento, and F.Manescalchi, *Synthesis*,
143 (1980).
23. G.Gelbard and S.Colonna, *Synthesis*, 113 (1977).
24. F.Manescalchi, M.Orena, and D.Savoia, *Synthesis*, 445 (1979).
25. G.Cainelli and F.Manescalchi, *Synthesis*, 472 (1976).
26. G.Cainelli, G.Cardillo, and M.Orena, *J.Chem.Soc., Perkin I*, 1597
(1979).
27. G.L.Borders,Jr., D.L.Donnell, and J.L.Chambers,Jr., *J.Org.Chem.*,
37, 3549 (1972).
28. G.Cainelli and F.Manescalchi, *Synthesis*, 723 (1975).
29. G.Cainelli, F.Manescalchi, A.Umani-Ronchi, and M.P.Panunzio,
J.Org.Chem., **43**, 1598 (1978).
30. G.Cardillo, M.Orena, and S.Sandri, *Tetrahedron Lett.*, 3985
(1976).
31. G.Cainelli, G.Cardillo, M.Orena, and S.Sandri, *J.Amer.*
Chem.Soc., **98**, 6737 (1976).
32. M.Gordon, M.L.Depamphilis, and C.E.Griffin, *J.Org.Chem.*,**28**, 698
(1963).
33. R.H.Grubbs and L.C.Kroll, *J.Amer.Chem.Soc.*, **93**, 3062 (1971).
34. R.L.Lazcano and J.E.Germain, *Bull.Soc.Chim.Fr.*, 1869 (1971).

35. M.Capka, P.Svoboda, M.Cerny, and J.Hetflejs, *Tetrahedron Lett.*, 4787 (1971).
36. J.P.Collman, L.S.Hegedus, M.P.Cooke, J.R.Norton, G.Dolcetti, and D.N.Marquardt, *J.Amer.Chem.Soc.*, **94**, 1789 (1972).
37. J.I.Crowley and H.Rapoport, *Acc.Chem.Res.*, **9**, 135 (1976).
38. R.H.Grubbs, C.Gibbons, L.C.Kroll, W.D.Bonds,Jr., and C.H.Brubaker,Jr., *J.Amer.Chem.Soc.*, **95**, 2373 (1973).
39. W.D.Bonds,Jr., C.H.Brubaker,Jr., E.S.Chandrasekaran, C.Gibbons, R.H.Grubbs, and L.C.Kroll, *J.Amer.Chem.Soc.*, **97**, 2128 (1975).
40. R.F.Heck, *Organic Reactions*, **27**, 345 (1982).
41. W.H.Daly and C.H.Sun, *Polymer Preprints*, **26**, 90 (1985).
42. H.R.Allock, *Proc.28th IUPAC Macromol.Symp.*, 207 (1982).
43. L.F.Fieser and M.Fieser, "Reagents for Organic Synthesis", Vol.1, John Wiley and Sons, New York, N.Y., (1976), pp.511-519.
44. D.C.Neckers, D.A.Kooistra, and G.W.Green, *J.Amer.Chem.Soc.*, **94**, 9284 (1972).
45. E.C.Bloosey, L.M.Turner, and D.C.Neckers, *J.Org.Chem.*, **40**, 958 (1975).
46. E.Bayer and V.Schurig, *Angew.Chem.Int.Ed.*, **14**, 493 (1975).
47. E.C.Bloosey and D.C.Neckers, *J.Amer.Chem.Soc.*, **95**, 5820 (1973).
48. G.Manecke, *Chimia*, **28**, 9 (1974).
49. O.Zaborsky, "Immobilized Enzymes", CRC Press, Cleveland, Ohio, (1973).
50. G.Manecke and W.Stork, *Angew.Chem.Int.Ed.Engl.*, **17**, 657 (1978).
51. R.A.Messing and A.M.Filbert, *Agric.Food.Chem.*, **23**, 920 (1975).
52. J.Chibata, T.Tosa, T.Mori, Y.Matsuo, and G.Terui, *Proc.4th Int.Ferment.Symp.*, 383 (1972).

