1983

Polymeric Catechols.

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POLYMERIC CATECHOLS

A Dissertation

Submitted to the Graduate Faculty of the
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Agricultural and Mechanical College
in partial fullfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by

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ABSTRACT

Polymeric catechols have been synthesized by two general procedures: (a) incorporation of catechol synthons into preformed polymers, or (b) synthesis and polymerization of a monomer containing a formal-protected catechol substituent. The utilization of condensation polymers containing oxy-phenylene repeat units as alternative supports to polystyrene has been evaluated. The techniques of functionalization of the polymers *via* chloromethylation 1,4-bis(chloromethoxy)butane were highlighted. The effects of concentration, reaction time, and types of Lewis acid catalysts on the extent of chloromethylation were studied.

Incorporation of catechol synthons such as 1,3-benzodioxole, 2,2-dimethyl-1,3-benzodioxole, or *o*-phenylene carbonate into the polymeric matrices having oxy-1,4-phenylene backbone *via* the Friedel-Crafts reactions afforded only low to moderate loadings and was often accompanied by side reactions. The halide of the chloromethyl group could be replaced quantitatively by azide, thiocyanate, xanthate, or *t*-butyl thiocarbonate nucleophiles. A polymer-bound catechol precursor with relatively high loadings has been prepared by nucleophilic addition of 3,4-methylenedioxybenzyl alkoxide.

A protected vinyl monomer, 5-vinyl-1,3-benzodioxole (**49**) was prepared from either catechol or piperonal; homopolymerizations of this monomer using radical, cationic, and anionic initiators were studied. Radical copolymerization parameters of the monomer **49** (M_1) with methyl methacrylate (M_2) and with styrene (M_2) were $r_1 = 1.1$; $r_2 = 0.45$ and $r_1 = 1.02$; $r_2 = 0.6$ respectively. Based upon these results, Q and e values for 5-vinyl-1,3-benzodioxole were calculated to be Q = 2.9 and e =

-1.11. Crosslinked beads (1:1:ca 0.02; 49 :styrene:divinylbenzyl chloride) were prepared and were used in subsequent chemical modifications. Boron trichloride or boron trichloride/n-butyl mercaptan have been found to be the most efficacious agents for effecting the deblocking. The resultant immobilized catechols could be oxidized to the corresponding o-benzoquinone with such oxidizing agents as hydrogen peroxide or potassium nitrosodisulfonate (Fremy's radical).

Treatment of the catechol resin with BH_3.THF produced immobilized catecholborane, which could effect the reduction of benzaldehyde and cyclohexanone. The catechol resin was elaborated with phosphorous oxychloride to an o-phenylene phosphorochloridate resin having a maximum loading of 1.431 meq/g.

INTRODUCTION

A. POLYMER-SUPPORTED REACTIONS

The use of polymeric materials as chemical reagents has received wide attention from chemists in a variety of fields.[1-8] Merrifield's[9,10] first successful application of synthetic polymers as a solid support for polypeptide synthesis stimulated much additional research on binding monomeric reagents onto polymer side-chains for a variety of end uses. The application of polymers in organic synthesis in general may be categorized into the two main classes to be discussed in more details later; they are:

1. Passive participants: those in which a polymer serves as a heterogeneous matrix to which a low-molecular weight substrate is covalently bound, allowed to react with various reagents and subsequently cleaved from the polymer in a modified form.

2. Active participants: those in which a polymer itself acts to transform low-molecular weight soluble substances. This can be subdivided further into: (a) polymer bound catalysts, in which the active site effects numerous transformations without loss of activity and (b) polymer bound reagents, in which the active site undergoes chemical change during the course of the reaction.

A considerable number of polymeric and inorganic materials have been investigated as support matrices. Linear and crosslinked organic macromolecular species have found wide application in more recent years, the latter in particular being experimentally very attractive because of their ease of filtration and purification. For example, the most frequently used support has been the polystyrene matrix.[11] Crosslinked

polystyrene resins are prepared by copolymerizing styrene with concentrations of divinylbenzene ranging from 0.5-20%. Resins containing 1-2% divinylbenzene are highly swollen in polystyrene solvents but higher crosslink densities produce rigid matrices which hinder diffusion of reagents through the particle. High-crosslink densities are used to produce macroporous or macroreticular resins with high surface to volume ratios and low sensitivity to solvent selection since no swelling occurs.[12] The dominance of polystyrene supports in solid phase synthesis is no accident. Polystyrene fulfills the major criteria for a support, i.e., it is chemically stable but easily functionalized, mechanically strong and compatible with most organic solvents. A hydrocarbon backbone is resistant to attack by most reagents, so various transformations can be effected without degrading the polymer chain. Although linear or soluble polymer substrates are not as widely used as crosslinked polymer substrates, they are useful both as model systems for the resin and as soluble reagents which are not subject to diffusion control. In addition, the optimum reaction conditions for attaching the reactive group to the substrate can be ascertained using soluble derivatives. Inorganic oxides and glasses have been employed more widely in large-scale applications, particularly in plants operating high-temperature catalytic processes. However, there have also been some attempts to reproduce the elegant syntheses of structurally well-defined, polymer-supported reagents employing various inorganic supports.[13-15]

As with any technique, the use of polymeric materials in organic syntheses processes both advantages and disadvantages. Some of the advantages are:

1. Reaction work-up is simplified because the supported species are easily separated from the non-supported species by filtration.

2. Multistep syntheses can be simplified by having each of the successive products remain bound to the polymer, thereby facilitating their isolation.

3. Reaction yields can be very high since large excess of reagents can be used and the loss of product during isolation can be minimized.

4. When a polymer-supported reagent is used, the spent reagent is easily recovered and can possibly be recycled.

5. If the reaction proceeds very readily, it can be carried out using a column of the supported reagent or substrate and passing the other reactants down the column in turn, much in the same way as ion-exchange resins.

6. If the reaction proceeds virtually to completion, so that filtration and washing of the polymer are all that is required to work-up the reaction, it becomes feasible to automate the process.

7. When a reaction depends on the diffusion of a substrate to a reactive site, control over the size of the molecules reaching the site can be exerted by changing the polymer pore sizes. This may offer an advantage in situations where selective transformations of various sized molecules are carried out.

8. Because crosslinked polymers are insoluble and nonvolatile, polymer-supported reagents will be nontoxic and odorless.

As with any other synthetic method, syntheses employing polymeric materials also have many limitations, some of which are:

1. The yield of the products in reaction carried out using

polymeric reagents can be lower than those in solution. The lower yields could be caused by polymer-generated steric hindrance of the reaction site, by electronic, i.e., charge, incompatiblity of the reactants and the polymer, and by absorption of the products to the resin.

2. Elaborate, lengthy, and, sometimes, costly methods of preparing the polymeric reagent or catalyst may be necessary. This effectively limits their application to very special cases or those of academic interest only.

3. When polymeric rather than low molecular weight reagents are employed, changes in the mechanism of the reaction may be encountered.

4. Characterization of chemical changes carried out on supports, particularly, with insoluble, crosslinked resins and inorganic oxide supports represents one of the big problems associated with "supported chemistry". Many techniques which are applicable to small molecule chemistry are no longer of use.

5. Although some polymeric reagents may be regenerable in principle, the degree of functionalization has been found to be reduced during the regeneration process.[16-18]

Although there are limitations to the use of polymeric reagents as outlined above, the merits frequently outweigh the limitations of the method. Often this approach offers possibilities not attainable in other ways. In other instances high yield and pure products make the method attractive for laboratory use and even on a large scale. Finally, as this is still a relatively new field, probably not all possible advantages of the use of polymeric reagents have been explored.

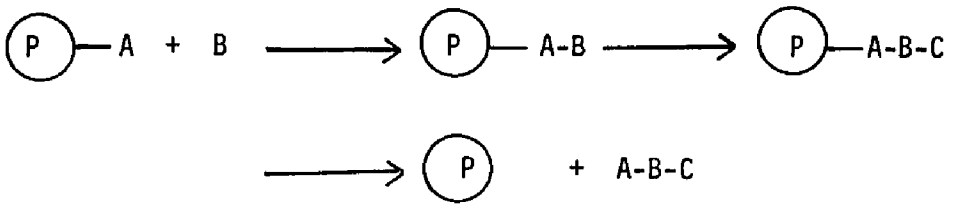
I. Passive Participants

The concept of passive participants as employed in polypeptide, polynucleotide or polysaccharide synthesis was to increase the efficiency of intermediate manipulation and product recovery by attaching soluble substrates to insoluble supports. Transformations of the substrate could be effected in a heterogeneous system and products could be isolated by filtration and washing. This reaction type can be

Scheme 1

Organic Synthesis on Polymeric Carrier

(Merrifield-type Synthesis)



P = insoluble polymer

A,B,C = soluble reactants

represented by Scheme 1. Here the polymer acts as a carrier in the stepwise construction of molecules made up of repeating similar units. Excess soluble reagent is usually employed. After completion of the synthesis the product is cleaved from the polymer. A number of other

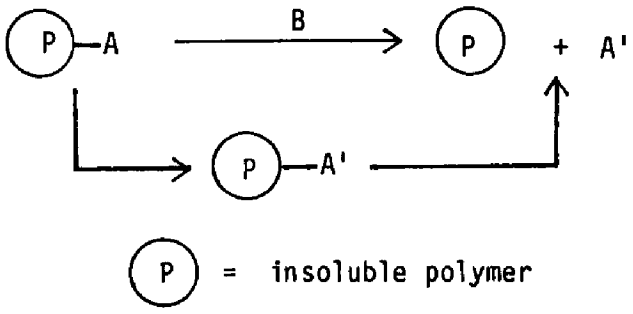
organic syntheses may be represented by a similar scheme. Criteria for selection of the support were limited to properties which maintain the pore structure and allow free diffusion of the reagents to the substrate. Thus, the primary contribution of the support was to impart the inherent advantages of macromolecules, i.e., insolubility, mechanical stability and variations in physical forms.

Intramolecular and other "matrix isolation" reactions on polymeric carriers as represented by Scheme 2 also fall into this class. In this reaction type a rigid polymer helps in directing intramolecular reactions (e.g. cyclizations) of polymer-attached molecule, A, by reducing intermolecular reactions between them. The product, A', is obtained in solution either directly or after a separate cleavage step.

Scheme 2

Intramolecular (and "Matrix-isolation")

Reactions on Polymeric Carriers



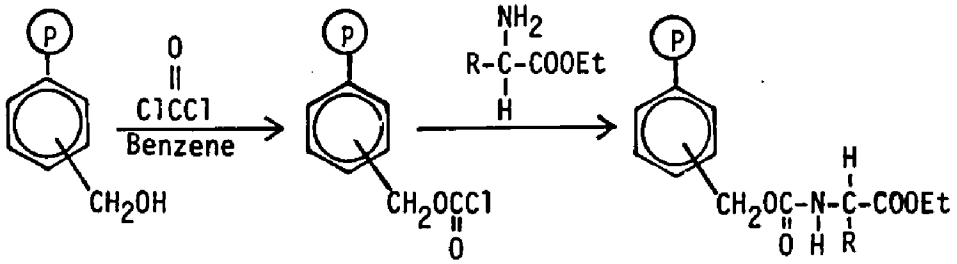
a. Polypeptide synthesis

The utilization of solid supports in polypeptide syntheis was developed nearly simltaneously by Professor Merrifield[6] and by Professor Letsinger.[19] Details regarding the syntheis of polypeptides can be

studied in the excellent review of Bodonsky and Ondetti.[17] Merrifield immobilized an amino acid to the backbone of a polystyrene derivative and carried out sequential peptide bond formation with the original amino acid serving as an anchor to the polystyrene resin. Because every amino acid has both amino residue and a carboxy residue, blocking groups must be used which will prevent the functional group which one does not wish to react, from participating in the sequence. Thus, sequential polypeptide synthesis will involve a few more steps. These are the coupling of the specific amino acid to the original amino acid previously attached to the polymer support, followed by unblocking of the blocked amino group and the next coupling step. These steps are repeated until the desired polypeptide chain length is obtained. The grown polypeptide must then be removed from the backbone of the polymer support. The synthesis of polypeptide via the Merrifield solid-state method is illustrated in Scheme 3.

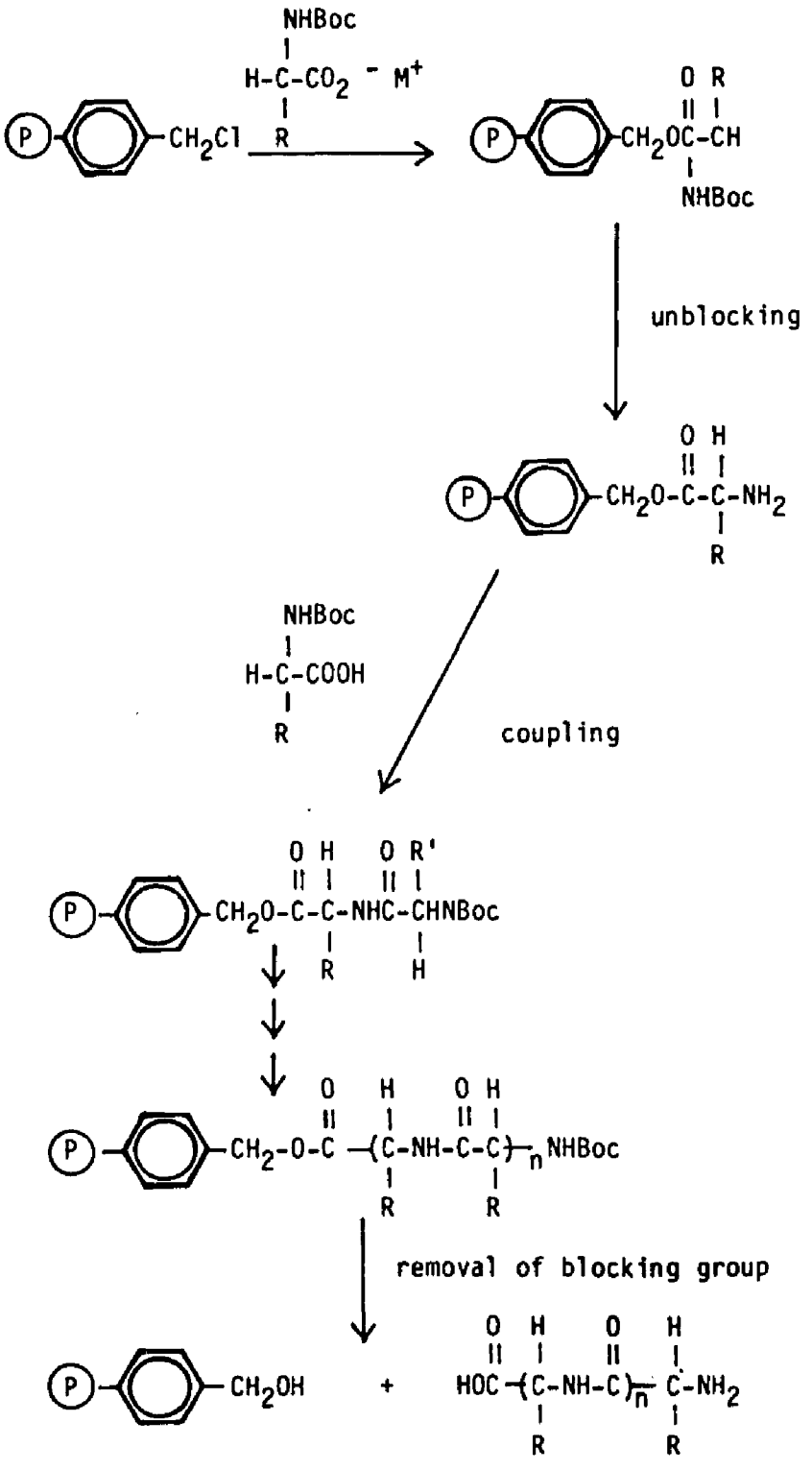
Letsinger and Kornet[19] use another approach to prepare polypeptides by converting a styrene-divinylbenzene copolymer to a hydroxymethyl derivative and then to chloroformyl derivative which was then reacted with the terminal amino group of the N-terminus amino acid (Equation 1).

(1)

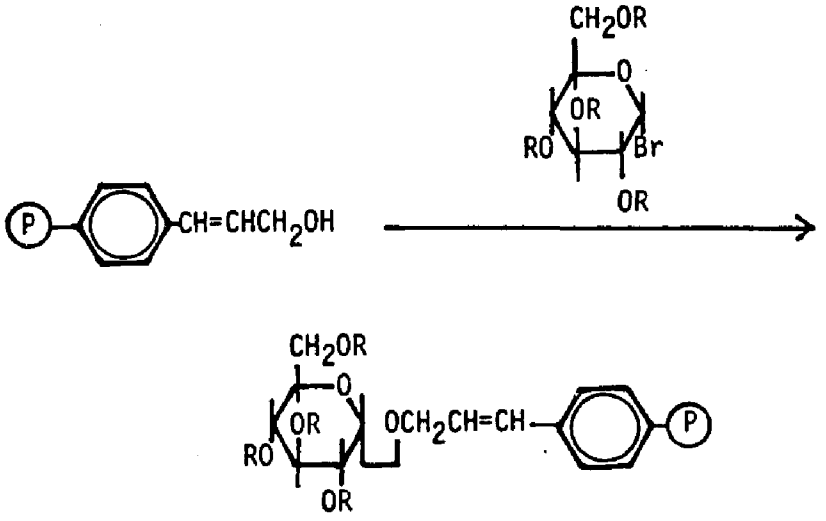


Scheme 3

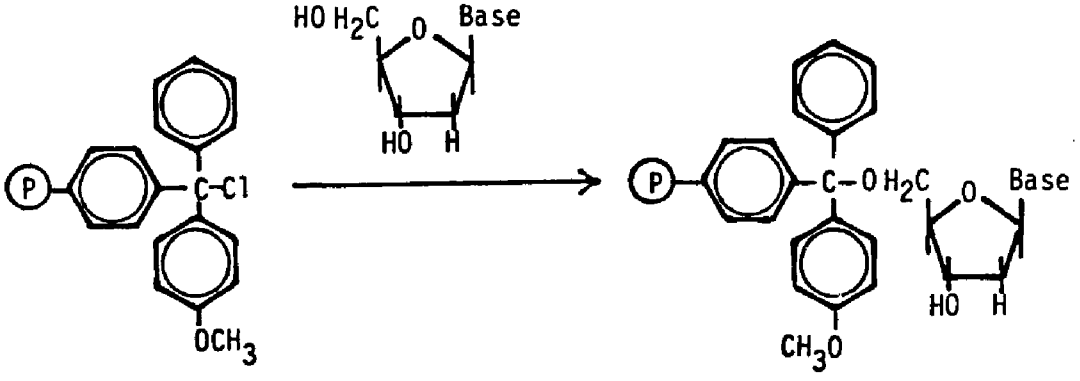
Merrifield Synthesis of Polypeptide



(2)


CH2OR
O
OR
RO
Br
OR
P
CH=CHCH2OH
CH2OR
O
OR
OCH2CH=CH
P
RO
OR

(3)


HO H2C
O
Base
HO
H
P
C-Cl
OCH3
P
C-O H2C
O
Base
HO
H
CH3O

The same principle outlined above can be applied to the synthesis of oligosaccharides and polynucleotides as well, but other polymeric derivatives and coupling procedures are required. For example, Frechet and Schuerch[20] developed an allyl alcohol functional group on a polystyrene for oligosaccharide synthesis on a polymer support (Equation 2). For the synthesis of polynucleotides on polymer supports, Khorana and coworkers[21] developed a polystyrene supported p-methoxytrityl chloride (Equation 3).

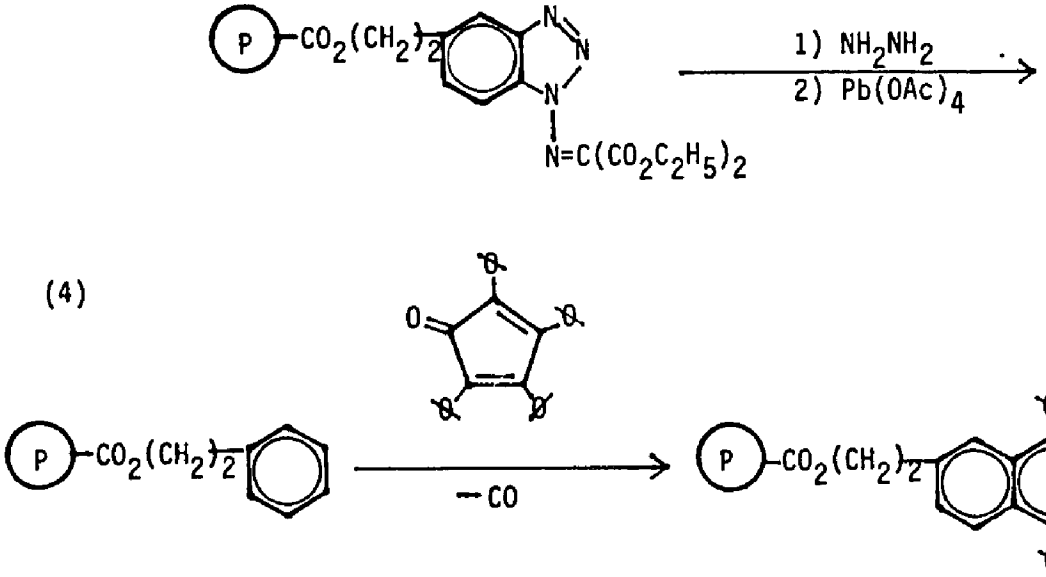
b. Polymers as immobilizing media

The use of crosslinked polymers for isolating organic reactive species from each other to minimize undesired interaction has long been known. Synthesis of a cyclic peptide on a polymeric carrier was, in fact, the first reaction in which this approach was utilized.[22] Traditionally, a high dilution technique is employed in many cyclization reactions in order to prevent intermolecular and to promote intramolecular reactions. Obviously, this method has its limitations. This technique may be replaced by using a rigid polymer as a carrier on which the molecules to be cyclized are immobilized. In principle, infinite dilution at finite concentration is created since the concentrations allowable on the polymer are expected to be considerably higher than those in solution.

Patchornik and Kraus,[23] and Crowley and Rapoport[24] have studied the Dieckmann cyclization of diester in which one of the ester alkoxy groups is attached to a crosslinked polymer. It was found that simple five- and six-membered rings could be prepared in good yields. However, in attempts to prepare larger rings, extensive intrapolymeric intermolecualar reactions occurred.[25,26] Still, an advantage of this

procedure over cyclization in solution is the easy separability of the cyclization products.

The concept of site isolation within a polymer matrix was also used successfully to prevent undesired interactions in other organic and biochemical processes. For instance, the facile dimerization of benzyne to biphenylene can be completely suppressed by generating in a polymer-attached site.[27] When a trapping agent (tetracyclone) was added to the polymeric benzyne, a considerable yield of polymeric tetraphenylnapthalene was obtained (Equation 4). The yield decreases with increasing time interval between benzyne formation and trapping. With more highly crosslinked polymer and lower functionalization, a higher yield of product was obtained.



II. Active Participants

Active supports require interaction of the reacting species with substituents attached to the polymer matrix. These immobilized reagents are similar in behavior to their low molecular weight analogs, but have the inherent advantage of insolubility. They offer the chemist ease of separation and utility similar to the well developed application of ion-exchange resin. In solvent swollen reactive polymer, the microenvironment within the vicinity of the polymer chain may appear to be the same or may differ from that of the corresponding reaction in solution. This may lead to interesting rate and specificity effects. One possibility is simply that the microenvironment of the polymer chains is a more favorable medium for the reaction. Another is that the difference in polarity between the polymer and the reaction solvent might cause the substrate to concentrate within the polymer, thereby causing an increase in reaction rate. Furthermore, the bulkiness of the insoluble phase which might impose steric constraints on the transition state may lead to regioselective and/or stereospecific reactions.

The design of a new reactive polymer must be carefully planned considering important factors such as: support stability, the types of solvents and reagents to which the polymer must be subjected during the course of its subsequent reactions, and the mechanical constraints on the system. Generally, one would like to choose the polymer support that has the following properties:

1. The support should be totally insoluble in the solvent used and either be rigid or able to swell so that the contact with solvent is maximized.

2. The support should have a reasonable high degree of

substitution of reactive sites, i.e., a high concentration of reagent per gram of polymer.

3. The reaction sites should be easily available to reagets in the solution.

4. The polymer should be easy to handle and not suffer from mechanical breakdown during handling.

Crosslinking confers insolubility, rigidity, and strength to a polymer. A low degree of crosslinking results in an easily swollen polymer matrix, but one which also fractures easily and has low mechanical strength. Thus a compromise among these properties has to be made.

Another factor that must be considered is the means of incorporating the active functionality into the polymer substrate. Three methods have been used: (1) preparation of the reactant as a vinyl monomer that can be homopolymerized or copolymerized with another appropriate vinyl monomer, then used in the reaction as is or after further modifications, (2) attachment of the active group to a preformed polymer by reaction with functional group on the polymer, and (3) entrapment of the reactive compound within the polymer by means other than covalent bonding. Although the first method does have a number of advantages such as: composition of the product is known with increased certainty, the degree of functionalization of the product is more readily controlled, and the product is readily characterized; nevertheless, the second method has been used to prepare most of the polymeric reagents cited in the literature. This may be due to the relative difficulty of monomer preparation and conversion of functionalized monomers into high molecular weight polymers.

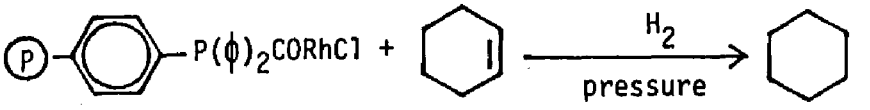
Another important factor in the design of a reactive polymer is the physical form desired. Most often, small, spherical, crosslinked beads are preferred because of the extremely convenient physical form of the bead products, which lends itself to further batchwise chemical modification. These are easily obtained by the free-radical suspension polymerization of vinyl monomer/divinyl monomer mixtures.

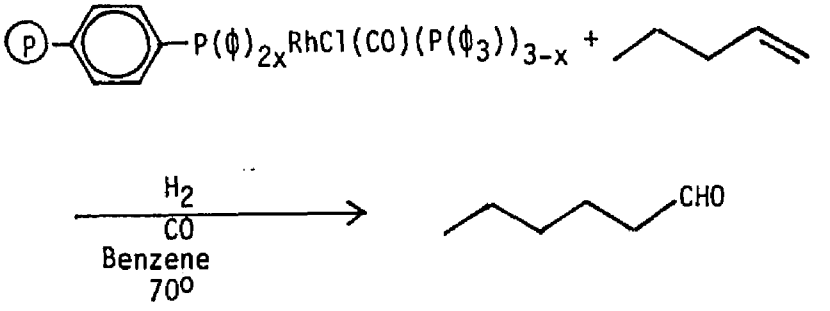
a. Polymer bound catalysts

Nonenzymic polymeric catalysts, i.e., ion-exchange resin were used in organic chemistry long before the more sophisticated polymeric reagents were prepared.[28] The ion-exchange resins in either the acid (H^+) or basic (OH^-) forms have been used for some time to catalyze general acid or general base-catalyzed reactions.[29] More recently, many known homogeneous catalysts, like some organometallic derivatives used in hydrocarbon dimerization and in hydrogenations and carbonylations, have been "heterogenized" by attaching them to polymer substrates thus producing catalysts combining the advantages of selectivity associated with homogeneous catalysis and the ease with which the catalyst is separated from the reaction products and left over reactants. Many catalysts on the insoluble matrix also show enhanced stability to hydrolysis and oxidation. In practice the use of polymeric catalysts is very similar to that of polymeric reagents. However, these "reagents" according to definition must be recovered unchanged at the end of the reaction. The preparation and properties of polymer bound catalysts have been reviewed extensively.[8,30-33]

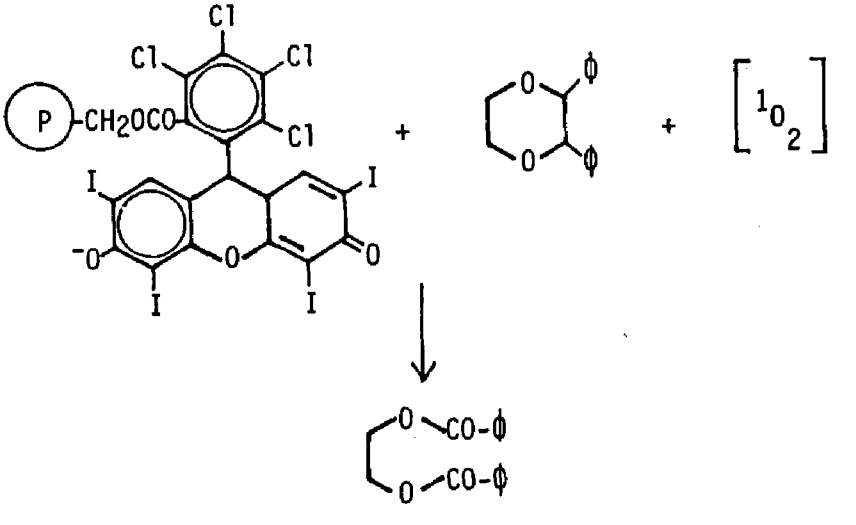
Some sample uses of the polymer bound catalysts are the reductions of hydrocarbons with polymer based rhodium catalysts (Equation 5) and

hydroformylation reactions using a similar catalyst (Equation 6) [34-37]

(5) 

(6) 

Polymer-attached Rose Bengal was also used as an insoluble photosensitizer in the generation of singlet molecular oxygen which was trapped by various acceptors (Equation 7),[38,39] the main advantage being ease of separation and reuse.

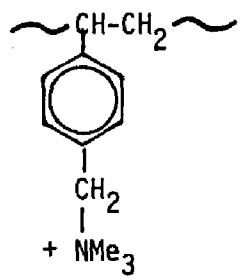
(7) 

More recently, the use of polymeric reagents as catalysts in reactions involving both an aqueous and an organic phase have been reported. These processes have been termed "triphase catalysis",[40,41] "immobilized micelles",[42] and "immobilized phase transfer catalysts",[43] but all seem to involve the same mechanism. However, many phase transfer reactions are extremely simple and relatively fast, so that polymeric phase transfer catalysts apparently offer a substantial advantage mainly in special or difficult reactions. Still, such polymeric reagents may offer microenvironmental conditions not easily attainable in reactions utilizing only soluble phase.

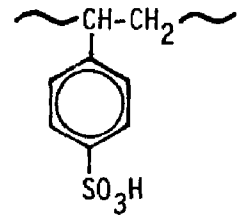
b. Polymer bound reagent

Polymer bound reagents can be divided into two main parts: (1) reactions using reagents ionically bound to polymer supports and (2) reactions using reagents covalently bound to polymer supports. Several polymer supported ionic reagents have been known for many years and are easily prepared from commercial ion-exchange resins. The most common strongly basic anion-exchange resins are crosslinked polystyrene containing quaternary ammonium groups (1) . The desired anions may be bound to these polymers either by displacing a relatively weakly bound anion, or by treating the hydroxide form of the resin with the acid corresponding to the anion. The latter is usually the method of choice when the desired anion is only weakly bound. The common cation-exchange resins contain either benzenesulfonic acid groups (2) (strongly acidic resins) or aliphatic carboxylic acid group (3) (weakly acidic resins). The desired cations may be bound to these either by treating the acid form of the resin with the appropriate metal hydroxide or by

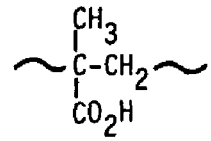
displacing a weakly bound cation. Since most commercial ion-exchange



1



2



3

resins are designed for aqueous applications, early efforts to utilize ammonium resins in organic synthesis met with limited success.[44] The development of macroreticular resins which retained a reasonable porosity in organic media enhanced substrate interaction and prompted the development of ion-exchange supported reagents. A limited selection of the reported application of ion-exchange bound reagents are tabulated in Table 1.

The preparation of polymer bound reagents by covalent bonding to lipophilic functionalized supports to increase the compatibility of the reagents with organic substrates can be achieved by using the method described earlier, either by preparation of the reactant as a vinyl monomer, or by attachment of the active group to a preformed polymer. The utilization of polymer reagents in organic synthesis has increased tremendously in recent years. Some representative reactions of polymer bound reagents (via covalent bonding) are compiled in Table 2. Polymer

Table 1

Organic Synthesis Using Ion-Exchange-Bound Reagents

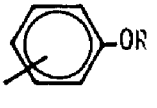
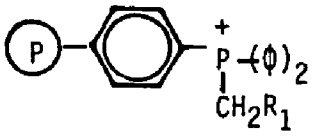
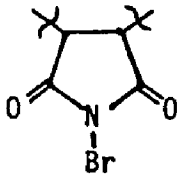
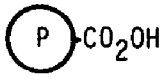
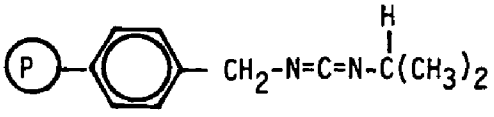
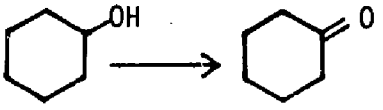
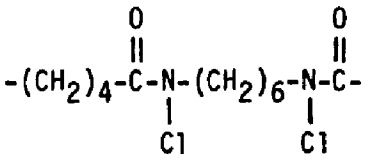
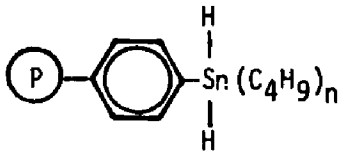
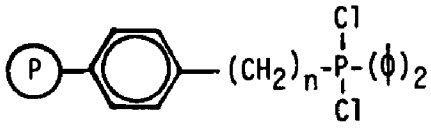
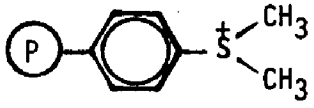
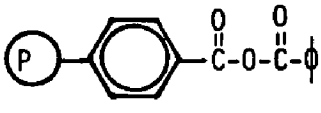
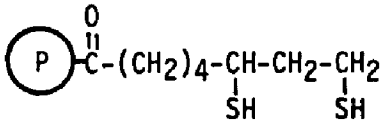
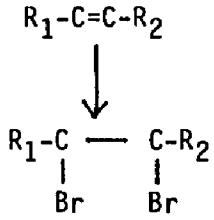
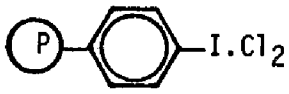
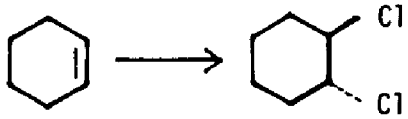
Anion	Reaction	Yield %	Reference
^-CN	RX ⟶ RCN	70	45
^-CN	Ketone to cyanohydrins	60	46
$R\text{-}CO_2^-$	R'OH ⟶ R-C(=O)-OR'	60-98	47
	RX ⟶ 	50-95	48
NO_2^-	RX ⟶ RNO_2	30-90	48
OCN^-	RX ⟶ R-NH-C(=O)-NHR	40-90	49
^-SCN	RX ⟶ R-SCN	75-90	49
Br_3^-	R'-C(H)(R")-C(H)(Br)-R"	55-75	50
$^-O\text{-}CrO_3H$	$R\text{-}CH_2Br$ ⟶ R-C(=O)-H	95-98	51
$^-BH_3CN$	Typical reduction	50-90	52
$^-BH_3$	Reduction of carbonyl Cpds.	12-74	53
F^-	$Ar\text{-}SO_2Cl$ ⟶ $ArSO_2F$	82-94	54

Table 2

Organic Synthesis using Polymer-bound Reagents

Polymer-bound Reagents	Reaction	Reference
Polystyrene-bound witting Reagents 	$R_2R_3C{=}O \longrightarrow R_2R_3C{=}CHR_1$ (olefin synthesis)	57,58
Poly N-bromosuccinimide 	benzylic bromination	59
Polymer Based Peroxidizing Agents 	$R\text{-}CH{=}CH_2 \longrightarrow R\text{-}CH\text{-}CH_2$ (epoxidation)	60
Insoluble Polymeric Carbodiimide 	 (Mofatt oxidation)	16,17
N-Chloropolyamide 	Oxidation of organic and inorganic substrate	61

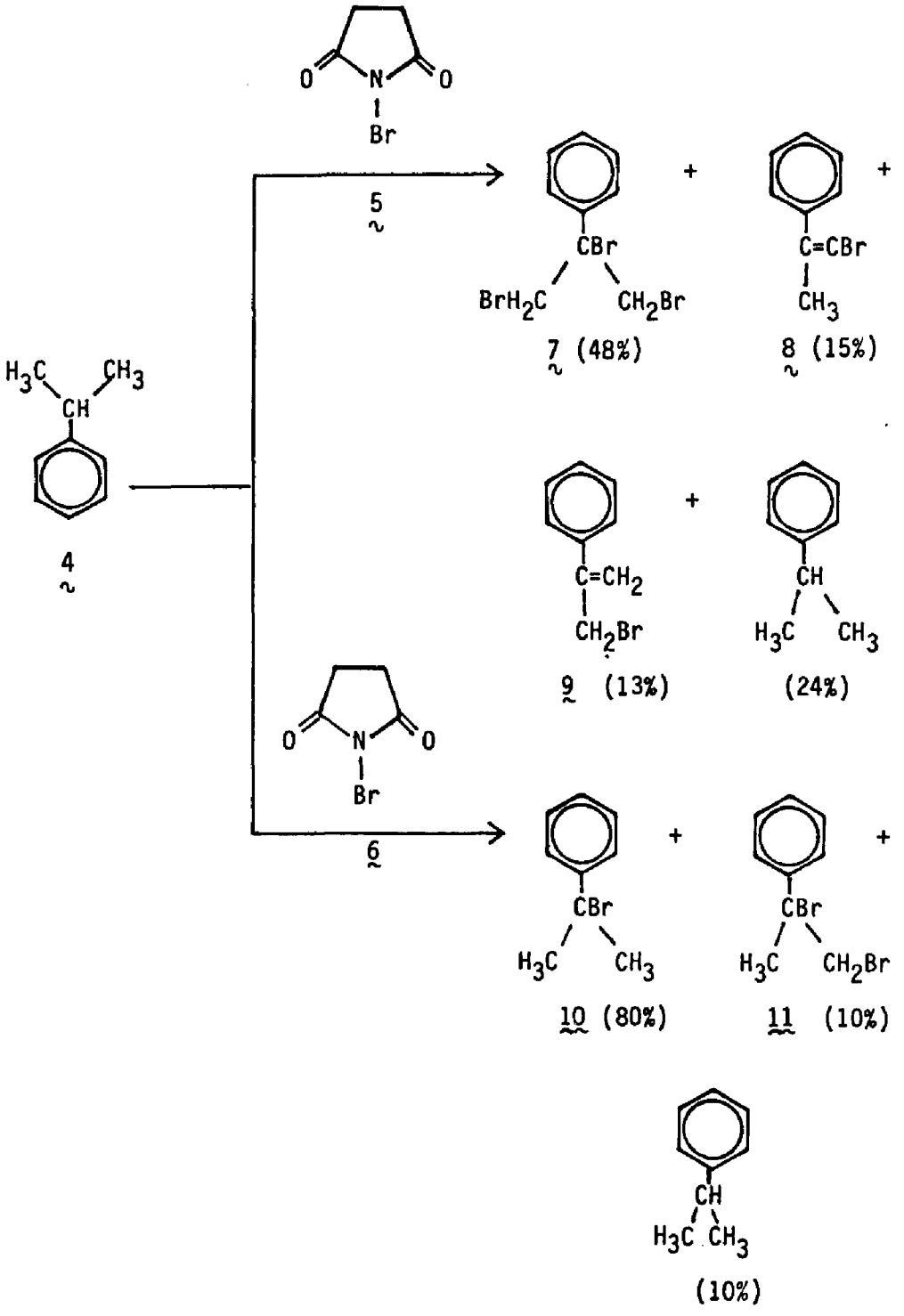
Polymer-bound Reagents	Reaction	Reference
Polymeric organotion dihydride 	Reduction of carbonyl compounds	18
Trisubstituted phosphine dichloride of copoly(styrene, divinylbenzene) 	Acid chloride, alkyl chloride, chloro olefin, nitrile synthesis	62
Polymeric sulfonium salt 	$C_6H_5CHO \longrightarrow C_6H_5CH(O)CH_2$	63
Benzoic anhydride of copoly (styrene, divinylbenzene) 	$\text{Q-NH}_2 \longrightarrow \text{Q-NH-C(=O)-Q}$; $\text{EtOH} \longrightarrow \text{EtO-C(=O)-Q}$	64
Polymeric disulfide Reducing agent 	$R_1\text{-S-S-}R_2 \rightarrow R_1(SH)\,R_2(SH)$	65

Polymer-bound Reagents	Reaction	Reference
Polymeric brominating agent 		66
Polymeric chlorinating agent 		67

reagents usually give products similar to those obtained from their monomeric analogues. However, poly-N-bromomaleimide and poly-N-chloromaleimide showed unique reaction paths, different from those obtained from the same reactions with monomeric counterpart, N-halosuccinimide.[55,56] The reaction of N-bromopolymaleimide, 5, with cumene, 4, in the presence of benzoyl peroxide in refluxing carbon tetrachloride yielded a mixture of 1,2,3-tribromo-2-phenylpropene, 9 (Scheme 4). No 2-bromo-2-phenylpropane, 10 , or 1,2-dibromo-2-phenylpropane, 11 , the only products found into the analogous reaction with N-bromosuccinimide, 6, were found (Scheme 4). The explanation of this difference lies in the polar nature of the polymeric backbone, providing a special microenvironment during halogenation, irrespective of the solvent used. This causes the dehydrobromination of the initially-formed 2-bromo-2-phenylpropane, 10, to α-methylstyrene . Then by consecutive bromination and dehydrobromination steps the formation of products 7, 8, and 9 may easily be explained. When the solvent in reactions with monomeric N-bromosuccinimide, 6, was changed from CCl_4 to CH_3CN, the product distribution was similar to that obtained with the polymer. A similar effect was observed for the chlorination of ethyl benzene, 12, with N-chloropolymaleimide, 13, in the absence of free-radical initiator: exclusively aromatic monochlorination was obtained; wheareas, with monomeric N-chlorosuccinimide, 14, a variable mixture of aromatic and aliphatic substituted products were isolated (Scheme 5). However, in the presence of added succinimide, monomeric N-chlorosuccinimide behaved similarly to the polymer reagent, yielding exclusively aromatic substitution.