53. J.M.J.Frechet and C.Schuerch, *J.Amer.Chem.Soc.*, **93**, 492 (1971).
54. W.Heidmann and H.Koster, *Angew.Chem.Int.Ed.*, **88**, 577 (1976).
55. T.Kusama and Hayatsu, *Chem.Pharm.Bull.Jap.*, **18**, 319 (1970).
56. C.C.Leznoff and J.Y.Wong, *Can.J.Chem.*, **50**, 2892 (1972).
57. C.C.Leznoff and J.Y.Wong, *Can.J.Chem.*, **51**, 3756 (1973).
58. B.Sansoni, *Ger.Pat.1,005,734*, (1957).
59. H.R.Allock, K.D.Lavin, and G.H.Riding, *Macromolecules*, **18**, 1340 (1985).
60. A.Sittaturkul, PhD.Dissertation, Louisiana State University, (1985).
61. H.G.Cassidy, *J.Amer.Chem.Soc.*, **71**, 402 (1949).
62. E.L.Kopra and R.P.Welcher, *U.S.Pat.2,703,792*, (1955).
63. L.D.Taylor and H.S.Kolesinski, *J.Polym.Sci., B-1*, 117 (1955).
64. G.Wegner, N.Nakabayashi, and H.G.Cassidy, *J.Org.Chem.*, **32**, 3155 (1967).
65. G.Wegner, N.Nakabayashi, S.Duncan, and H.G.Cassidy, *J.Polym.Sci., A-1*, **6**, 3395 (1968).
66. G.Wegner, N.Nakabayashi, and H.G.Cassidy, *J.Polym.Sci., A-1*, **6**, 3151 (1968).
67. V.P.Parini, Z.S.Kasavoka, M.N.Okorakova, and A.A.Berlin, *Vysokomolekul.Soedin.*, **3**, 402 (1961).
68. Y.Suzuki and S.Tazuke, *J.Polym.Sci., Polym.Lett.Ed.*, **22**, 129 (1984).
69. Y.Iwakura, K.Kayashi, M.Shimuzu, and T.Watanabe, *Makromol.Chem.*, **95**, 228 (1966).
70. G.Manecke and G.Kossmehl, *Makromol.Chem.*, **80**, 22 (1964).

71. V.F.Dallal, M.H.Litt, and S.E.Rickert, *J.Polym.Sci.*,
Polym.Chem.Ed., **23**, 2659 (1985).
72. H.J.Harwood and H.G.Cassidy, *J.Amer.Chem.Soc.*, **79**, 22 (1964).
73. N.Nakabayashi, G.Wegner, and H.G.Cassidy, *J.Polym.Sci.*, A-1, **7**,
1269 (1969).
74. G.Izoret, *Compt.Rend.*, **253**, 274 (1961).
75. K.A.Kun, *J.Polym.Sci.*, Part A, 1833 (1965).
76. E.E.Ergozhin, B.A.Mukhitdinova, and S.R.Rafikov, *Izv.Akad.Nauk
SSR Ser.Khim*, **3**, 707 (1969).
77. K.A.Kun and R.Kunin, *J.Polym.Sci.*, A-1, **4**, 859 (1966).
78. K.A.Kun, *J.Polym.Sci.*, A-1, **4**, 847 (1966).
79. N.Kahana, A.Deshe, and A.Warshawsky, *J.Polym.Sci.*,
Polym.Chem.Ed., **23**, 231 (1985).
80. S.Iwabuchi, T.Nakahira, Y.Fakushima, O.Saito, and K.Kojima,
J.Polym.Sci., *Polym.Chem.Ed.*, **19**, 785 (1981).
81. S.Chotiwana, PhD.Dissertation, Louisiana State University, 1983.
82. G.Manecke, H.G.Vogt, and D.Polakowski, *Makromol.Chem.*, *Suppl.*,
3, 107 (1979).
83. H.Kamogawa, *J.Polym.Sci.*, B-3, 283 (1965) ; *J.Polym.Sci.*, A-1,
5, 2705 (1967).
84. G.Izoret, *Compt.Rend.*, **254**, 671 (1962).
85. I.H.Updegraff and H.G.Cassidy, *J.Amer.Chem.Soc.*, **71**, 407 (1949).
86. S.Iwabuchi, M.Ueda, M.Kobayashi, and K.K.Kojima, *Polymer J.*, **6**,
185 (1974).
87. M.Ueda, S.Iwabuchi, and K.Kojima, *J.Polym.Sci.*, B, **9**, 367
(1971).