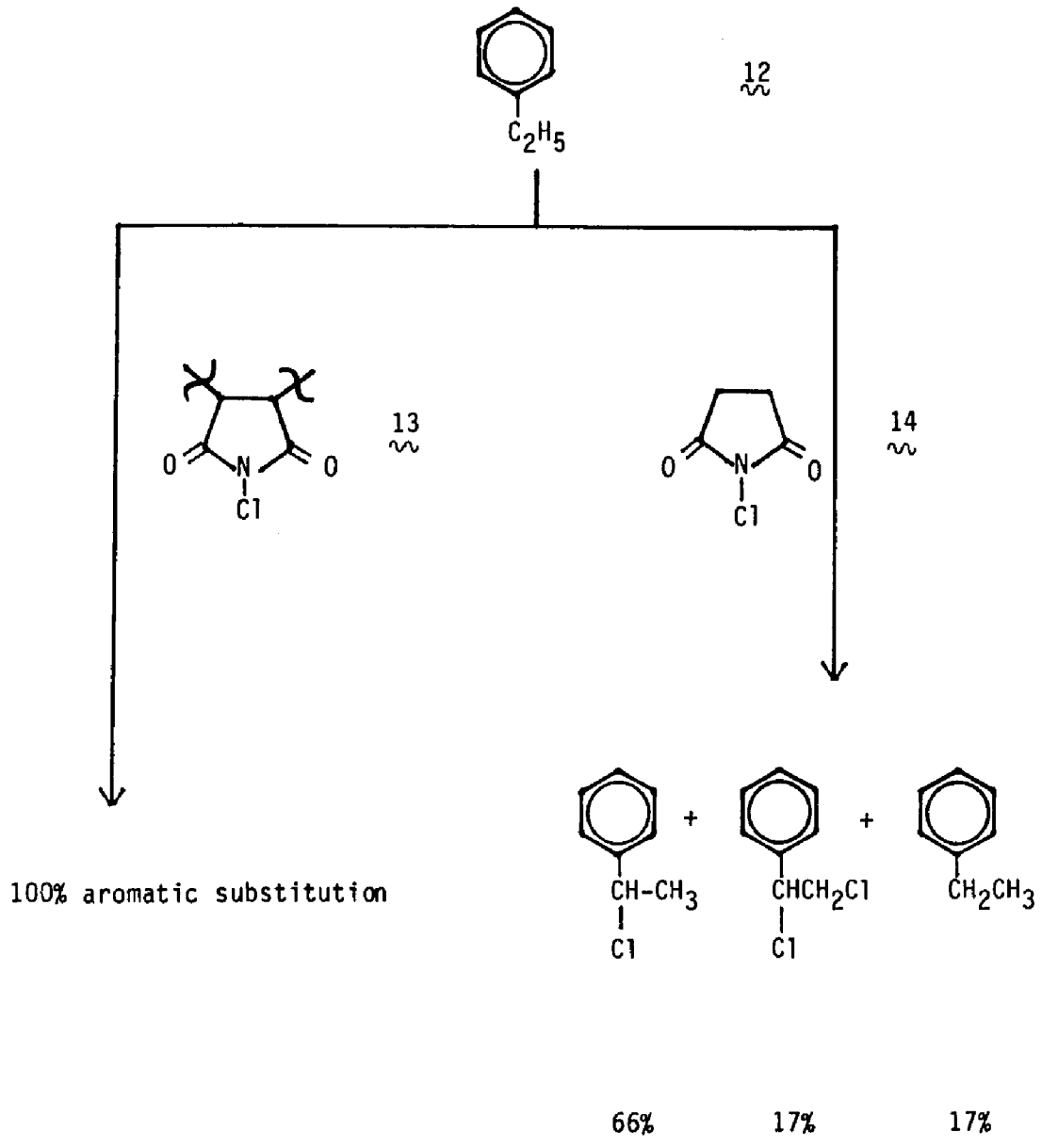
Scheme 4

The Reactions of N-Bromopolymaleimide and N-Bromosuccinimide with Cumene



Scheme 5

The Reactions of N-Chloropolymaleimide and N-Chlorosuccinimide with Ethylbenzene

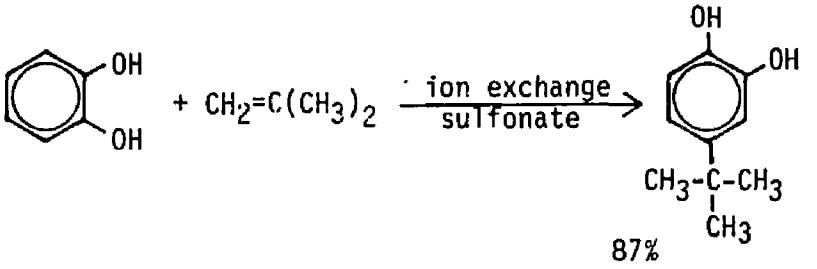


B. REACTIONS OF o-DIHYDROXYBENZENE (CATECHOL)

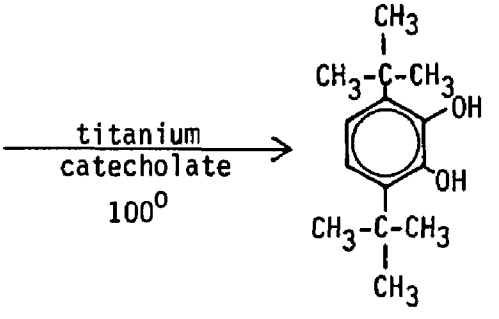
Pure ortho-dihydroxybenzene or catechol is a white crystal or flake with a low odor level and has a molecular weight of 110.11. X-ray diffraction studies of catechol show that all C-C bonds in the ring are equal and have a length of 1,385 Å while C-O bonds distance is 1.372 Å and O-H bond distance, 2,801 Å [68] Catechol can function as: (1) an active benzenoid substrate, (2) a weak acid, and (3) an orthodihydric phenol. Thus, catechol can take part in a wide variety of chemical reactions. The chemical and structural properties that characterize the reactivities of catechol and its ring substituted. derivatives are (1) high reactivity towards electrophilic aromatic substitution, (2) the relatively high stability of the catecholate anion, (3) low redox potential, and (4) the coplanar, bidentate nature of the ortho-dihydroxy groups.

1. Electrophilic aromatic substitution

The presence of the strongly electron-donating dihydroxy substituents will activate the ring of catechol and make it even more susceptible toward electrophilic attack. For example, catechol can be alkylated by all of the common agents which alkylate phenol such as olefins, alcohols, alkyl halide, etc. The usual Friedel-Crafts catalysts, like sulfuric acid, boron trifluoride or aluminum chloride, can be used in alkylation. Mono-substitution usually occurs in the para- or 4-position of catechol (Equation 8).[69] With the appropriate catalyst, it is also possible to obtain substitution in the 3- or 3,6-positions in catechol (Equation 9).[70]

(8) 

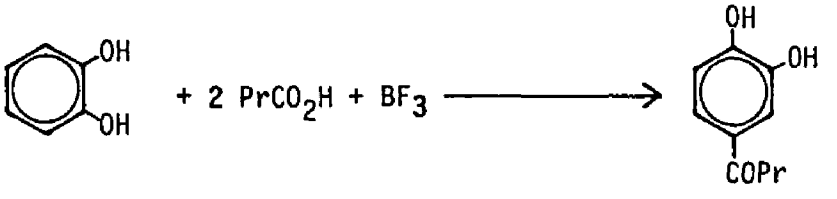
87%

(9) " " 

96%

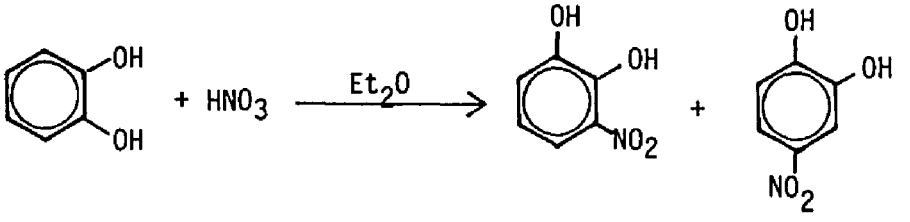
Catechol also undergoes Friedel-Crafts acylation by acid chloride, carboxylic acids, or anhydride in the presence of Lewis acid catalysts. Substitution usually occurs in the 4 position. A representative reaction is shown in Equation 10.[71]

Catechol has been nitrated under various conditions to yield the 3- and 4-nitrocatechol as well as the 3,4- and 3,5-dinitrocatechols.

(10) 

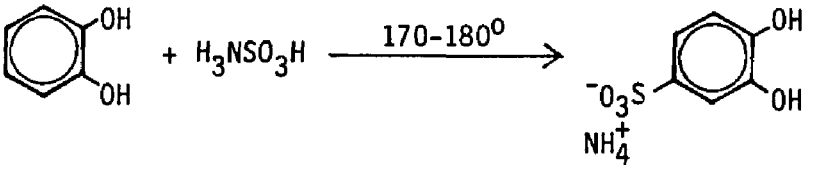
61%

Direct nitration with nitric acid gives varible yields of the products with a complex workup required (Equation 11).[72]

(11) 

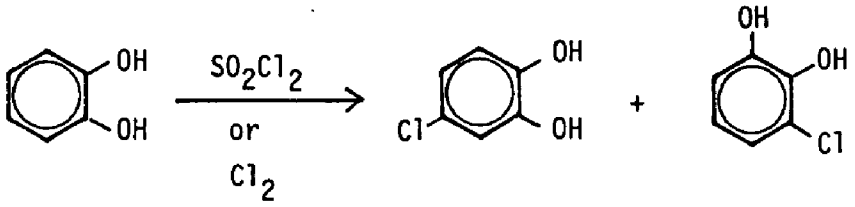
38-43% 27-31%

Sulfonation of catechol with conc. H_2SO_4 or sulfamic acid gives good yield of the 4-catechol sulfonic acid or its ammonium salt (Equation 12).[73]

(12) 

85-92%

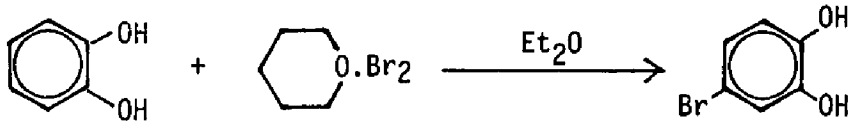
Chlorination of catechol can be effected with the action of gaseous chlorine or sulfuryl chloride yielding 4-chlorocatechol as the major isomer (Equation 13),[74] while excess halogen produces the 4,5-dichlorocatechol (Equation 14).[75] On the other hand, halogenation of

(13) 

85.5% 9.5%

(14) 

catechol with the more reactive bromine will yield polybromocatechol. However, monobromocatechol can be prepared in excellent yield if dioxane dibromide is used as brominating agent (Equation 15).[76]

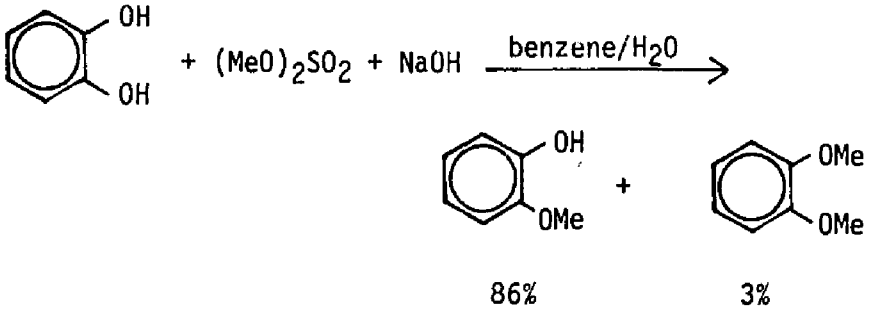
(15) 

85-92%

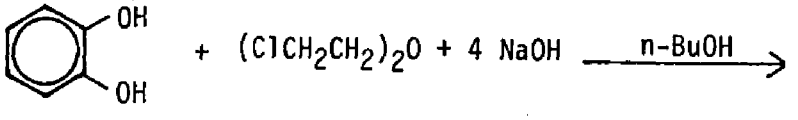
2. Catecholate anion

The catecholate anion that serves as a nucleophile can be generated

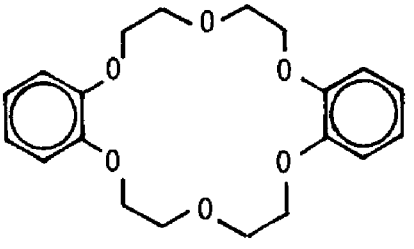
in aqueous solution in the presence of alkali. Etherification can be achieved by the usual methods to give both mono- and diethers of catechol. However, it is often difficult to confine the etherification to the monoether stage (Equation 16).[77] A crown ether such as dibenzo-18-crown-6-polyether has been successfully prepared by the action of catechol and 2-chloroethyl ether in the presence of excess sodium hydroxide but the yield is relatively low (Equation 17).[78]



(16)



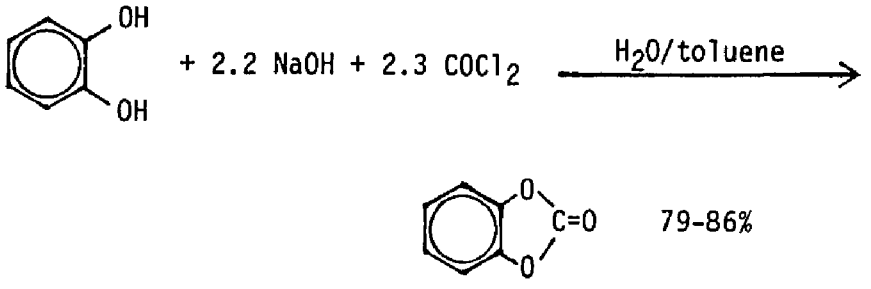
(17)

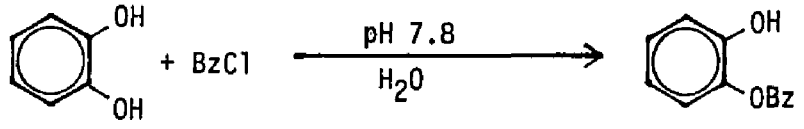


39-48%

Catechol can be esterified easily to form the corresponding diester or cyclic ester derivatives (Equation 18),[79] while the preparation of

monoester requires careful control of pH or preparation of intermediates (Equation 19).[80]

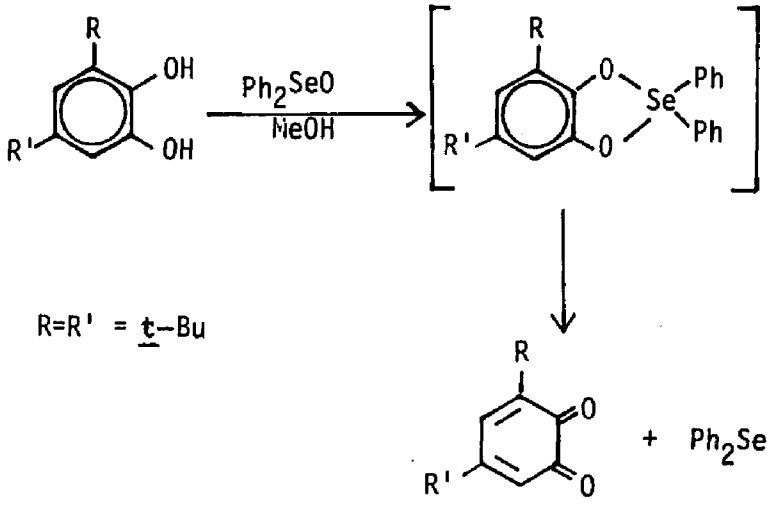
(18) 

(19) 

Bz = Benzoyl

3. Oxidation of catechol and its derivatives

Due to its relatively low redox potential, the oxidation of o-catechol to the corresponding o-benzoquinone can be effected by a number of different oxidizing agents such as ferricyanide, Fremy's salt, o-chloranil.[81] Other common oxidants include ceric ammonium nitrate,[82] silver carbonate,[83] ceric sulfate,[84] etc. Diphenyl selenoxide has also been reported to function as a mild oxidant for catechol in acetic acid, this reaget in anhydrous methanol can oxidize the 3,5-t-butyl catechol in quantitative yield in short time even at 0^{o} (Equation 20).[85]



(20)

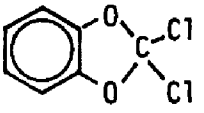
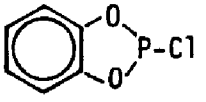
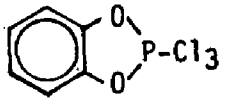
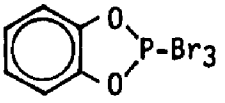
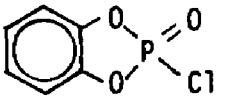
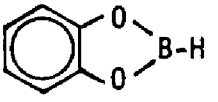
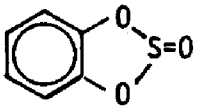
R=R' = t-Bu

4. The coplanar bidentate nature of o-dihydroxybenzene

The presence of o-dihydroxy groups on the catechol molecule will allow the formation of five-membered rings by nucleophilic attack on electron deficient atoms possessing two or more leaving groups such as those of phosphorous, boron, and sulfur (Table 3). These bicyclic derivatives, which are themselves susceptible to nucleophilic attack at the electron-deficient atom, have been found to be valuable reagents. Some of those reagets have been utilized extensively in organic synthesis in the last fifteen years. Specific applications include: (1) carboxylation of aromatic rings with catechol carbonate dichloride (2,2-dichloro-1,3-benzodioxole, 15),[86,87] (2) activation of alcohols by treating with o-phenylene phosphorochloridite (2-chloro-1,3-benzodioxaphosph(III)ole, 16) to form the phosphite intermediate for S_N2 displacement,[88] (3) halogenation and dehydration of acid derivatives with catechyl phosphorous trichloride (2,2,2-trichloro-1,3-

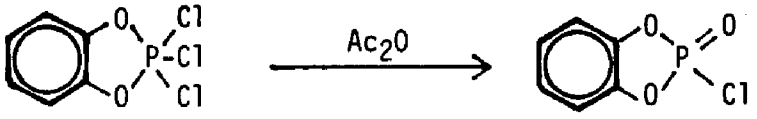
Table 3

Synthesis of Catechol's Cyclic Derivatives

Substrate	Reagents	Products		Reference
Catechol	1. $COCL_2$ 2. PCl_5		(15)	86,87
"	PCl_3		(16)	100
"	PCl_5		(17)	89
"	PBr_5		(18)	92
"	$POCl_3$		(19)	101
"	B_2H_6		(20)	102
"	$SOCl_2$, Pyridine		(21)	103

benzodioxaphosph(V)ole, 17),[89-93] e.g., the conversion of carboxylic acid and anhydride to acid halide, amide to nitriles, N-alkyl-substituted amide to nitriles and alkyl halide, and thiocarbonate to isocyantes and alkyl halide (Table 4), (4) phosphorylation of alcohol (including polysaccharide and nucleoside derivatives) with o-phenylene phosphorochloridate, 19 [94-97] (Scheme 6), and (5) selective reductions of various functional groups by catecholborane (1,3,2-benzodioxaborole, 20) [98,99] (Table 5). The latter two applications are of particular interest in this study.

Although o-phenylene phosphorochloridate, 19, can be prepared from catechol by reacting with phosphorous oxychloride as shown in Table 3; this particular reagent may also be obtained in high yield employing a superior method by heating 2,2,2-trichloro-1,3,2-benzodioxaphosph(V)ole, 17 , with slight excess of acetic anhydride (Equation 21).[96] The

(21) 

17 19

reagent, 19, has been reported to be the most generally useful reagent for the conversion of an alcohol into the corresponding monophosphate ester.[96] It reacts rapidly and quantitatively with stoichiometric amounts of alcohols in the presence of suitable base such as triethylamine or 2,6-lutidine to give virtually quantitative yields of

Table 4

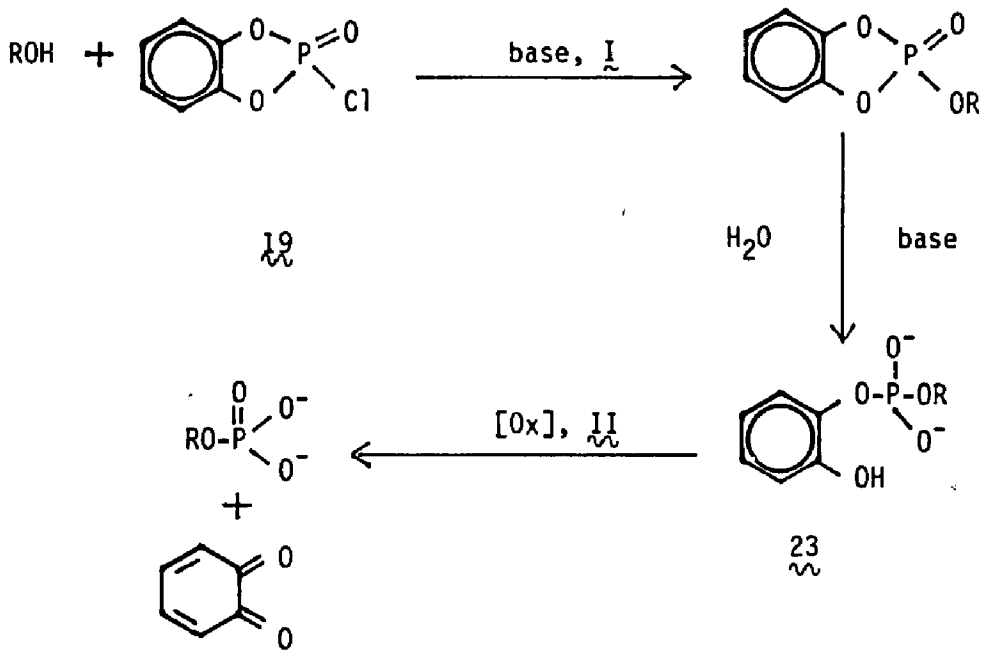
Representative Reactions of Catechyl

Phosphorous Trichloride

Substrate	Product	Condition		Yield
		Hrs.	Temp.	%
C_6H_5-CO-CH_3	C_6H_5-CCl-CH_2	0.5	100	64
$C_6H_5CO_2H$	C_6H_5COCl	1	100	81
$(CH_3CO)_2O$	CH_3COCL	0.5	100	79
$HCO_2C_4H_9$	Cl_2CH-OC_4H_9	0.5	50-60	68
$C_6H_5CH_2CONH_2$	$C_6H_5CH_2CN$	1	100	80
C_6H_5CO-N⬡	C_6H_5CN and	0.3	200	67
	Cl-$(CH_2)_5$-Cl			(55)
C_6H_5NH-CO-OC_2H_5	C_6H_5-NCO	0.5	100	80
C_6H_5-NH-CS-OC_2H_5	C_6H_5NCO	12	20	53

Scheme 6

Phosphorylation of Alcohol with o-Phenylene Phosphorochloridate



I = triethylamine or 2,6-lutidine

II = Br_2/H_2O and $Ba(OAc)_2$, periodic acid, or $Pb(OAc)_4$/dioxane

alkyl o-hydroxyphenyl phosphate salts, 22 . The intermediate phosphodiesters, 22 , can then be converted into the corresponding monoalkyl phosphates via oxidative path by treatment with either (a) bromine in neutral aqueous buffer solution, (b) periodic acid in aqueous solution, or (c) lead tetra-acetate in dioxane solution followed by alkaline hydrolysis (Scheme 6).

Catecholborane (1,3,2-benzodioxaborole, 20) , which has been recently developed by Brown and Gupta[102] by treating catechol with borane in THF (Table 3), has been shown to be an important and versatile reducing agent for many selective reductions.[98] It exhibits some reductive properties which are unique and complementary to other substituted boranes, such as thexylborane, disiamylborane, and 9-borabicyclononane. A review article on some of the chemistry of catecholborane has appeared recently.[99] Representative examples of reduction of various functional groups with catecholborane are shown in Table 5.

C. OBJECTIVES

From the literature reviewed, the catechol moiety and derivation seems to be ideal for attachment to polymeric matrices for subsequent utilization as immobolized reagents. In this study, a catechol resin was prepared and converted to a selective hydroborating reagent and phosphorylating reagent. The efficacy of these reagents in the elaboration of low molecular weight substrates was investigated. However, whether the preparations of these polymeric reagents and their applications in organic synthesis will be successful or not, the preparation of catechol resin is still desired. Although a linear

Table 5

Reduction of Various Functional Groups with Catecholborane*

Reduction	Substrate	Ratio of H/substrate	% overall redn (time, h)
Aldehyde → alcohol	C_6H_5CHO	1:1	85 (2)
	C_6H_5CHO	2:1	92 (1.5)
Ketone → alcohol	Cyclohexanone	1:1	84 (24.7)
Hydrazone → hydrazinoborane	$C_6H_{13}C(CH_3)$=NNHTs	1:1	100 (0.92)
Acid salt → alcohol	$C_{17}H_{35}CO^-{}_2Na^+$	3:1	100 (6.5)
Anhydride → alcohol	$(C_3H_7CO)_2O$	4:1	86 (24)
Epoxide → alcohol	Propylene oxide	2:1	100 (1)
RC≡CH → α-alkenyl-1,3,2-benzodioxaborale	$C_4H_9C{\equiv}CH$	1:1	79 (25.3)
Acetal → ether	$C_6H_{13}CH(OC_2H_5)_2$	1:1	20 (24)
Ketal → ether	1,1-Diethoxycyclohexane	1:1	100 (1)
RCOCL → alcohol	CH_3COCL	2:1	20 (72)
RC≡N → amine	$C_2H_5C{\equiv}N$	2:1	54 (63)
RCO_2H → alcohol	$C_6H_5CO_2H$	3:1	28 (20)
	p-$NO_2C_6H_4CO_2H$	3:1	87 (97)
$RCONR_2$ → amine	$CH_3CON(CH_3)_2$	2:1	40 (96)
RCO_2R	$C_3H_7CO_2C_2H_5$	1:1	0
RSSR	$(CH_3S)_2$	1:1	0
RSO_2R	Tetramethylenesulfone	1:1	0

Reduction	Substrate	Ratio of H/substrate	% overall redn (time, h)
RCH=CHR	Cyclohexene	1:1	0
RBr	n-$C_8H_{17}Br$	1:1	0
RI	n-$C_5H_{11}I$	1:1	0

*Reactions were carried out in $CHCL_3$ at room temperature except that of sodium stearate which was reduced in THF.

poly(3-vinylcatechol) was first successfully prepared on a micro scale and was reported in the literature in 1957 by Cassidy, et al.,[104] the structure of the poly(vinylcatechol) has not been proved spectroscopically. In addition, the potential applications of catechol resin itself are expected to be superior to those of the well-established hydroquinone resin in terms of redox properties (i.e., as antioxidizing agent), absorption of metallic ions, and other industrial applications.

RESULTS AND DISCUSSION

A. SYNTHESIS OF POLYMERIC CATECHOLS

Two primary methods have been investigated for immobilization of functionalized catechol derivatives. The first entails incorporation of a catechol synthon into preformed polymers by either nucleophilic or electrophilic substitution. The second approach is the synthesis of an easily polymerized monomeric precursor, suitably blocked to assure the formation of high molecular weight polymer. Some of the blocked catechols that were considered as possible precursors were: 1) 1,3-benzodioxole; 2) 2,2-dimethyl-1,3-benzodioxole; 3) and o-phenylene carbonate. Since a number of natural products containing the 1,3-benzodioxole nucleus are available, 1,3-benzodioxole was given the most attention. Benzodioxole is functionalized readily and should be hydrolysed easily to free catechols.

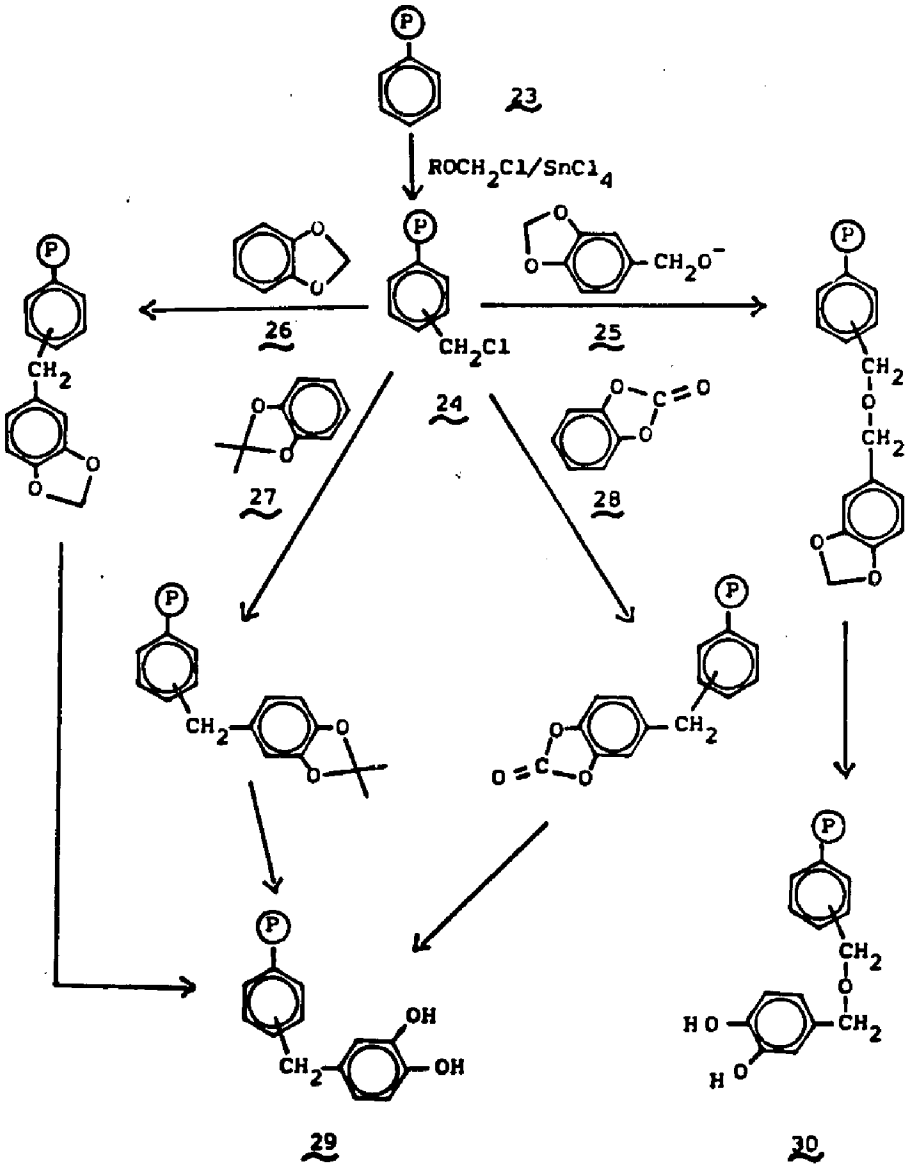
I. Chemical Modification of Polymeric Matrices

Lithiation was considered as an alternative route to functionalized polymer at the very beginning of this work; however, this approach was abandoned due to the fact that only a limited amount of polymer matrices could be utilized as supports. For example, polymers containing C-O bonds in the backbone have a tendency to degrade; extremely dry conditions had to be maintained throughout the reaction sequence and the selection of catechol precursors suitable for coupling reactions was limited.

Our approach to prepare resins with catechol units as pendent groups involved the following steps; (a) chloromethylation of the

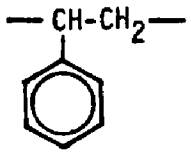
Scheme 7

Preparation of Catechol Resin: Chemical Modification Approach



preformed polymer, 23, (b) nucleophilic substitution (S_N2) of a chloromethylated polymer, 24, by alkoxide of piperonyl alcohol (3,4-methylenedioxybenzyl alcohol), 25, with 1,3-benzodioxole, 26, 2,2-dimethyl-1,3-benzodioxole, 27, and o-phenylene carbonate, 28, (c) removal of the protected groups to yield free catechol resins 29, and 30. The synthetic sequence directed ultimately towards the preparation of catechol resin is outline in Scheme 7.

Chloromethylation has been proved in this study to be the most versatile and reliable route to functionalized polymers. A wide range of loadings can be achieved with reasonable reproducibility. The only problems encountered in chloromethylation are intra- and/or intermolecular side reactions producing additional crosslinking and a reduction in the accessibility of sites. However, we were able to keep this side reaction to a minimum by choosing proper conditions. Chloromethylation of polystyrene, 31, and several commercially available condensation polymers such as poly(2,6-dimethyl-1,4-phenylene oxide), PPO, 32; poly(phenylene ether sulfone), 33; polycarbonate, 34; and phenoxy resin, 35, were studied.



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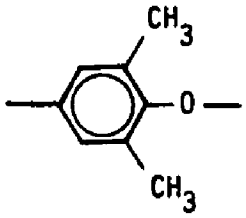

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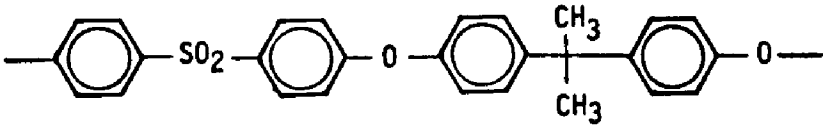

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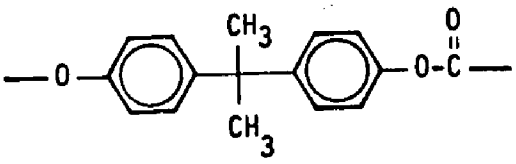

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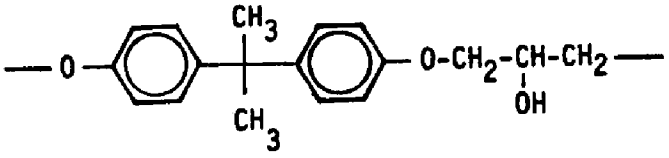

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1. Preparation of chloromethylating agents

The potent carcinogenic properties of chloromethyl alkyl ethers such as chloromethyl methyl ether or chloromethyl ethyl ether prompted us to focus our attention on the less volatile 1,4-bis(chloromethoxy)butane, 36, and 1-chloromethoxy-4-chlorobutane, 37, as chloromethylating agents. Olah, et al.,[105] had applied these reagents successfully to chloromethylation of activated low molecular weight aromatic compounds. The preparation of 1,4-bis(chloromethoxy)butane, 36, was conducted by contacting 1,4-butanediol with parafomaldehyde in

$$ClCH_2\text{-}O\text{-}(CH_2\text{-}CH_2)_2\text{-}O\text{-}CH_2Cl \ , \ 36$$

$$Cl\text{-}(CH_2\text{-}CH_2)_2\text{-}O\text{-}CH_2Cl \ , \ 37$$

the presence of hydrogen chloride. The reaction was carried out at around 20°C. An excess of hydrogen chloride over the stoichiometric requirements was employed and the reaction time ranged from 2-3 hours after the solid residue in the reaction mixture had been completely dissolved. Since the rate of reaction was found to depend on rate of stirring and rate of passage of hydrogen chloride, it was somewhat difficult to obtain a reproducible result. Nevertheless, the yield was no lower than 60% and could reach a maximum of 70% depending on the factors mentioned above.

1-Chloromethoxy-4-chlorobutane, 37, could be prepared in a similar fashion using tetrahydrofuran instead of 1,4-butanediol and a reaction temperature of 60°. An unsuccessful attempt to prepare 1,2-bis(chloromethoxy)ethane, 38, from 1,3-dioxolane under the same

$$ClCH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2Cl \ , \ 38$$

conditions or even in the presence of a Lewis acid catalyst such as zinc chloride indicates that the formal linkage is unexpectedly strong.

2. Chloromethylation of the preformed polymers

Chloromethylation of polystyrene, 31, with a 1:1 molar equivalent or 2:1 molar excess of 36 proceeded at room temperature in chlorinated hydrocarbons (i.e., chloroform, dichloromethane, tetrachloroethane, etc.) in the presence of stannic chloride or anhydrous zinc chloride. With stannic chloride as a catalyst, a high degree of substitution (70-80%) was achieved with extended reaction times (17-20 hr. at 25°). However, when the reaction was run at a higher temperature or when higher concentrations of stannic chloride were used, crosslinking associated with gelation phenomena was often unavoidable. On the other hand, when anhydrous zinc chloride, a weaker Lewis acid catalyst, which is less soluble in chlorinated hydrocarbons, was employed, the reaction was found to be more easily controlled. Although only low degrees of substitution were obtained at ambient temperature, a high degree of substitution could be achieved at elevated temperatures with no major complication of crosslinking.

Under more extreme conditions, the chloromethylation of polysulfone, 33, could be catalysed by a number of Lewis acids (Table 6). Low catalyst to polymer ratios were employed to achieve a maximum of two chloromethyl substituents per repeat unit; no substitution was detected on the aryl sulfone rings. The failure of poly(phenylene ether sulfone), a polymer with a sulfone substituent attached to every ring, to undergo chloromethylation confirms the powerful deactivating influence of the sulfone group. Facile crosslinking of polysulfone was

not observed but an increase in $\overline{M}_w$ was apparent. Since no crosslinking occurred in the absence of chloromethylating agent, the increase in molecualr weight was believed to be attributed to intermolecular alkylation. The maximum $\overline{M}_w$ increase was obtained using the most reactive alkylation catalyst, $SbCl_5$; minimal changes in $\overline{M}_w$ were observed with harder Lewis acids such as titanium tetrachloride (Table 6).

Reaction of phenoxy resin, 35, with 36 was accompanied by crosslinking but 4.67 meq of Cl/g resin was introduced (Table 6). This may be due to the fact that the unprotected hydroxy group has a tendency to complex with Lewis acids. Polycarbonate, 34 , failed to react with 36 under normal condition but was found to undergo substitution reactions if more than a stoichiometric amount of the catalyst (preferably, a softer acid) was used and the temperature was raised to 110-115° (Table 6). It was assumed that complexation of the catalyst to the carbonyl oxygen prevented chloromethylation unless the amount of the catalyst was more than molar equivalent.

The chloromethylation of poly(oxy-2,6-dimethyl-1,4-phenylene), PPO, 32, with 36 proceeded at room temperature in chlorinated hydrocarbons in the presence of stannic chloride (Table 6). The degree of substitution was limited to one chloromethyl substituent per aromatic ring but active chloride concentrations comparable to those found in chloromethylated polystyrene were achieved. Nevertheless, the rate of chloromethylation of PPO was found to be extremely fast compared to a similar reaction with polystyrene (i.e., the extent of substitution approached 100% within 1 hour of reaction). Introduction of 5.5 meq/g active chloride was accompanied by broadening of molecualr weight distribution. The weight average molecular weight ($\overline{M}_w$) of

Table 6

Chloromethylation of Oxy-1,4-Phenylene Polymers[a]

Reactions			Conditions		Products		
Polymer	1,4-bis(chloro-methoxy)butane, mmol	Catalyst, mmol	Temp., °C	Time, hr.	Chlorine[b] Content, meq/g	$\bar{M}w \times 10^{-3}$[c]	$\bar{M}n \times 10^{-3}$
Poly[oxy-2,6-dimethyl-1,4-phenylene]	2.14	$SnCl_4$, 0.85	25	1	1.36	47.5	17.5
"	8.56	" , "	"	"	3.01	56.4	16.4
"	"	" , 4.3	"	"	5.49	85.6	17.7
"	17.12	" , 2.13	"	"	4.91	54.5	16.9
"	"	" , 4.25	"	"	5.72	63.2	17.1
Polysulfone	18.7	" , 2.3	110	"	3.56	108.5	19.4
"	16.6	$SbCl_5$, 0.33	"	"	3.23	99.6	21.1
"	10.7	$AsCl_3$, 0.55	"	"	2.48	88.4	18.4
"	"	$TiCl_4$, 0.53	"	"	2.30	78.8	20.6
"	16.6	$SbCl_5$, 0.33	25	"	0.6	70.4	21.0
Phenoxy Resin	23.0	$SnCl_4$, 4.6	50	3	4.67	crosslinked	-
Polycarbonate	20.0	$SbCl_5$, 12	110	7	0.68	-	-

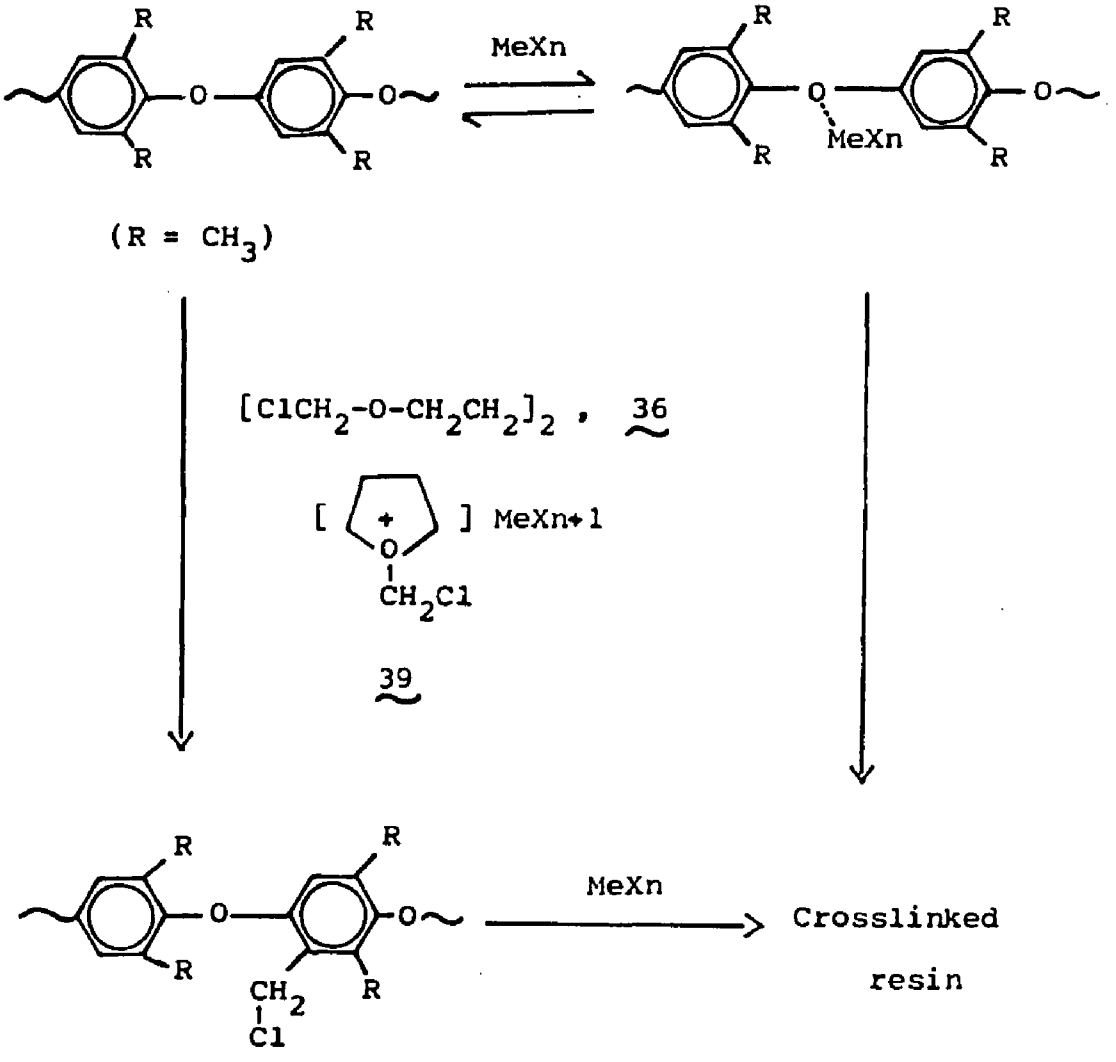
[a]Reactions were conducted on 8.3 meq PPO, 4.5 meq polysulfone, 7.0 meq phenoxy resin and 10 meq polycarbonate as described in the experiment methods.