88. S.Iwabuchi, K.Kojima, T.Nakahira, M.Ueda, K.Kobayashi, and M.Iwakura, *J.Polym.Sci., Polym.Chem.Ed.*, **12**, 280 (1974).
89. S.Iwabuchi, T.Nakahira, A.Inohana, H.Uchida, and K.Kojima, *J.Polym.Sci., Polym.Chem.Ed.*, **21**, 1877 (1983).
90. R.Stern, J.English, and H.G.Cassidy, *J.Amer.Chem.Soc.*, **79**, 5797 (1957).
91. R.E.Moser, H.Kamogawa, H.Hartmann, and H.G.Cassidy, *J.Polym.Sci., A-2*, 2401 (1964).
92. S.Iwabuchi, K.Kojima, T.Nakahira, T.Uchiyama, J.Sakata, and H.Shimuzu, *J.Polym.Sci., Polym.Chem.Ed.*, **15**, 405 (1977).
93. R.A.Barns, *J.Amer.Chem.Soc.*, **75**, 3004 (1953).
94. H.G.Cassidy and K.A.Kun, "*Oxidation-Reduction Polymers*", Interscience, New York, N.Y., (1965).
95. M.Ezrin, I.H.Updegraff, and H.G.Cassidy, *J.Amer.Chem. Soc.*, **75**, 1610 (1953).
96. K.A.Kun and H.G.Cassidy, *J.Polym.Sci.*, **56**, 83 (1962).
97. G.Manecke and G.Bourweing, *Chem.Ber.*, **95**, 1413 (1962).
98. M.Hashimoto, K.Uno, and H.G.Cassidy, *J.Polym.Sci., A-1*, **5**, 993 (1967).
99. G.Manecke, *Pure Appl.Chem.*, **38**, 181 (1974).
100. G.Manecke and W.Stork, *Chem.Ber.*, **94**, 300 (1961).
101. I.H.Spinner, J.Yannopoulous, and W.Metanonski, *Can.J.Chem.*, **39**, 2529 (1961).
102. I.H.Spinner, W.D.Raper, and W.Metanonski, *Can.J.Chem.*, **41**, 483 (1963).