[b]Determined by nmr and confirmed by elemental analysis, maximum theoretical content: PPO, 5.9; polysulfone, 3.71; phenoxy resin, 5.26; polycarbonate, 5.54 meq/g.

[c]Calculated from GPC data; values observed for starting materials: PPO, $\bar{M}w$, 46.0; $\bar{M}n$, 15.9; polysulfone, $\bar{M}w$, 65.05; $\bar{M}n$, 25.5.

Scheme 8

Lewis acid-base Complex Formation between Poly(oxy-2,6-dimethyl-1,4-phenylene) and the Catalyst



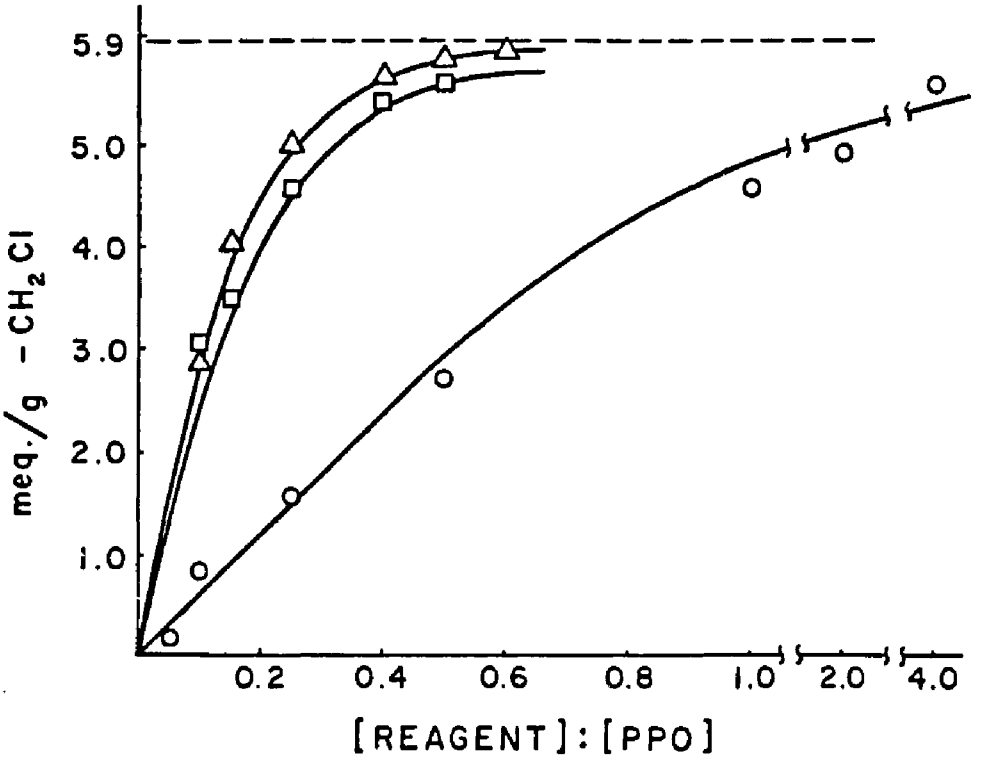


Figure 1: Extent of substitution achieved at varying molar ratios of $SnCl_4$ or 36 to PPO; □, 1:1 PPO to 36, reagent $SnCl_4$; △, 1:2 PPO to 36 reagent $SnCl_4$; ○, 1:0.25 PPO to $SnCl_4$, reagent 36; _ _ _ maximum substitution.

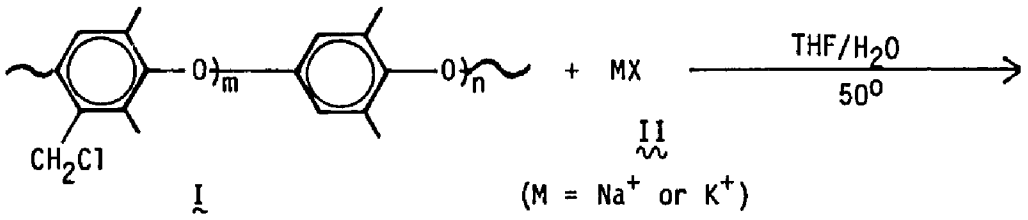
chloromethylated polymers prepared with high catalyst ratios increased significantly indicating that chain coupling was occurring. A crosslinked insoluble derivative was obtained when a Lewis acid was added to a solution of PPO and 36 at higher reaction temperatures (i.e.,>30°).

The unique reactivity of PPO stems from the facile Lewis-acid-base complex formation with the catalyst (Scheme 8). Complexed polymer crosslinked if no chloromethylating agent was present. The catalyst selection was dictated by the rate of complex dissociation to produce the active chloromethylating species, 39; stable complexes were formed with aluminum chloride, boron trichloride, titanium tetrachloride, zinc chloride, and arsenic trichloride and no substitution was observed but crosslinking occurred if higher concentration of the catalyst was used or/and the reaction time was extended. The complex derived from antimony pentachloride tended to crosslink rapidly but a low degree ~ 10%) of substitution was observed. A more acceptable balance between the rate of crosslinking and substitution was achieved with stannic chloride, where catalyst to polymer molar ratios as high as 0.6 could be used without producing an insoluble derivative (Figure 1). Corresponding lower catalyst concentrations were used to minimize concommitant crosslinking reactions. In addition, intermolecuar alkylation was initiated by catalyst residues in the chloromethylated polymers, so rigorous purification of samples with low substituent contents was required to prevent crosslinking during the drying stage or on storage.

3. Chemical modifications of chloromethylated polyphenylene oxide

Chemical modification of chloromethylated PPO is of particular

interest in this study because the polymer backbone of PPO exhibited relatively high reactivity toward chemical reactions (e.g., chloromethylation) due to semiorthogonal conformation of phenylene groups. In our experiment, the modified PPO (III) was prepared by nucleophilic displacement of the chlorine atom on the chloromethyl group of the polymeric substrate (I) with the appropriate nucleophile (II) according to the following scheme (Equation 22):



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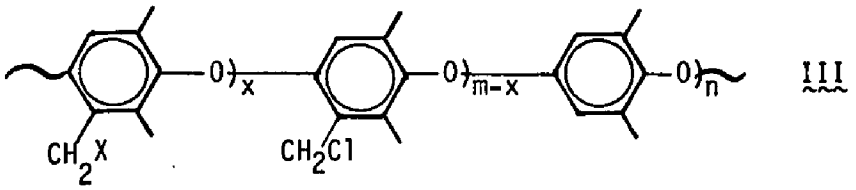

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Either THF or dioxolane containing small amounts of water was used as a reaction medium. Although both THF and dioxolane are good solvents for the polymer, I; without trace amount of water, the reaction proceeded poorly due to low solubility of the salts (nucleophiles) in the media. However, phase separation occurred if too much water was used.

Examination of the results of chemical modification of chloromethylated PPO's (Table 7) reveals that essentially quantitative replacement of the halide by azide, thiocyanate, xanthate, t-butyl

Table 7

Chemical Modification of Chloromethylated PPO (I)
via Nucleophilic Substitution with Appropriate
Nucleophile (II)

Nucleophile (II) (MX)	Solvent	Temp (°c)	Time (hr.)	Conversion (%)	IR* (cm^{-1})
$M = K^+$, $X = N_3^-$	THF	50	4	96.9	2100 ($-N_3$)
$M = Na^+$, $X = N_3^-$	"	55	6	96.6	"
$M = K^+$, $X =$ $^-S-\overset{\overset{O}{\|}}{C}-C(CH_3)_3$	"	50	4	99.2	1730 (-C=O)
$M = K^+$, $X =$ ^-SCN	"	55	6	96.6	2130 (-SCN)
$M = K^+$, $X =$ $^-S-\overset{\overset{S}{\|}}{C}-OC_2H_5$	"	55	6	97.4	1600 (-C=S)

*Representative IR bands

thiocarbonate nucleophiles has been achieved. It was concluded that chemical modification of the chloromethylated PPO using the method *via* nucleophilic approach described above would not only give us a method of introducing various functional groups which would affect the physical properties of the PPO's backbone but also an alternative means to remove the reactive chlormethyl groups when they are not needed.

4. *Preparation of "blocked" catechols*

1,3-Benzodioxole, **26**, used in this study was either obtained commercially or synthesized by the reaction of biscatecholate anion and dibromomethane in the presence of tricaprylylmethylammonium chloride (Aliquat 336), a phase transfer catalyst. The reaction was carried out in two phases under a nitrogen atmosphere in order to prevent oxidation of the anion. The yield obtained in this work was somewhat lower than the similar method reported by J.F. Collin, *et al.*,[106] with methyltrialkyl (C_8-C_{10}) ammonium chloride (Adogen 464) being used as a catalyst.

The preparation of 2,2-dimethyl-1,3-benzodioxole, **27**, was a straight-forward application of the method of condensation of catechol with absolute acetone.[107] The rate of reaction was found to be increased by removal of water during condensation with phosphorous pentoxide. Reasonable yields of **27** were obtained in spite of the heterogeneous nature of the reaction mixture.

Crystalline *o*-phenylene carbonate, **28**, was prepared by treating catecholate anion with phosgene solution at below ambient temperature. The reaction was carried out under an inert atmosphere due to the fact that the catecholate anion is susceptible to oxidation.

5. Friedel-Crafts reactions of the chloromethylated polymer and catechol precursors

A catechol synthon, i.e., 1,3-benzodioxole, 26, was introduced into polymeric matrices by reacting with chloromethylated polymer under the standard Friedel-Crafts alkylation conditions. The attachment of 26 to poly(phenylene oxide) backbone was achieved using either zinc chloride or stannic chloride as a catalyst and a high degree of substitution was obtained. In contrast, the reaction of poly(vinylbenzyl chloride) with 26 in dioxane failed under the normal conditions of this study. Due to the high reactivity of chloromethylated PPO and susceptibility of 26 toward multiple electrophilic aromatic substitution, a large excess of 26 was used to prevent side reactions such as polysubstitutions of 26 or intermolecular alkylation between the polymer chains from occuring. These reactions introduce crosslinks and lead to a reduction in incorporation of 26 to the polymeric supports. In addition, the complexation of the Lewis acid catalyst, i.e., $SnCl_4$, with the formal oxygen, as confirmed by NMR spectra, may be responsible in some ways for crosslinking.

Moderate loadings of 2,2-dimethyl-1,3-benzodioxole, 27, were attained with the reaction of chloromethylated polystyrene resin and 27 using 1:1 molar equivalent at room temperature. Under more vigourous conditions, the reaction of poly(vinylbenzyl chloride) with 27 in dioxane could not be affected.

o-Phenylene carbonate, 28, a less reactive catechol precursor, was reacted with chloromethylated PPO to yield a polymer having o-phenylene carbonate as pendant groups. The extent of substitution achieved with this particular protected catechol was relatively low, however.

Table 8

Friedel-Crafts Reactions of the Chloromethylated Polymers and Catechol Precursors

Polymer, 1 meq $-CH_2Cl$	Catechol Precursor, mmol	Solvent	Catalyst mmol	Conditions	% Substitution
PVBCl	1,3-benzodioxole, 3.7	dioxane	$ZnCl_2$,1	Reflux, 12 h	negligible
PPO-CH_2Cl	" , "	$CHCl_3$	" ,0.6	60°, 4 h then RT, 48 h	72.7[a]
"	" , 4.8	"	$SnCl_4$,0.25	RT, 4 h	70.1[b]
"	o-phenylene carbonate, 2	"	" , "	"	16[c]
PVBCl	2,2-dimethyl-1,3-benzodioxole, 3	dioxane	" ,0.4	RT, overnight then 75°, 24h	negligible
(P)-CH_2Cl (resin)	" , 1	DCM	" ,0.12	RT, 24h	51.5[c]

[a] From elemental analysis

[b] From area integration of NMR spectrum

[c] Based upon oxygen analysis

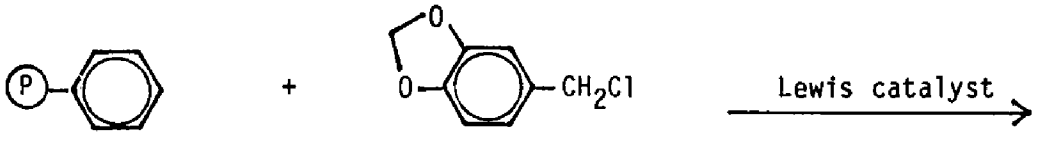
Intermolecualr alkylation between the polymer chains was extensive as indicated by comparing the oxygen-chlorine ratios in the elemental analysis. Friedel-Crafts reactions of the chloromethylated polymers and catechol precursors are summarized in Table 8.

6. Attempted reduction of unreacted pendant chloromethyl groups with lithium triethylborohydride (Super Hydride)

Because only a low to moderate degree of incorporation of catechol synthons into the polymeric matrices could be achieved under standard Friedel-Crafts alkylation conditions, a considerable amount of the introduced chloromethyl group still remained unreacted. Consequently, removal of the chloromethyl groups, preferably *via* reduction, had to be considered since the unreacted chlormethyl groups might cause unfavorable side reactions and effects in the subsequent transformation. We preferred to choose a reductive method because we believed that the physical properties of the polmer backbone such as polarity and solubility would not be altered significantly. Lithium triethylborohydride which had proved to be a versatile reducing agent in organic synthesis, was used for this study. At the onset, the reduction of unsubstituted chloromethyl PPO (a model compound) with lithium triethylborohydride was attempted. The reduction was run at room temperature for 30 minutes, unfortunately, degradation of the polymer backbone occurred. Milder conditions were employed (i.e., *ca*-60°) in order to avoid degradation, but no reduction was observed. Finally, when the reduction was performed on the chloromethylated PPO partially substituted as 1,3-benzodioxole at room temperature over the period of 5 min., no significant reduction could be substantiated by an NMR analysis.

7. Friedel-Crafts reaction of the preformed polymers and piperonyl chloride (3,4-methylenedioxybenzyl chloride, 40)

Low degrees of incorporation of catechol synthons into the polymeric matrices in normal Friedel-Crafts reactions of chloromethylated polymers and monomeric catechol derivatives, combined with the failure to reduce unreacted residual chloromethyl groups with lithium triethylborohydride prompted us to focus our attention on an alternative way of introducing the catechol synthons into the polymeric matrices. Piperonyl chloride was prepared and was reacted with the preformed polymers under the standard Friedel-Crafts alkylation condition to yield a polymer, 41, having methylenedioxybenzyl groups as pendant groups (Equation 23). With this approach, the side reaction



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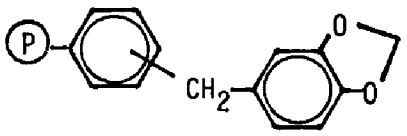

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associated with the presence of chloromethyl groups was avoided.

a. Preparation of piperonyl chloride (40): In the beginning of this study, chloromethylation of the polymeric supports under mild conditions with 36 or 37 had proved to be very successful in our laboratory; this led us to an attempt to prepare piperonyl chloride by chloromethylating 1,3-benzodioxole, a monomeric catechol derivative. However, under the conditions of this study, the yield of desired product obtained was relatively low. The desired product tended to

undergo polymerization in the presence of Lewis acid catalysts both during the reaction and purification, i.e., distillation.

Chloromethylation of 1,3-benzodioxole was also carried out using a classical method by treating with paraformaldehyde and hydrogen chloride in the presence of anhydrous zinc chloride; nevertheless, a low yield was obtained due to the formation of a low molecular weight polymeric residue in a distilling flask. With careful removal of the catalyst before distillation by extracting with 10% sodium carbonate, the yield was improved somewhat. Due to the difficulty to eliminate completely the presence of the catalyst before distilling and/or to avoid the use of the Lewis acid catalyst during the synthesis, an althernative method using piperonyl alcohol as a precursor for the synthesis of piperonyl chloride was utiilized. As expected, piperonyl alcohol which is a derivative of benzyl alcohol was rapidly converted into the corresponding chloride in quantitative yield by treatment at room temperature with excess conc. hydrochloric acid. Piperonyl chloride was also obtained in quantitative yield from piperonyl alcohol by reacting with thionyl chloride in the presence of pyridine.

b. Reaction of unfunctionalized polymers and piperonyl chloride: Because piperonyl chloride has a tendency to self-polymerize to form a low molecular weight polymer, particularly, in the presence of a Lewis acid catalyst, our initial attempt to react unfunctionalized polymers and piperonyl chloride under standard Friedel-Crafts condition was to employ a low concentration of piperonyl chloride with an excess of active sites on the reactive polymeric matrices. An excess molar ratio of PPO was used for this purpose. When piperonyl chloride was reacted with PPO in the presence of anhydrous zinc chloride or stannic chloride

Table 9

Friedel-Crafts Reactions of Unfunctionalized Polymers and Piperonyl Chloride

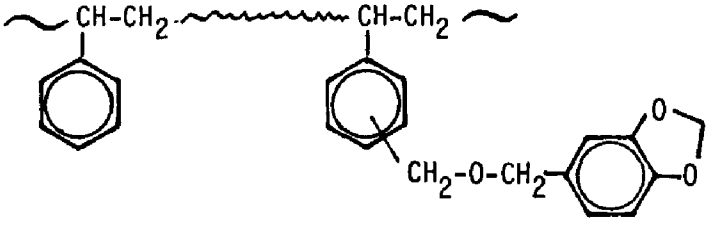
Polymer, meq	Piperonyl Chloride	Solvent	Catalyst, mmol	Temp, °c	Time, hr	% Substitution
PPO, 10	5	DCM	$ZnCl_2$, 1.0	25	6	crosslinked
" , "	5	"	$SnCl_4$, 0.42	"	1.5	"
" , "	-	"	" , "	"	"	"
Polystyrene 10	"	"	" , "	"	"	40.6 and gray polymeric residue

under the condition of this study, crosslinking was unexpectedly obtained. Furthermore, when polystyrene was used as a substrate, only a fraction of available piperonyl chloride (40.6%) was found to be incorporated into the polymeric matrices. The remaining unreacted piperonyl chloride precipitated out from the reaction mixture as a gray polymeric residue.

In addition, when a solution of PPO and anhydrous zinc chloride only, was stirred under identical conditions, the polymer was found to crosslink. These observations led us to conclude that the facile Lewis acid-base complex formation between the oxygen on the polymeric backbone of the PPO and the Lewis acid catalyst was leading to side reactions and crosslinking. Due to this fact, incorporation reactions of chloromethylated reagents could be used to modify polystyrene only. Friedel-Crafts reactions of unfunctionalized polymers and piperonyl chloride are summarized in Table 9.

8. Reaction of Poly(vinylbenzyl chloride) and 3,4-methylenedioxybenzyl alkoxide

When poly(vinylbenzyl chloride) was reacted with the alkoxide of 3,4-methylenedioxybenzyl alcohol under S_N2 conditions, the



methylenedioxybenzyl groups were introduced into the polymeric matrices with a high degree of incorporation to yield the polymer, 42. Unfortunately, this polymer was found to be of little significance in this work. Because the formal linkage was found to be relatively stable, selective removal of the formal catechol blocking group in the presence of a benzyl ether linkage was not possible.

II. Synthesis of Vinyl Monomer

Our initial plan to prepare a catechol-bound polymer via chemical modification of a preformed support has been found short of our expectations. The two main obstacles encountered are the problems associated with controlling the loading and distribution of a monomeric protected-catechol in the polymeric matrices. The other is the difficulty in minimizing the side reactions that often leads to crosslinking. An alternative technique of preparing the catechol-bound polymer was then pursued and was carried out in the following steps; (a) the synthesis of vinyl catechol derivative, (b) a suspension copolymerization of the vinyl monomer with appropriate comonomer, i.e., styrene, and (c) removal of the protected group with an appropriate reagent to release free catechols.

Because it was very difficult, if not impossible, to introduce the unsaturated side chain by the one-step reaction, a gradual build-up of the vinyl group had to be considered. In addition, unprotected phenolic functions react with organometallic reagents and dihydric phenol derivatives are powerful inhibitors in free radical polymerizations. Therefore, it was imperative to block the hydroxy functions of the catechols with a protecting group that would suffer cleavage under very

mild conditions. In this study a formal linkage was chosen as the protecting group, since demethylenation of the methylenedioxy group could be accomplished by treating with boron trichloride or a mixture of boron trichloride and 1-butanethiol to yield the corresponding catechols in short time under mild conditions.