103. W.H.Daly, R.L.S.Chang, and C.K.Liu, "Use of Anionic Membranes for Hemofiltration", *Proc. 12th Annual Contractors Conference, NIAMD, AKCU, NIH*, 154 (1979).
104. C.A.Mehta, *Chem.Abstr.*, **100**: 52239n (1984).
105. S.Iwabuchi, K.Kojima, and H.Hosoya, *Makromol.Chem.*, **176**, 255 (1975).
106. S.Iwabuchi, K.Kojima, T.Nakahira, and H.Hosoya, *Makromol.Chem.*, **177**, 1643 (1976).
107. S.Iwabuchi, T.Nakahira, Y.Ikebukuro, T.Tahada, and K.Kojima, *Makromol.Chem.*, **182**, 2715 (1981).
108. N.M.Kruglikova, A.B.Pashkov, and A.A.Kruglikova, *U.S.S.R.Pat.232,499*, (1968); *Chem.Abstr.*, **70**, 100043e (1969).
109. N.M.Kruglikova and A.B.Pashkov, *Zh.Prikl.Khim.*, **41**, 551 (1968); *Chem.Abstr.*, **68**, 115345n (1968).
110. I.D.Robinson, M.F.Rofojo, and H.G.Cassidy, *J.Polym.Sci.*, **29**, 47 (1959).
111. L.Luttinger and H.G.Cassidy, *J.Polym.Sci.*, **22**, 271 (1956).
112. G.Manecke and H.J.Foster, *Makromol.Chem.*, **52**, 147 (1962).
113. G.Manecke, H.J.Foster, and H.J.Panoch, *Electrochim. Acta*, **13**, 1101 (1968).
114. G.Manecke and W.Stork, *Chem.Ber.*, **104**, 1207 (1971).
115. W.Stork and G.Manecke, *Makromol.Chem.*, **176**, 97 (1975).
116. G.Manecke, G.Kossmehl, G.Hartwich, and R.Gawlik, *Angew.Makromol.Chem.*, **2**, 86 (1968).
117. G.Manecke, G.Kossmehl, R.Gawlik, and G.Hartwich, *Angew.Makromol.Chem.*, **6**, 89 (1969).
118. G.Manecke, C.Bahr, and C.Reich, *Angew.Chem.*, **71**, 646 (1959).

119. H.S.Haas and N.W.Schuler, *J.Appl.Polym.Sci.*, **5**, s-2 (1961).
120. V.Verplank and H.G.Cassidy, *J.Polym.Sci.*, **19**, 307 (1956).
121. G.Manecke, *Z.Elektrochem.*, **58**, 363 (1954).
122. G.Manecke, *Angew.Chem.*, **67**, 613 (1955).
123. H.G.Cassidy, *Proc.Natl.Acad.Sci.U.S.*, **38**, 934 (1952).
124. A.J.Parker, *Quat.Rev.(Lond.)*, **16**, 163 (1962).
125. W.E.Jones, L.R.Carey. and T.W.Swaddle, *Can.J.Chem.*, **50**, 2739 (1972).
126. L.M.Minsk and W.O.Kenyon, *U.S.Pat.2,710,801*, (1955).
127. M.S.Harding, *U.S.Pat.2,831,045*, (1958).
128. G.Manecke, *Z.Elektrochem.*, **58**, 363 (1954).
129. G.Manecke, *Z.Elektrochem.*, **58**, 369 (1954).
130. H.P.Gregor and M.Beltzer, *J.Polym.Sci.*, **53**, 125 (1961).
131. T.Winnicki, *Polimery*, **11**, 416 (1966); *Chem.Abstr.*, **66**, 66255f (1967).
132. S.V.Burinskii, L.A.Vol'F, and A.I.Meos, *Zh.Prikl.Khim.*, **38**, 2604 (1965); *Chem.Abstr.*, **64**, 6805g (1968).
133. S.V.Burinskii, L.A.Vol'F, and A.I.Meos, *Vysokomolekul. Soedin.*, **8**, 65 (1966); *Chem.Abstr.*, **64**, 14356d (1966).
134. H.Kamogawa, *J.Polym.Sci.*, **B-3**, 283 (1965).
135. S.Iwabuchi, Y.Watanabe, T.Nakahira, and K.Kojima, *J.Polym.Sci.*, *Polym.Chem.Ed.*, **17**, 172 (1979).
136. W.M.Clark, "Oxidation Reduction Potentials of Organic Systems", Williams and Wilkins, Baltimore, Maryland, 1960.
137. W.Bonthrone and J.W.Cornforth, *J.Chem.Soc.*, (C), 1202 (1969).
138. A.P.Bashall and J.F.Collins, *Tetrahedron Lett.*, **40**, 3489 (1975).

139. J.H.Clark, H.I.Holand, and J.M.Miller, *Tetrahedron Lett.*, **30**, 3361 (1976).
140. V.Grignard, *C.R.Acad.Sci.Paris*, **151**, 332 (1910).
141. G.Odian, "*Principles of Polymerization*", 2nd Ed., John Wiley and Sons, New York, (1981).
142. W.Tagaki, I.Inoue, Y.Yano, and T.Okonogi, *Tetrahedron Lett.*, **30**, 2587 (1974).
143. R.Broos and M.Anteunis, *Synth.Comm.*, **6**, 53 (1976).
144. J.Bandrup and E.H.Immergut, "*Polymer Handbook*", 2nd Ed., John Wiley and Sons, New York, (1975).
145. M.Mayen and E.Marechal, *Bull.Soc.Chim.Fr.*, **12**, 4662 (1972).
146. J.M.Rooney, *Polymer Commun.*, **26**, 164 (1985).
147. Y.Imanishi, S.Y.Matsushita, T.Higashimura, and S.Okamura, *Makromol.Chem.*, **70**, 68 (1964).
148. R.Alexander, A.Jefferson, and P.D.Lester, *J.Polym.Sci., Polym.Chem.Ed.*, **19**, 695 (1981).
149. S.Cabbidu, A.Maccioni, P.P.Piras, and M.Secci, *J.Organometal.Chem.*, **136**, 139 (1977).
150. A.Luttinghaus, G.Wegner-V-Saaf, E.Sucker, and G.Borth, *Justus Liebigs Ann.Chem.*, **557**, 46 (1945).
151. T.J.Alfrey, and C.C.Price, *J.Polym.Sci.*, **2**, 101 (1947).
152. F.R.Mayo and F.M.Lewis, *J.Amer.Chem.Soc.*, **66**, 1594 (1944).
153. T.J.Alfrey and G.Goldfinger, *J.Chem.Phys.*, **12**, 205 (1944).
154. M.Fineman and S.D.Ross, *J.Polym.Sci.*, **5**, 259 (1950).
155. H.Kamogawa and H.G.Cassidy, *J.Polym.Sci., Part A*, **2**, 2409 (1964).
156. W.Y.Lau and C.M.Burns, *Can.J.Chem.*, **47**, 2057 (1969).

157. C.G.Overberger and G.F.Endres, *J.Amer.Chem.Soc.*, **75**, 6349 (1953); *ibid.*, **77**, 2701 (1955); *J.Polym.Sci.*, **16**, 283 (1955).
158. P.M.Kamath and H.C.Haas, *J.Polym.Sci.*, **24**, 143 (1957).
159. G.A.Olah, D.A.Beal, S.H.Lu, and J.A.Olah, *Synthesis*, 560 (1974).
160. M.Kaneko, S.Nemoto, A.Yamada, and Y.Kurimura, *Inorg.Chim.Acta*, **44**, L289 (1980).
161. D.Braun, *Makromol.Chem.*, **30**, 85 (1959).
162. A.J.Chalk, *J.Polym.Sci., Part B*, **6**, 649 (1968).
163. D.C.Evans, L.Phillips, J.A.Barrie, and M.H.George, *J.Polym.Sci., Polym.Chem.Ed.*, **12**, 247 (1974).
164. D.M.White and H.J.Klopper, in *Polyethers*, Ed.E.J.Vandenberg, Washington,D.C., 169 (1975).
165. W.Heitz and R.Michels, *Makromol.Chem.*, **148**, 9 (1971).
166. F.Camps, J.Castells, M.J.Fernando, and J.Font, *Tetrahedron Lett.*, 1713 (1971).
167. J.Moreto, J.Albaiges, and F.Camps, *An.Quim.*, **70**, 636 (1974).
168. M.J.Farrall and J.M.J.Frechet, *J.Org.Chem.*, **41**, 3877 (1976).
169. L.A.Yanovskaya, A.P.Terentyev, and L.I.Belenky, *J.Gen.Chem.USSR*, 1594 (1952).
170. G.C.Levy, R.L.Lichter, and G.L.Nelson, "Carbon-13 Nuclear Magnetic Resonance", 2nd Ed., John Wiley and Sons, New York, (1980).
171. H.E.Zaugg, *Synthesis*, **2**, 49 (1970).
172. J.F.Klebe and T.J.Windish, *U.S.Pat.* 3,780,052, (1974).
173. R.T.Swiger, *J.Polym.Sci., Polym.Chem.Ed.*, **13**, 1555 (1975).
174. A.R.Mitchell, S.B.H.Kent, B.W.Erikson, and R.B.Merrifield, *Tetrahedron Lett.*, 3795 (1976).