1. Preparation of 5-vinyl-1,3-benzodioxole (49)

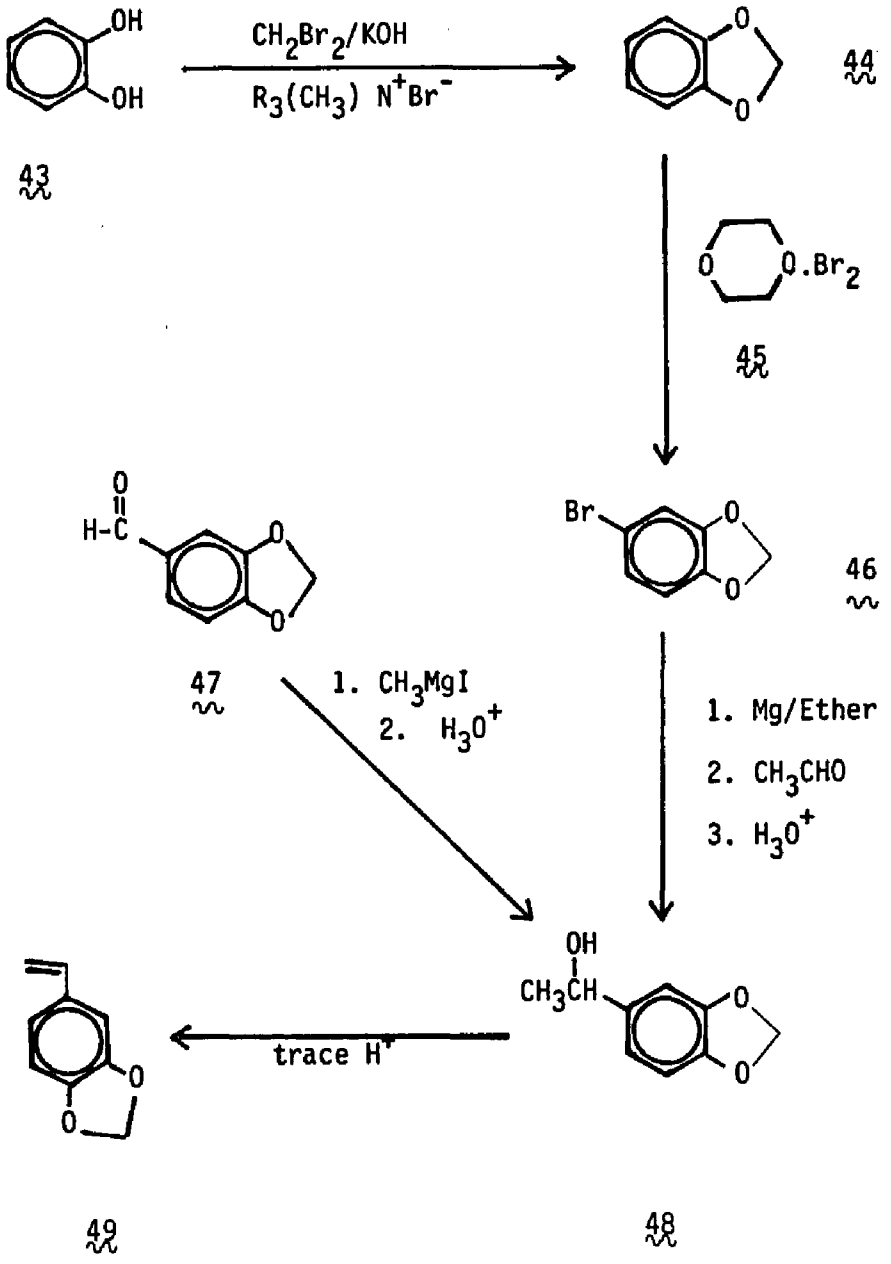
The synthetic sequence directed ultimately towards the preparation of the polymeric catechols for subsequent utilization as versatile immobilized reagents is outlined in Scheme 9. Our initial approach to prepare the monomer, 49, was to employ simple reactions resulting in high overall yield. Those factors had to be taken into consideration because the polymeric reagents to be prepared must compete favorably with the monomeric analogs in term of both reactivity and cost factors.

In order to protect the hydroxy functions of a catechol, 43, methylenation was performed by treating the catecholate anion with dibromomethane in the presence of Aliquat 336 (tricaprylylmethylammonium chloride) using conditions similar to those employed by J.F. Collin, et al.[106] The phase transfer catalyst technique proved to be more effective than homogeneous reactions in aprotic polar solvents as described by Bonthorne and Cornforth.[108] A third method reported by Miller, et al.,[109] was also considered but large amounts of cesium fluoride had to be used.

Monobromination of 1,3-benzodioxole, 44, was achieved with the action of dioxane dibromide, 45, to yield 5-bromo-1,3-benzodioxole, 46. The attachment of a bromine atom to the aromatic ring at position 5 was somewhat surprising. This might be partly due to steric

Scheme 9

Preparation of 5-Vinyl-1,3-benzodioxole (49)



requirements and an electronic factor of the particular brominating reagent. When 44 was allowed to react with one equivalent of bromine at ambient temperature, a mixture of non-specifically brominated products was obtained, containing mainly the monosubstituted product ($\geq$ 50%). In addition, the reaction of 2,2-dimethyl-1,3-benzodioxole, 27, with bromine was found to be more facile but less selective than the reaction of 47 and bromine. This observation was believed to be due to the partial complexation of Br_2 with the oxygen atoms of the methylenedioxy functions. In the case of 2,2-dimethyl-1,3-benzodioxole the presence of a dimethyl group might prevent or retard the initial complexation and reduce the stereoselectivity. The Grignard reagent of 46 was readily prepared by the reaction with magnesium metal in absolute ether; the α-hydroxyethyl derivative, 48, resulting from the reaction between the Grignard reagent and acetaldehyde, was used in elimination in the subsequent step without further purification. However, a small portion of the crude alcohol was seperated for identification and it solidified upon prolonged standing. The α-hydroxyethyl derivative, 48, was also conveniently prepared from piperanal, 47, by the reaction with methylmagnesium iodide prepared in situ in absolute ether.

Elimination of the corresponding alcohol was effected upon heating and the 5-vinyl-1,3-benzodioxole, 49, was distilled under reduced pressure from the vessel equipped with an appropriate fractionating column (20x1.2 cm) and was collected in a receiver. If a fractionating column was not used, a lower conversion resulted and crude product containing α-hydroxy ethyl derivative, 48, was obtained. Passing nitrogen under the liquid while distilling also improved the yield because the distillate came out from the fractionating column faster

with less exposure to heat in the flask. Water, a by-product was collected in a dry-ice acetone trap.

The monomer, 49, was also obtained from the corresponding alcohol, 48, by distillation from sodium hydrogen sulfate or in the presence of a few drops of conc. H_2SO_4, but the monomer had a propensity to undergo polymerization and perhaps charring. The 5-vinyl-1,3-benzodioxole with the highest purity was obtained by passage through a silica gel column and was redistilled under reduced pressure using a nitrogen ebulator. The pure monomer was utilized in polymerization and in kinetic studies.

2. Polymerization reaction of 5-vinyl-1,3-benzodioxole (49)

(a) Homopolymerization

Polymerization of the pure 5-vinyl-1,3-benzodioxole, 49, in the presence of azobisisobutyronitrile proceeded without complications. The formal blocking group did not appear to act as a chain transfer agent as the high molecular weight polymer was obtained. Cationic polymerization in the presence of boron-trifluoride etherate at 20° was accompanied by intense color development but only low molecular weight polymer could be isolated in 75-80% yield. It was assumed that the methylenedioxyphenyl pendant groups of poly(5-vinyl-1,3-benzodioxole) are more susceptible to electrophilic aromatic substitution than the unsubstituted phenyl groups in polystyrene. Therefore, electrophilic attack by developing cations of the growing chains with the substituted phenyl pendant groups might occur, both as an interpolymeric and intrapolymeric process (back-biting), resulting in early termination of the growing chains. As a result, only low molecular weight polymer was obtained. Anionic

polymerization could be effected in THF at -70° using either butyl lithium or sodium naphthalide as catalysts. Conversions of 50-60% were obtained within 18 hours; no evidence for ring metalation for formal cleavage[110] could be detected.

(b) Dilatometric studies of the homopolymerization of 5-vinyl-1,3-benzodioxole (49)

The rate of polymerization (R_p) of the monomer, 49, was evaluated dilatometrically and the result was compared to the R_p of styrene under identical conditions. The initial rate of polymerization (R'_p) of the monomer was obtained by using the following equation:

$$R'_p = \frac{\Delta V}{\Delta T} \frac{(1)}{VK}$$

where $\frac{\Delta V}{\Delta T}$ is the rate of volume change, V is the total volume of the system, and K is the contraction, a characteristic quantity for a given monomer and was estimated for gravimetric conversion data. The overall rate of polymerization was then calculated from R'_p value by the following relationship.

$$R_p = R'_p[M]$$

where M is the monomer concentration.

Under the condition of study (i.e., 0.317 wt% AIBN used as an initiator), the initial rate of polymerization, R'_p was found to be 2.107×10^{-3} and the rate of polymerization, R_p, 1.534×10^{-2} mol l^{-1} min^{-1}, which are more or less comparable to the corresponding values of R'_p (1.637×10^{-3}) and R_p (1.357×10^{-2} mol l^{-1} min^{-1}) calculated for styrene under the same conditions.

(c) Copolymerization of 5-vinyl-1,3-benzodioxole (49)

The copolymerization characteristics of 5-vinyl-1,3-benzodioxole, 49, were determined by measuring the relative reactivity (copolymerization parameters r_1 and r_2) of 49 toward styrene and methyl methacrylate. These comonomers represent a range of copolymerizabilities, extending from the resonance stabilized styrene with negative polarity (Q, 1.0; e, -0.8) to the positively polarized methyl methacrylate (Q, 0.74; e, 0.4).[111] Thus, the reactivity ratios observed when 49 was copolymerized with each of these comonomers should define the Q, e parameters for 49 and indicate the types of comonomers which would yield random copolymers.

Among the reactivity ratio determination methods, the most used are those based on the differential equation derived almost simultaneously by Mayo and Lewis,[112] and by Alfrey and Goldfinger[113] in 1944 which describes the copolymer composition (Equation 24).

$$(24) \qquad \frac{d[M_1]}{d[M_2]} = \frac{m_1}{m_2} = \frac{[M_1]}{[M_2]} \frac{(r_1[M_1]/[M_2] + 1)}{([M_1]/[M_2] + r_2)}$$

where $[M_1]/[M_2]$ is the comonomer ratio in feed and m_1/m_2, the structural unit ratio in low conversion (10%). All experimental techniques based on equation 24 require variation of a known $[M_1]/[M_2]$ and the determination of relative m_1/m_2. For the r_1-r_2 determination in this study, the method of Fineman and Ross[114] was adopted in which $[M_1]/[M_2]$ may be replaced by F and m_1/m_2 is defined as f. Equation 24 can be arranged to

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

If $F(F-1)/f$ is plotted vs F^2/f, a straight line with a slope of r_1 and an intercept of r_2 is obtained. However, the difficulty with experimental work that was often encountered was to control the extent of conversion of monomer to polymer. In principle, the conversion of monomer to polymer must be low (3-5%) in order that the monomer concentrations be, to a close approximation, unchanged from the initial concentrations. In spite of all precautions, the copolymerizations frequently proceeded so rapidly that conversions greater than 10% were obtained.

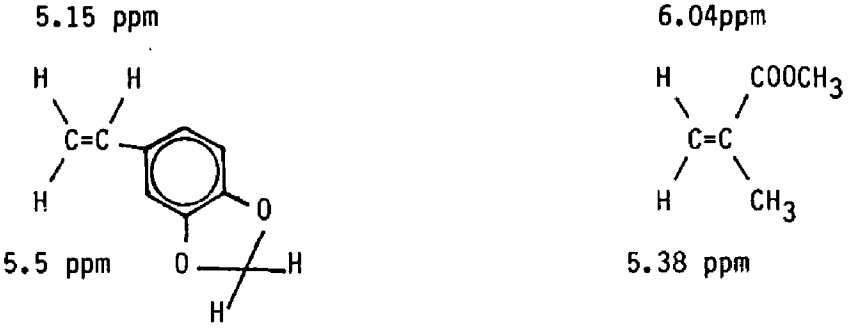
For the majority of r_1-r_2 determinations in this work, the method of Mayo and Lewis was preferred, utilizing the Equation 25 derived by integration of Equation 24:

$$(25) \qquad r_2 = \frac{\log ([M_2]_0 / [M_2]) - (1/p) \log (1-px)/(1-px_0)}{\log ([M_1]_0 / [M_1]) + \log(1-px) / (1-px_0)}$$

where $x = [M_1]/[M_2]$, the ratio of unreacted monomer concentrations at a given moment, and $p = (1-r_1)/(1-r_2)$ is assigned. The method is based on $[M_1]$ and $[M_2]$ determination at a given moment (knowing $[M_1]_0$ and $[M_2]_0$) and obtaining a straight line $r_2 = f(r_1)$ for each experiment. The intersection of the experimental straight lines can specify r_1 and r_2. In addition, utilizing the method of Mayo and Lewis makes the determination of r_1 and r_2 in high conversion copolymerization possible. Various techniques for instantaneous determination of unreacted comonomer concentrations, $[M_1]$ and $[M_2]$, have been described by Guyot, et al.,[115,116] and Narita, et al.,[117] utilizing the chromatographic methods and by A. Natansohn[118] utilizing high resolution NMR spectroscopy.

In this work the reactivity ratios for the 5-vinyl-1,3-benzodioxole (M_1)-methyl methacrylate (M_2) was determined by using the integrated Mayo-Lewis equation (Equation 25) with the copolymerizations being carried out in an NMR sample tube. Hexamethyl disiloxane which is chemically relatively inert was used as a reference replacing the conventional but very volatile tetramethyl silane.

The ^1H NMR spectrum of the comonomer mixture with x_0=0.9265 is shown in Figure 2; the protons resonating in the olefinic region are



On the integral curve the signal area at 5.15 ppm represents one proton from 5-vinyl-1,3-benzodioxole and at 6.04 ppm for one proton from methyl methacrylate. The integral amplitude was adjusted so that the respective areas corresponding to $[M_1] + [M_2]$ totaled unity with respect to the reference signal. From the spectra taken every 60 minutes the instantaneous comonomer concentrations were measured and the evolution of these is given in Figure 3.

A computer program for processing the integrated Mayo-Lewis equation and calculating r_1-r_2 values from the unreacted comonomer concentration data is shown on page 72. The notations are A = $[M_2]_0/[M_2]$ and B = $[M_1]_0/[M_1]$. For each experiment, three p values are

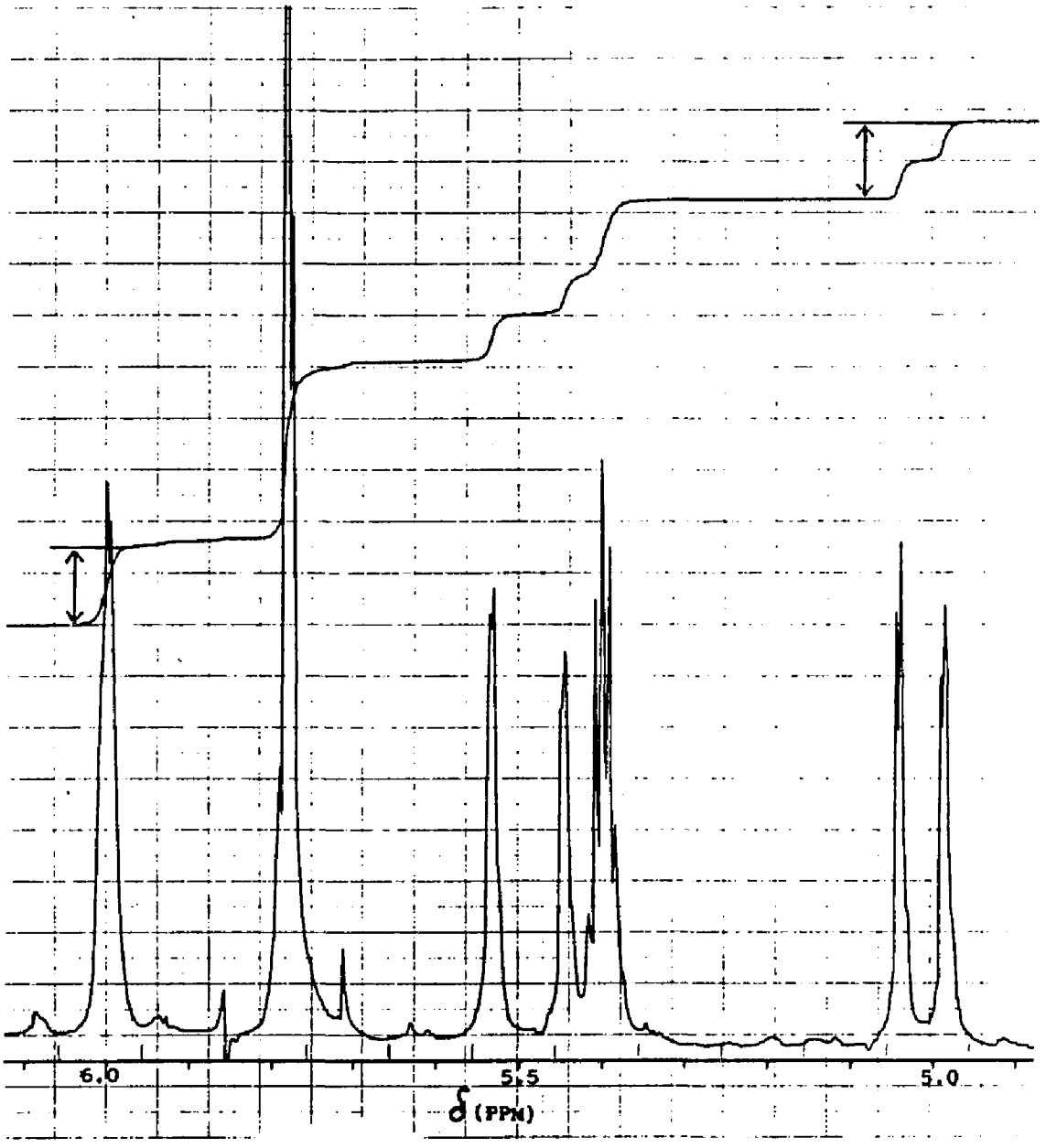


Figure 2: ^{1}H n.m.r. spectrum of the olefinic region for a comonomer mixture

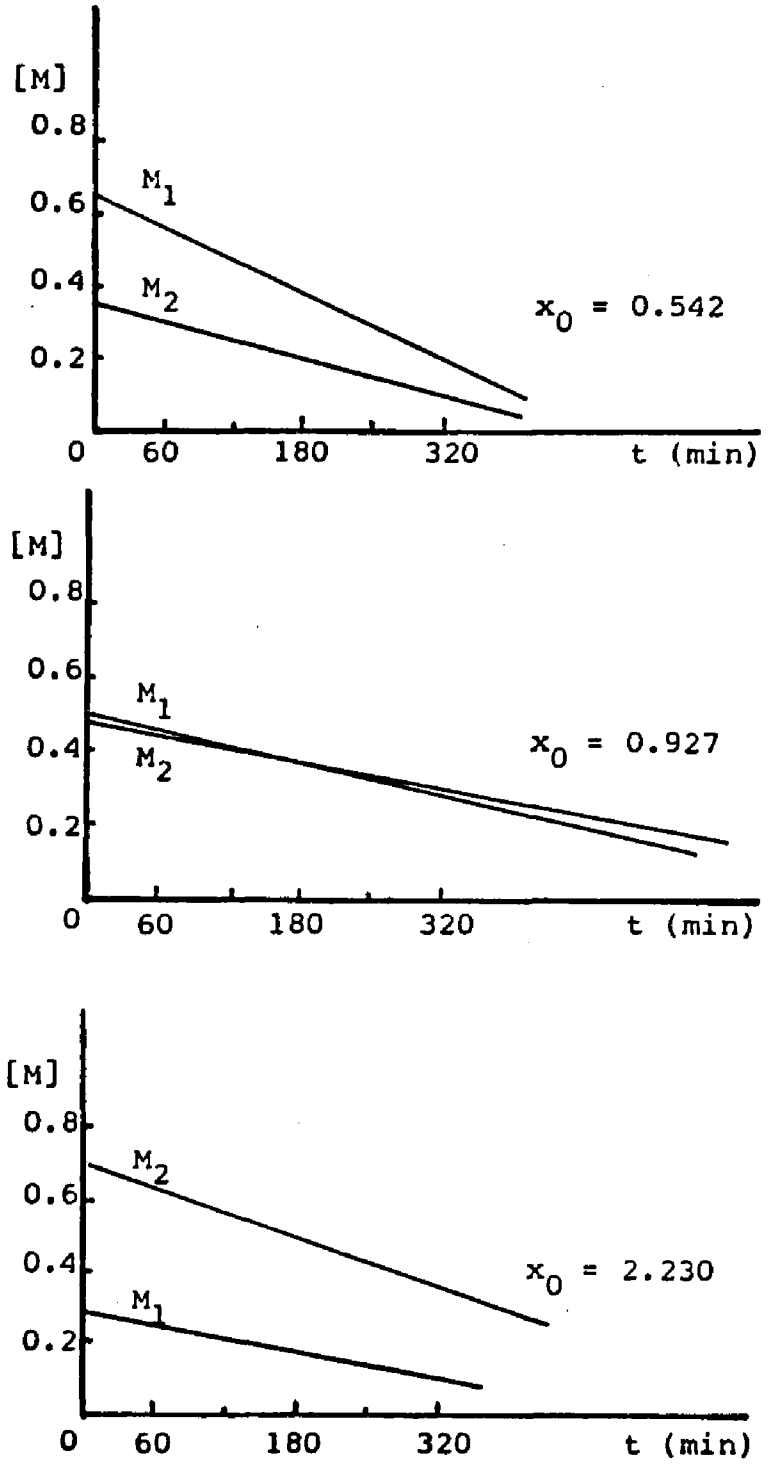


Figure 3: Comonomer concentrations as a function of time

A Computer Program for Processing the Integrated Mayo-Lewis Equation

```
      DIMENSION P(3)
10    READ(5,100,END=99)NTIMES,XO,P
100   FORMAT(I1,F6.4,3F3.1)
      WRITE(6,300)XO,P
300   FORMAT(1X,4F10.4)
      DO 50 I=1,NTIMES
      READ(5,200)A,B,X
200   FORMAT(3F6.4)
      WRITE(6,400)A,B,X
400   FORMAT(1X,3F10.4)
      WRITE(6,500)
500   FORMAT(1X)
      DO TO J=1,3
      R2=(ALOG10(A)-((1.0/P(J)*ALOG10((1.0-P(J)*X)/(1.0-
        P(J)*XO)))) & (ALOG10(B)+ALOG10((1.0-P(J)*X)/(1.0-
        P(J)*XO)))
      R1=1.0-P(J)*(1.0-R2)
      WRITE(6,600)R2,R1
600   FORMAT(2F10.5)
50    CONTINUE
      WRITE(6,700)
700   FORMAT(1X)
      GO TO 10
99    STOP
      END
```

chosen according to the restrictive conditions: $p = 0$; $p<(1/x)$ and $p<(1/x_0)$; and $p>(1/x)$ and $p>(1/x_0)$. The initial feed ratio, x_0 and the three p are fed into the computer, followed by experimental values for A, B and x obtained from NMR spectra recorded at 60 minute intervals. For each A, B and x the computer gives three r_2-r_1 values, corresponding to the three p values. The value of r_2 as a function of r_1 is then plotted and is shown in Figure 4. Each experiment is represented in Figure 4 as a family of straight lines intersecting each other. Due to experimental error, the center of the area enclosed by the family of lines is taken as the best values for r_1 and r_2; r_1 was found to be 1.1 and r_2, 0.45.