175. A.R.Mitchell, S.B.H.Kent, M.Engelhard, and R.B.Merrifield, *J.Org.Chem.*, **43**, 2845 (1978).
176. W.H..Daly, S.Chotiwana, and Y.C.Liou, "Amination of Condensation Polymers" in *Polymeric Amines and Ammonium Salts*, Ed.E.J.Goethals, Pergamon, New York, 1980.
177. T.Ogawa and C.S.Marvell, *J.Polym.Sci., Polym.Chem.Ed.*, **23**, 1231 (1985).
178. A.Noshay and L.M.Robeson, *J.Appl.Polym.Sci.*, **20**, 1885 (1976).
179. B.C.Johnson, C.Tran, I.Ylgor, M.Iqbal, J.P.Wightman, D.R.Lloyd, and J.E.McGrath, *Polymer Preprints*, **24**, 31 (1983).
180. N.Both, F.Doscher, J.Klein, and H.Widdecher, *Polymer*, **20**, 849 (1979).
181. F.Doscher, J.Klein, F.Pohl, and H.Widdecher, *Makromol.Chem., Rapid.Comm.*, **1**, 297 (1980).
182. A.D.Patel, *P.M.C.E.Prep.*, **51**, 102 (1983).
183. R.L.Burwell,Jr., *Chem.Rev.*, **54**, 615 (1954).
184. W.Gerrard and M.F.Lapport, *Chem.Rev.*, **58**, 1081 (1958).
185. S.Teital, J.O'Brien, and A.Brossi, *J.Org.Chem.*, **37**, 3368 (1972).
186. W.A.Pryor and D.Church, Private Communication.
187. D.C.Kaufman, PhD.Dissertation, Louisiana State University, (1973).
188. P.Carre and D.Libermann, *Compt.Rend.*, **199**, 791 (1934).
189. H.S.Mason, *J.Amer.Chem.Soc.*, **67**, 1538 (1945).
190. D.D.Perrin, W.L.F.Amarego, and D.R.Perrin, "Purification of Laboratory Chemicals", Pergamon Press, New York, N.Y., 1966.
191. S.McLean and J.Mehlan, *Can.J.Chem.*, **51**, 2457 (1973).

192. I.Ikeda, K.Suzuki, T.Maekawa, and T.Higashimura, *Polymer J.*, **12**, 423 (1980).
193. G.Mahecke, *Angew.Chem.*, **68**, 582 (1956).

VITA

Saad Moulay was born in Oued Ghomara (El-Hachimia), Algeria on February 10, 1954. He entered Ain-Bessem Elementary School in 1960 and ten years later he attended El-Ghazali High School from which he graduated with a Baccalaureat degree in mathematics in 1973. In 1979, he graduated from Université des Sciences et Technologie d'Alger with a Bachelor of Science in Inorganic Chemistry (Diplome des Etudes Supérieures en Chimie Minérale). He spent the following year in intensive english program at University of Texas in Austin. In 1981, he joined the chemistry department at Louisiana State University, Baton Rouge where he is currently a candidate for the degree of Doctor of Philosophy with a major in organic polymer chemistry and a minor in inorganic chemistry. In 1979, he married his cousin Aicha and is now father of three children. Asma (girl) was born in Austin (Texas) on July 4, 1980. Zacharia (boy) was born in Baton Rouge (LA) on March 1, 1983. Selma (girl) was born in Baton Rouge (LA) on March 5, 1986.

DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Saad Moulay

Major Field: Organic Chemistry

Title of Dissertation: Synthesis of Poly(vinylcatechols)

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination: July 7, 1986