The application of the integrated Mayo-Lewis equation to determine the reactivity ratios of 5-vinyl-1,3-benzodioxole (M_1) and styrene (M_2) by working with high resolution NMR spectroscopy was attempted but we were not able to find clearly seperated signals in the ^1H NMR spectrum for the two comonomers. Nevertheless, the reactivity ratios of the two comonomers was estimated using the methods of Fineman and Ross as a series of bulk copolymerization was carried out as usual to low conversion and the copolymer composition was determined by either elemental analysis or NMR spectrometry. From these data, it can be determined that $r_1 = 1.02$ and $r_2 = 0.6$.

The data obtained from the copolymerization of 49 with styrene were used to calculate the Q and e copolymerization parameters employing equations 26 and 27.[111]

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

(27) $$Q_2 = Q_1/r_1 \exp^{-e_1 (e_1-e_2)}$$

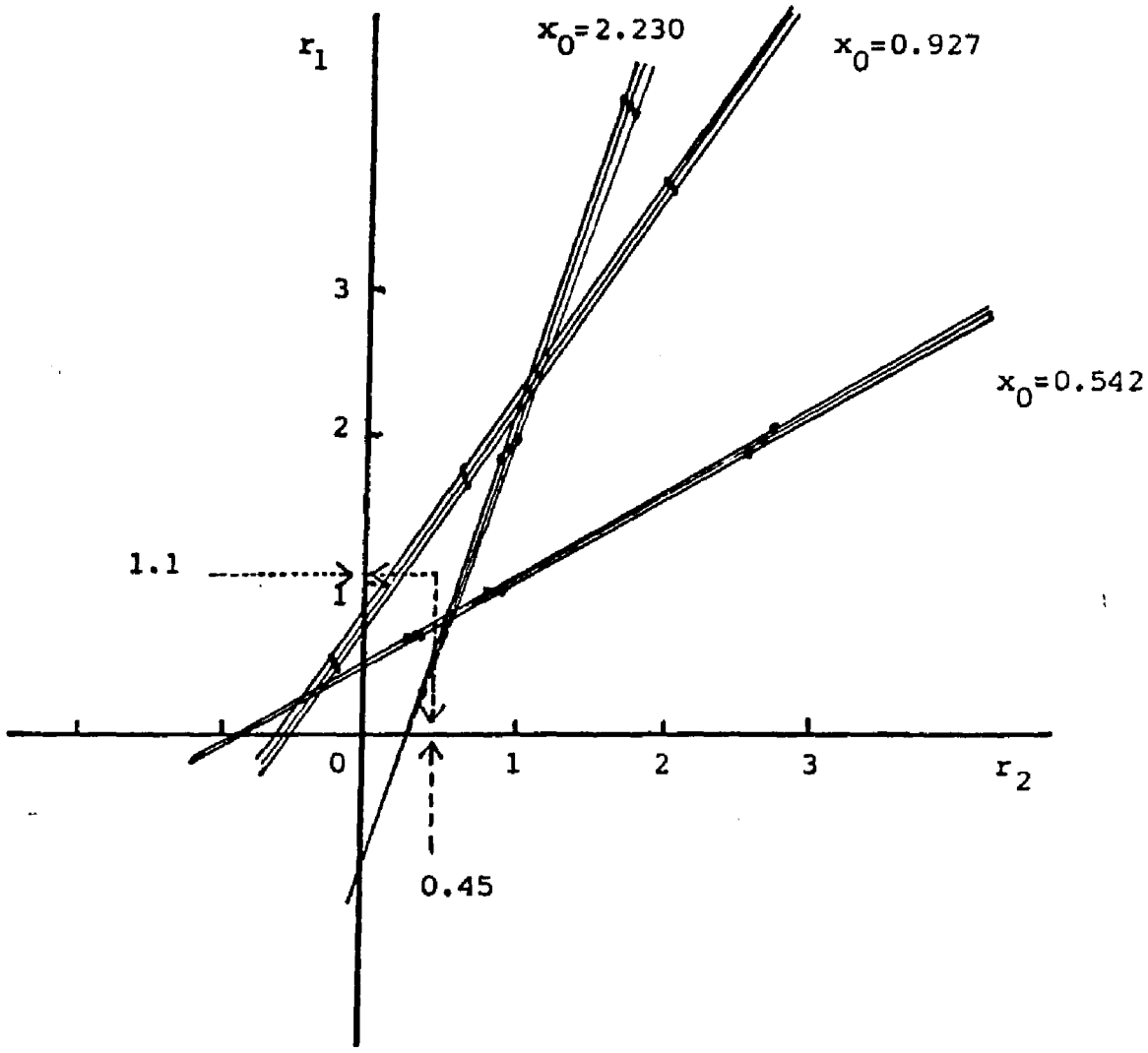


Figure 4: The Mayo-Lewis treatment for 5-vinyl-1,3-benzodioxole (M_1)-methyl methacrylate(M_2) copolymerization

The value of e for 49 was found to be -1.5 and Q, 2.9. The large negative value of e observed for 49 as compared to styrene (e=-0.8) or p-methoxystyrene (e=-1.11) indicates that the formation of the five-membered ring may enhance electron density of the double bond by perhaps constraining the system into the optimum configuration for conjugation. The relative high value obtained for Q which normally determines the relative polymerizability of the monomer confirms the stabilizing influence of methylenedioxy substituent.

3. Suspension copolymerization of 5-vinyl-1,3-benzodioxole (49) and styrene

Crosslinked terpolymers of 49 and styrene (1:1) with divinylbenzene (2-3%) as crosslinking agent were prepared by suspension ("pearl") polymerization,[119] a technique that results in spherical beads suitable for further modifications. Eventhough the physical stability of the beads with 2% crosslinking was satisfactory in most applications in this study, there were a few cases where the beads disintegrated into a fine powder during the reaction. Nevertheless, an improvement in the stability of the beads could be achieved with increased crosslinking but the ability of the network to expand in a 'good' solvent became reduced and penetration of reagents to the interior became impaired.

Our ultimate goal of copolymerization of 49 and styrene was to convert the obtained terpolymer into polymeric catechols in the subsequent step and eventually to the desired polymeric reagents; consequently, the ability to control the loadings of 49 into the copolymer had to be achieved. In principle, loadings of the bound reagents must be maximized in order to avoid the use of large amounts of

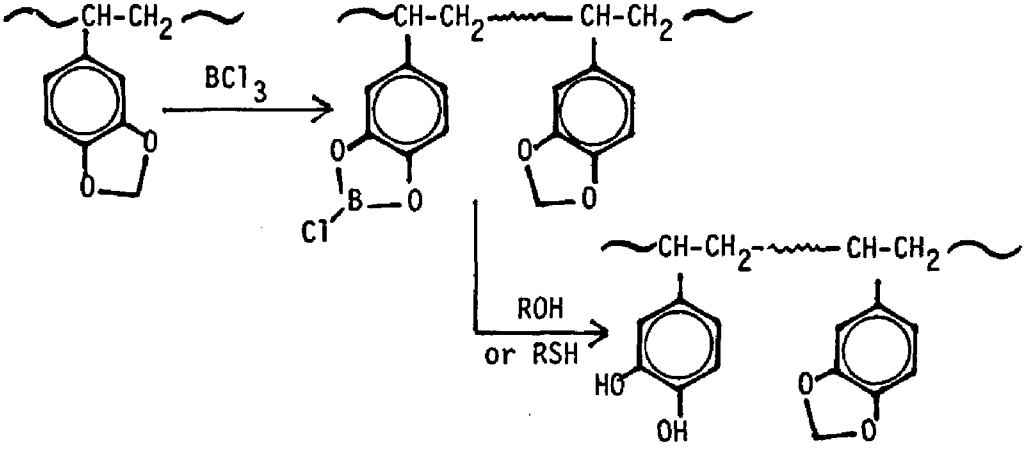
the polymeric species in subsequent reactions. However, the presence of high concentrations of hydrophilic functional groups significantly changes the rate at which hydrophobic reagents diffuse into the polymeric matrix. Thus, we employed 1:1 molar ratio of comonomers in the feed in copolymerization to high conversion in order to obtain approximately 50% of the segments carrying the required hydrophilic group and 50% styrene to retain the best hydrophilic/hydrophobic backbone. With this particular copolymer composition, the application involving the use of these relatively hydrophobic resins particularly in non-polar solvents in subsequent steps was proved to be useful. Chemical transformation of the bound reagent, intended to be carried out in non-polar medium during all transformations, would not alter significantly the solvent compatibility of the system in spite of change in nature of the functional group during the course of the reactions (i.e., non-polar to polar functional group or vice versa).

4. Removal of formal blocking group to free catechol

Cleavage of the formal blocking group to liberate the catechol moiety was thoroughly evaluated. In our preliminary study a linear, soluble poly(5-vinyl-1,3-benzodioxole) was employed as a model system for the terpolymer beads for the study of reactions involving removal of formal blocking group to free catechols. With this soluble system, chemical changes carried out on the support were easily monitored because a range of analytical techniques applicable to small molecule chemistry can be used.

D.C. Kaufman[120] has shown that a catechol synthon with an isopropylidene blocking group liberated catechol upon either direct acid

hydrolysis or thiolysis with butyl mercaptan and p-toluenesulfonic acid. However, an attempt to remove the formal blocking group in our soluble system with conc. H_2SO_4 or p-toluenesulfonic acid and butyl mercaptan failed under the same condition. Moreover, when 5,5-dimethyl-1,3-cyclohexanedione was added to the reaction in order to facilitate the separation of formaldehyde that might be formed during acid hydrolysis with sulfuric acid, it was found that the presence of 5,5-dimethyl-1,3-cyclohexanedione did not seem to alter the result. Boron trichloride which has been reported to be a useful reagent in the selective scission of cyclic acetals, particularly in o-demethylation,[121] was then employed in our study. It was found to be quite effective in removal of formal linkage in our system, presumably via the formation of borate esters (Equation 28) which had to be decomposed with either alcohols or mercaptans.



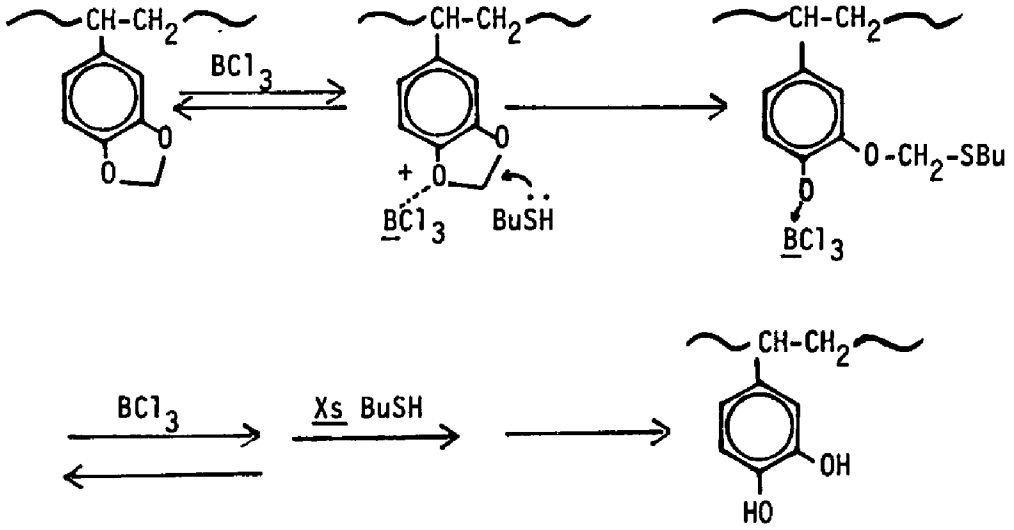
(28)

A boron trichloride-thiol system was believed to be even more effective in cleavage of a methylenedioxy group in the terpolymer because the mercaptans are hydrophobic and more compatible with the support

polymer. Unfortunately, when the linear poly(5-vinyl-1,3-benzodioxole) was treated with boron trichloride, phase separation occurred shortly after the reaction had commenced but the polymer could be redissolved by adding enough methyl alcohol. This was probably attributable to the formation of free catechols in the non-polar medium in contrast to the formation of the intermediate, borate ester, on treatment with boron trichloride alone. The reaction was believed to proceed *via* nucleophilic attack of the primary thiol on the less hindered and more electron-deficient carbon atom of the oxonium species formed initially by coordination of the Lewis acid (BCl_3) to oxygen, as shown in Scheme 10.

Scheme 10

Cleavage of Methylenedioxy Group by BCl_3-Thiol System



The extent of coordination of the Lewis acid, i.e., BCl_3 with "hard" base (oxygen), which may indicate the catalytic effectiveness of that particular Lewis acid, could be compared using ^1H NMR spectra of 1,3-benzodioxole, a model compound, in the presence of BCl_3, $SnCl_4$, BH_3-THF, etc. While only a slight paramagnetic shift of the proton signal (δ 7.05, s) of the aryl group was observed with excess ($\geq$2 molar equiv.) of $SnCl_4$ because of the coordination of the acid $SnCl_4$ with the oxygen of the methylenedioxy functional group, the proton signal of the aryl group shifted significantly downfield to exhibit a multiplet band between 7.1-7.4 ppm with only 1 molar equivalent of BCl_3, indicating a better complexation with BCl_3. In addition, the ^1H NMR spectrum has also shown that with increasing concentration of the Lewis acid, the methylene proton signal was observed to shift even further downfield which should indicate a significant decrease in electron density at the methylene carbon. Consequently, by increasing the concentration of the Lewis acid, the methylene carbon would be more electron-deficient, therefore, more susceptible to the attack by nucleophilic thiol.

The ^1H NMR spectrum of 1,3-benzodioxole in the presence of BH_3 THF, on the contrary, did not indicate any significant change in paramagnetic shift of the proton signals of both the aryl and methylene groups which might imply the absence of complexation of BH_3 with the oxygen of the methylenedioxy functional group. The ^1H NMR spectra of 1,3-benzodioxole with various Lewis acids are shown in Figure 5.

The soluble poly(vinyl catechol) was very unstable. Upon exposure to air, the dried polymer turned almost immediately to bluish purple and displayed a certain degree of irreversibility, i.e., crosslinking. It would be logical to assume that similar side reactions might occur in

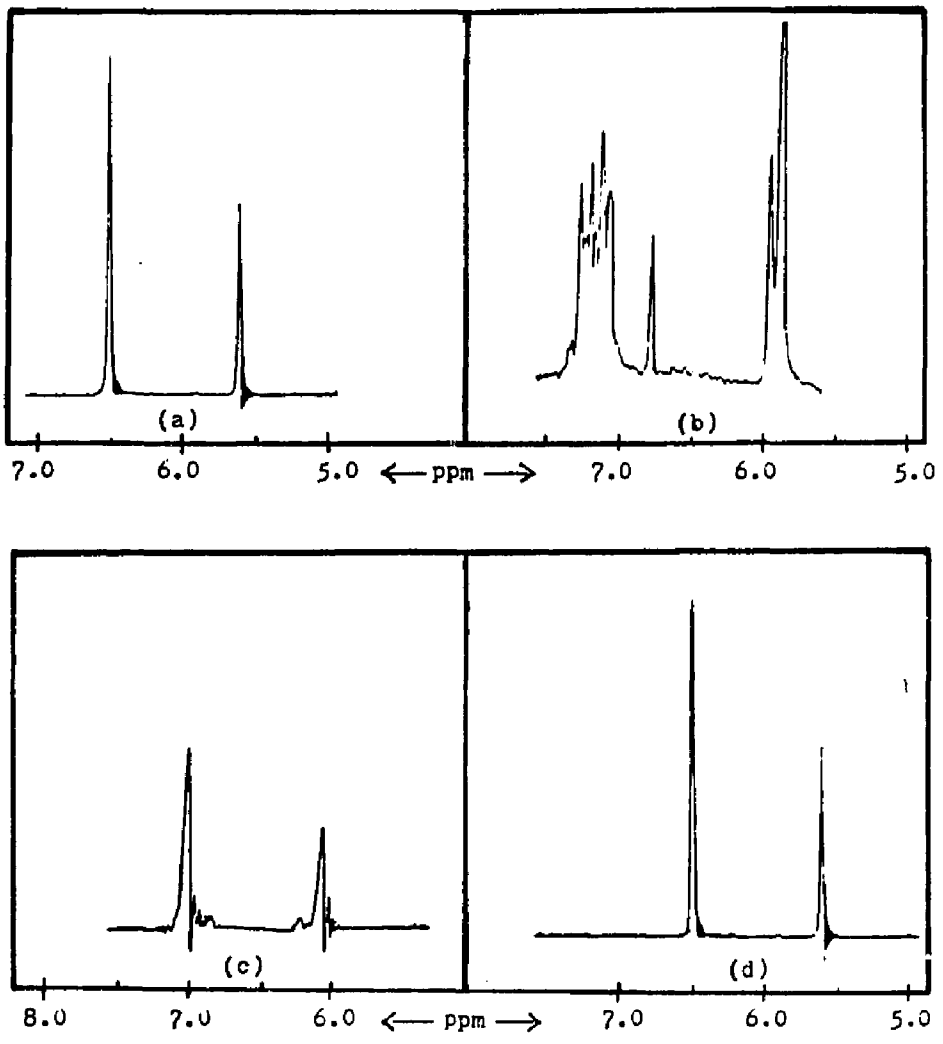
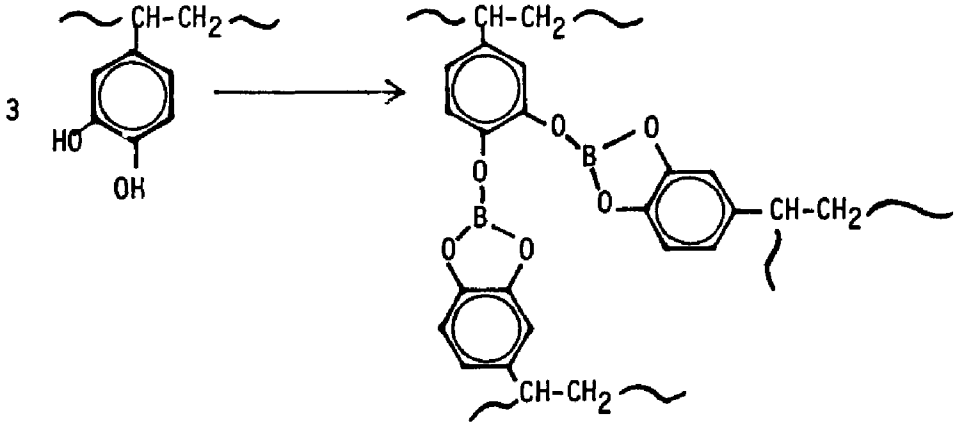


Figure 5: The ^{1}H NMR spectra of 1,3-benzodioxole; (a) with no catalyst, (b) with ca 1 molar equivalent BCl_3, (c) with $\geq$ 2 molar equivalent $SnCl_4$, (d) with excess BH_3.THF.

the crosslinked resins and the additional crosslinking would limit access to further modification of the resin. We ruled out the possibility of borate formation similar to the reation of a low molecular weight analog with BCl_3[122] (Equation 29) as being responsible for the crosslinking because the data obtained from elemental analysis of the polymer did not indicate the presence of elemental boron in

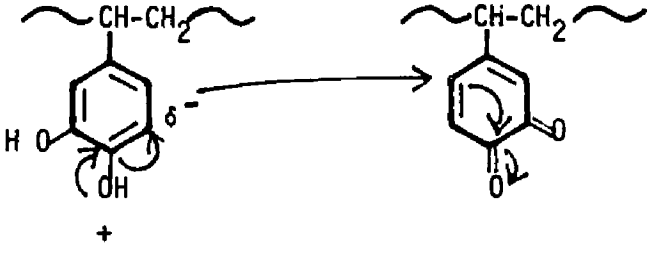
(29)



significat amount. However, we believed that under acidic conditions the crosslinking occurred because some of the catechol pendant groups of the poly(vinyl catechol) were transformed into quinoid moieties by auto-oxidation in air. The quinoid species then acted as electrophiles relative to catechol moieties and dimerization occurred (Figure 6)

Figure 6

Dimerization Reaction



between different polymer chains resulting in crosslinking. Furthermore, higher temperatures, i.e., heating seemed to accelerate the rate and extent of crosslinking. Direct bromination of freshly prepared Poly(vinyl catechol) in situ prior to separation from the reaction medium introduced two bromine atoms/catechol residue and a reduction in the rate of crosslinking was observed. Introduction of bromine to the unsubstituted rings was believed to stabilize the polymer by either increasing the redox potential of the system or by preventing the attack by radicals produced during oxidation of the hydroquinoid groups. In addition, the presence of quinhydrone-like moieties of the polymer was assumed to be responsible for the coloration of the polymer similar to the coloration observed from di-, tri-, and tetrahydroquinone upon autooxidation in air.[123]

The reaction of terpolymer with boron trichloride in dichloromethane proceeded without complication under inert atmosphere, generation of the borate ester functional groups did not alter noticeably solvent compatibility of the system during the course of the reaction. The pendant borate ester units in the terpolymer were decomposed successfully to catechols by either refluxing with methanol or treating with 1-butanethiol but the time required for decomposition was longer compared to the similar reaction in the soluble system. Elemental analysis and infrared analysis in KBr pellet (disappearance of the absorption peak at 2780 and 1033 cm^{-1} attributable to the formal fuctionality and appearance of a strong, broad band at 3600-3100 cm^{-1} attributable to OH stretching) indicated that the reaction had proceeded almost quantitatively.

The removal of the formal blocking group of the pendant

methylenedioxy unit in the terpolymer was also attempted in boiling 48% hydrobromic acid for 18 hours, the black beads obtained became hard and rigid with less swellability in 'good' solvents which indicated some degree of oxidation and further crosslinking.

B. OXIDATION OF CATECHOL RESIN TO THE CORRESPONDING o-BENZOQUINONE

The oxidations of catechol moieties in the terpolymer to the corresponding 1,2-benzoquinone were performed in our laboratory earlier employing oxidizing agents such as chlorine, cerium(IV) ammonium nitrate and a mixture of dimethyl sulfide (DMS), N-bromosuccinimide (NBS), and triethyl amine.[115] The oxidations were reported to be partially successful based on infrared evidence alone. In this study hydrogen peroxide and potassium nitrosodisulfonate (Fremy' radical) were used as alternative methods. The reaction of the terpolymer with hydrogen peroxide proceeded at room temperature to yield the oxidized resin possessing a brown color. Potassium nitrosodisulfonate was used in DMF/water containing Na_2HPO_4 buffer with equal success. The problem of identifying the oxidized product was particularly difficult since the overall loadings of catechol moieties were relatively small. The simple dilution factor made elemental analysis and change in weight less useful as the methods to indicate the success or failure of the reaction. The use of many of the invaluable spectroscopic means for identification of organic compounds was precluded by the total insolubility of the resin in all solvents. Consequently, we had to rely mainly upon data obtained from infrared spectra, although KBr pellets prepared were often opaque, and change in coloration of the resin. For instance, the resin with 1,2-benzoquinone moieties exhibited the characteristic carbonyl absorption at 1730 cm^{-1} in the infrared spectra and the color turned to brown from the bluish purple colored resin of partially oxidized catechol resin.

C. SYNTHESIS and APPLICATION of POLYMER-BOUND CATECHOL REAGENTS

Catechol resin was found to be very hygroscopic and rather unstable upon exposure to air. It was necessary to remove trace amounts of moisture remaining in the polymer before it was subjected to further modification, particularly when anhydrous conditions were required. It was also found that the copolymer bidentate nature of the the ortho-dihydroxy groups was partially destroyed upon prolonged storing of the resin. Not only the degree of conversion of the particular resin to another reagent was unexpectedly low but also the resin was swollen to a lesser extent in the solution. This was believed to be caused partly by the formation of the quinone moieties in the terpolymer upon autooxidation. Fortunately, this was a reversible process and the resin could be easily reduced to o-hydroquinone before use with sodium hydrosulfite in a THF-water mixture. The best approach for converting the catechol resin to another reagent was to use the freshly prepared, dried, catechol resin with minimal exposure to air and moisture. But, if an immediate conversion to another reagent was not planned, the resin had to be stored in an inert atmosphere.

1. Preparation and use of immobilized catecholborane

Immobilized catecholborane was prepared by allowing the swollen catechol resin to react with borane-THF in a nitrogen atomosphere at ambient conditions. Trace amounts of moisture in the polymer were removed prior to treatment with borane-THF by distilling a suspension of the resin in benzene until the distillate was clear. The resin was allowed to expand fully by suspending it in dried, redistilled THF at reflux. Infrared analysis (absorption peaks at 2360, 2260 cm^{-1}

attributable to B-H stretch and at 1420-1370 cm^{-1} attributable to B-O stretch) indicated the reaction had proceeded as expected, though not quantitatively (the absorption peak at 3700-3020 cm^{-1} was attributable to unreacted OH). Elemental analysis (based on per cent boron found) indicated that the available catechol moieties were more than 50% transformed to the catecholborane. The white beads were obtained at first but turned slightly purple upon prolonged storing.

Monomeric catecholborane has been reported to be a very versatile reducing agent, particularly in the important area of selective reductions.[98] We anticipated that the catecholborane resin that had been previously prepared in our laboratory would undergo the same reactions as its low molecular weight analog. In this study the efficacy of the reagent in the elaboration of low molecular weight substrates was investigated. In our preliminary study, those substrates possessing such functionalities as aldehyde, ketone, etc. which were considered to react relatively fast with monomeric catecholborane were tested with reagent. Therefore, benzaldehyde and cyclohexanone were investigated as representatives of aldehyde and ketone, respectively. The reactions were conducted at room temperature in a nitrogen atmosphere, generally in dried THF, with slight excess amounts of the resin. The extent of the reduction was followed by GLC by the determination of unreacted substrates at various time intervals. Hydroboration of benzaldehyde by the catecholborane resin was performed but proceeded very slowly under the condition of study, the reaction was complete after ca 110 hours of stirring in contrast to the reaction with monomeric catecholborane in which benzaldehyde was rapidly and quantitatively reduced to the corresponding alcohol in short time.

Change in coloration of the resin was evident during the transformation as the resin turned to blue. The rate of hydroboration of cyclohexanone by the resin was observed to be much slower, only 27% of the substrate was found to react with the resin over the period of ca 110 hours under the condition of study. Hydrolysis of the polymeric intermediate, alkoxy-1,3,2-benzodioxoborole, a derivative of both representative reactions at room temperature, proved futile. Although use of THF-water mixture as a solvent seemed to be more effective, nevertheless, only small amounts of the corresponding alcohol were detected in both cases. Hydroboration of benzaldehyde and cyclohexanone is summarized in Table 10.

Further investigations indicated that catecholborane resin would be a potential reducing agent to be employed in selective reductions. In competitive experiments, when various substrates, in equal molar quantities were allowed to compete for a limited quantity of catecholborane resin, the resin was found to preferentially reduce benzaldehye in the presence of cyclohexene and n-butyl bromide in quantitative yield. The selective reduction of benzaldehye in the presence of various functional groups is summarized in Table 11.

2. Preparation and use of immobilized o-phenylene phosphorochloridate

Immobilized o-phenylene phosphorochloridate was prepared by allowing the swollen catechol resin to react with phosphorous oxychloride ($POCl_3$) in the presence of pyridine under anhydrous conditions. Because the catechol resin employed in this experiment was stored for a certain period of time, the resin was treated first with 10% sodium thiosulfite in THF-water mixture and was dried carefully in

Table 10

Reduction of Carbonyl Function with Catechol-borane Resin

Functionality	Substrate	Solvent	Time (hr)	% Substrate Reacted
Aldehyde	Benzaldehyde	THF	0	0
			17.5	20.8
			41.5	24.7
			113	100
Ketone	Cyclohexanone	"	0	0
			114	26.7
			142	33.4

Table 11

Selective Reduction of Benzaldehyde in Presence of Various Substrates

Substrate	% Unreacted substrate	% Substrate reacted
C_6H_5-CHO	-	100
Ccyclohexene	100	-
n-C_4H_9Br	100	-

vacuo prior to use. The last traces of moisture on the resin were removed by refluxing with benzene. An elemental analysis of the resin after 18 hours of reaction indicated that the available catechol moieties were *ca* 50% transformed to the *o*-phenylene phosphorochloridate (1.43 meq/g).

EXPERIMENTAL METHODS

A. GENERAL INFORMATION

All reagents used in this study were either obtained commercially or synthesized in this laboratory by one of the methods described herein. Solvents of commercial reagent grade were purified before use following the methods described in "Purification of laboratry Chemicals", by Perrin,[124] et al. Melting points were determined on a Thomas-Hoover Capillary Melting Point Apparatus and are uncorrected.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee, or by Mr. Ralph Seab, Louisiana State University-Baton Rouge. Infrared spectra were recorded from 4000 to 600 cm^{-1} on a Perkin-Elmer 137 spectrometer. Nuclear magnetic resonance spectra (nmr) were recorded on a Varian Associates HA 60 or Bruker WP 200. Chemical shifts are given in ppm (δ) relative to the internal standard using either tetramethylsilane (TMS) or hexamethyldisiloxane. Gas chromatography (GC) was conducted on a Hewlett-Packard Model HP. 5700 A GC equipped with a Model HP. 3373 B Digital Integrator. The molecular weight distributions were obtained on a Waters Associates Model 200 Gel-Permeation Chromatograph (GPC) equipped with automatic injection and collection unit.

B. CHEMICAL MODIFICATION OF POLYMERIC MATRICES: ELECTROPHILIC APPROACH

(i) Preparation of Chloromethylating Agents

1. 1,4-bis(chloromethoxy)butane: The procedure of Olah, et al.,[105] was used with some modification. In a three-necked round flask

equipped with a mechanical stirrer, a HCl gas inlet, and a condenser, was added paraformaldehyde (80 g, 2.67 mole) and 1,4-butanediol (120 g, 1.33 mole). The flask was cooled to 5-10° in an ice-bath while anhydrous HCl was passed into the mixture until it was saturated. The mixture was stirred while the temperature was maintained below 20°. After all the solid residue disappeared, the mixture was stirred for an additional 2-3 hours.* The mixture was then transferred to a separatory funnel and was allowed to stand overnight in the refrigerator; during which time the mixture separated into 2 layers. The lower layer, after separation, was washed with cold water several times until the washing was neutral to pH paper and dried with anhydrous $MgSO_4$. The crude product was filtered and distilled under reduced pressure to give 154 g of a colorless oil,** b.p. 112-114°/14 mm of Hg (uncorrected).

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*Rate of reaction depends on rate of stirring and rate of passage of the hydrogen chloride.

**Yield was always more than 60% depending on the factors above.

2. 1-Chloromethoxy-4-chlorobutane: 1-Chloromethoxy-4-chlorobutane was prepared by treating a mixture of 30.3 g (1 mole) of paraformaldehyde and 72.1 g (1 mole) of tetrahydrofuran while passing anhydrous HCl to the mixture. After the solid dissolved (ca 30 min.), the reaction temperature was allowed to rise to 60° during the HCl addition and maintained at that temperature for an additional two hours. The resultant mixture was transferred to a separatory funnel, cooled to 10° and the lower phase was dried over anhydrous $MgSO_4$ and sparged with nitrogen until 127.1 g of clear oil remained. Fractional

distillation of the residue afforded 114.2 g (0.73 mole) of the product, b.p.70°/5 mm of Hg (uncorrected).

3. Attempted preparation of 1,2-bis(chloromethoxy)ethane: A mixture of 51.8 g (0.699 mole) of 1,3-dioxolane, 40 g (1.33 mole) paraformaldehyde, and 20 g (0.147 mole) of freshly fused $ZnCl_2$ in a three-necked flask equipped with a condenser, a mechanical stirrer, and a HCl inlet was stirred in an ice-bath while passing anhydrous HCl into the mixture. The temperature of the mixture was then allowed to rise to 60° and maintained at that temperature for 8 hours. At this point, most of the solid was still undissolved. The mixture was then filtered through glass wool and the filtrate was washed with cold water. It was, however, soluble in water, and no significant crude product was obtained.

(ii) Chloromethylation of the Performed Polymers

1. Chloromethylation of Poly[1,4-phenylene(1-methylethylidene)-1,4-phenylene carbonate] (Polycarbonate): Polycarbonate (2.54 g, 0.01 mole) was placed in a three-necked resin kettle equipped with a condenser, a mechanical stirrer, and a dropping funnel. Tetrachloroethane (80 ml) was added, and the mixture was stirred and warmed to 110-115° in an oil bath in order to facilitate dissolution. After dissolution was complete, the mixture was allowed to cool to room temperature and 1,4-bis(chloromethoxy)butane (3.74 g, 19.98 mmol) was added. Antimony pentachloride (1.5 ml) was injected into the solution, it was stirred at room temperature for about 5-10 min. and heated to 110-115° for an additional 7 hours. The product was isolated by pouring the solution into methanol; the precipitate was redissolved in

chloroform and reprecipitated in methanol and dried in vacuo at 40° overnight. An NMR spectrum of the product indicated that approximately 18% chlormethylation (based on mono substitution) had occurred. NMR ($CDCl_3$): δ 1.4-1.9 (s, 6H, gem CH_3), 4.6 (s, 0.36H, CH_2Cl), 7.23 (7.82H, ArH).

2. Chloromethylation of Poly[oxy-2,6-dimethyl-1,4-phenylene] (PPO): To a three-necked resin kettle equipped with a condenser, a mechanical stirrer, and a pressure-equalizing dropping funnel, was added a solution of 1,4-bis(chloromethoxy)butane (3.2 g, 17.1 mmole) in chloroform (20 ml). The flask was cooled to 0-5° under a positive nitrogen pressure and stannic chloride (0.5 ml, 4.3 mmole) was injected into the mixture. A solution of PPO (1.0 g, 8.2 meq) in chloroform (20 ml) was added dropwise into the mixture with vigorous stirring. After the addition was complete, the ice-bath was removed, and the mixture was stirred at room temperature for an additional 1 hour. Methanol (1 ml) was then added to deactivate the catalyst. Poly(oxy-2,6-dimethyl-3-dimethyl-3-chloromethyl-1,4-phenylene) was isolated by precipitation in methanol, reprecipitation and drying in vacuo at room temperature for 24 hours; NMR ($CDCl_3$): δ 2.04 (s, 3H, CH_3, trans and cis to CH_2Cl respectively), 4.95 (bs, 2H, CH_2), and 6.09 (s, 1H, ArH). A weak singlet at δ 6.46 confirms the presence of unsubstituted ring. Elemental analysis is consistet with 93% chloromethylation; Found: C, 65.44; H, 5.49; Cl, 19.53 (Calcd: C, 65.22; H, 5.47; Cl, 19.55).

3. Chloromethylation of Polystyrene: 1,4-Bis(chloromethoxy)butane (7.48 g, 0.04 mole) dissolved in 50 ml $CHCl_3$ was added into a three-necked resin kettle equipped with a mechanical stirrer, a condenser, and a pressure-equalized dropping funnel. While a positive nitrogen

pressure was maintained, the flask was cooled down to 0-5° in an ice-bath; and stannic chloride (0.7 ml, 6.02 mmole) was injected into the mixture. A solution of polystyrene (2.08 g, 0.02 mole) in chloroform (20 ml) was added slowly to the vigorously stirred solution. Addition was complete in 2 hours; the mixture was stirred at room temperature for an additional 1 hour. Methanol (1 ml) was then added to the solution to deactivate the catalyst. The mixture was filtered through glass wool and precipitated in methanol. The polymer was dried in vacuo at 40° for 48 hours; NMR ($CDCl_3$): δ 1-2.2 (bs, 3H, -CH-CH_2-), 4.58 (bs, -CH_2Cl), 6.2-6.85 (bs, ArH), 6.85-7.4 (bs, ArH). The area of the peak at δ 4.58 indicated 53% chloromethylation.

4. Chloromethylation of Polysulfone: To a solution of polysulfone (7.5 g, 17.0 meq) in 150 ml tetrachloroethane was added 20 g (0.13 mole) of crude 1-chloromethoxy-4-chlorobutane and 0.5 ml (3.93 mmole) of antimony pentachloride. The solution was heated to 110° for two hours during which time a deep orange color developed. After deactivating the catalyst with 5 ml of methanol, 8.85 g of chloromethylated polysulfone, was isolated by precipitation in methanol, dissolution in chloroform and reprecipitation in methanol; NMR ($CDCl_3$): δ 1.68 (s, 6H, gem CH_3), 4.53 (s, 3.5H, CH_2Cl), 6.9-7.4 (m, 10.5H, ArH), 7.9 (d, 4H, ArH ortho to -SO_2). Elemental analysis was consistent with the introduction of 3.1 meq/g active chloride; Found: C, 65.89; H, 4.81; Cl, 11.02; S, 5.39.

5. Chloromethylation of Phenoxy resin: A solution of stannic chloride, 1.2 g (4.6 meq) in 25 ml tetrachloroethane was cooled to 5° for 1 hour before raising the temperature to 50° for 3 hours. The crosslinked chloromethylated resin was separated by filtration and washed with chloroform (50 ml) and methanol (200 ml). After drying at

60° in vacuo, 2.3 g of the crosslinked product was obtained. Analysis indicated the presence of 4.67 meq/g active chloride; Found: C, 63.14; H, 5.76; Cl, 16.58.

(iii) Chemical Modifications of Chloromethylated PPO

In a typical reaction, a solution of nucleophile (1.1 mmole) in a mixture of THF/H_2O or Dioxolane/H_2O (10:1 v/v) was added to THF or dioxolane solution of polymer containing ~ 1 meq of active chlorine. The mixture was heated to about 50° and was maintained at that temperature with constant stirring for approximately 4 hours. The mixture was then allowed to come to room temperature and was filtered to remove unreacted nucleophile and by-product salt. The filtrate was poured into methanol, the precipitate was isolated and dried in vacuo at 40° to constant weight. The extent of substitution was estimated by elemental analysis. The results are summarized in Table 7, page 59.

(iv) Preparation "Blocked" Catechols

1. 1,3-Benzodioxole: In a three-necked round flask equipped with a condenser, a nitrogen inlet, a dropping funnel, and a mechanical stirrer; a mixture of H_2O (20 ml), dibromoethane (26.08 g, 0.15 mole), and tricaprylylmethylammonium chloride (0.4 g, 1mmole) was stirred vigourously and heated to reflux. The air in the system was displaced with nitrogen. A solution of catechol (11.0 g, 0.25 mole) in H_2O (50 ml) was added slowly to the stirred mixture at such a rate that the addition was complete in 1.75 hours. The reaction mixutre was refluxed and stirred vigorously for an additional 1.3 hours. The mixture was allowed to come to room temperature and was extracted with ether (3 x 50

ml). The extract was dried with anhydrous $MgSO_4$ and concentrated to yield 7.4 g of the crude product. Distillation of the crude oil at reduced pressure gave 1,3-benzodioxole (6.2 g) as a colorless oil, b.p. 60°/9 mm of Hg (Lit.[125] b.p. 172-75°/755 mm of Hg). NMR ($CDCl_3$): δ 5.87 (s, 2H, $-CH_2-$), 6.8 (s, 4H, ArH).

2. 2,2-Dimethyl-1,3-benzodioxole: A mixture of catechol (25 g, 0.227 mole) and acetone (14 g, 0.24 mole) was slurried in a flask fitted with an efficient condenser and a calcium chloride drying tube. Phosphorous pentoxide (50 g, 0.352 mole) was added in several portions over 0.25 hour with rapid shaking; the solution darkened as the exothermic reaction occurred. The flask was shaken in a water bath at 50° for an additional 2.4 hours. The liquid was decanted and the solid residue was washed several times with acetone; the washings were combined with the liquid phase. After evaporating the acetone, the crude product was isolated by distillation under reduced pressure in a Kugelrohr apparatus. Fractional distillation at reduced pressure yielded 21 g of the product, b.p. 68°/10mm of Hg (uncorrected). IR: 1460 (s), 1220 (s), 970 (m), 838 (m), 815 (m), and 7355 cm^{-1}. NMR ($CDCl_3$): δ 1.55 (s, 6H, $(CH_3)_2-C-$), 6.63 (S, 4H, ArH).

3. o-Phenylene carbonate: In a nitrogen-flushed 300 ml three-necked flask, catechol (15 g, 0.136 mole) was dissolved in deaerated water containing 13 g (0.325 mole) of sodium hydroxide. A solution of 30.7 g (0.31 mole) of commercial phosgene in 100 ml of toluene was then added to the flask in several portions over a period of 1 hour with constant stirring. During the addition the temperature was maintained at 0-5°. After addition of the phosgene solution was completed, the mixture was stirred at 5° for an additional 2 hours. The mixture was

allowed to come to room temperature, filtered, and the solid was pressed on the suction funnel to remove as much water as possible. The aqueous portion of the filtrate was separated and discarded. The solid in the funnel was redissolved in toluene layer. The warm toluene solution was filtered and distilled under reduced pressure (water aspirator) until the product began to crystallize. The residue was warmed to redissolve the solid, and then chilled. The crystalline o-phenylene carbonate was collected on a suction filter and recrystallized one from toluene. It was dried in a vacuum desiccator to constant weight; the yield was 15.4 g, m.p. 119-120° (lit.[126] m.p. 119-20°).

(v) Friedel-Crafts Reactions of Chloromethylated Preformed Polymers and the Catechol Synthons

1. Reaction of Chlormethylated Poly[oxy-2,6-dimethyl-1,4-phenylene] with 1,3-benzodioxole

(a) $ZnCl_2$ as a catalyst

In a three-necked flask equipped with a condenser, a pressure-equalized dropping funnel, and a mechanical stirrer, a slurry of dried zinc chloride (1 g, 7.34 mmole) in chloroform (ca 40 ml) was heated to 58-60°. A solution of 1,3-benzodioxole (5.6 g, 45.86 mmole), and chloromethylated PPO (2.3 g, 12.3 meq Cl) in 40 ml cchloroform was then added dropwise to the hot catalyst slurry. After 3-4 hours at 60°, the heating bath was removed and stirring continued at room temperature for an additional 48 hours. The reaction mixture was then filtered through glass wool and poured into methanol. The precipitated white polymer (2.6 g) was dried in vacuo at 60° overnight. The elemental analysis, based on % unreacted chlorine, indicated 72.7% substitution; Found: C,

72.91; H, 5.78; Cl, 3.99.

(b) $SnCl_4$ as a catalyst

In a flask containing chloromethylated PPO (2.0 g, 10.3 meq Cl) and 1,3-benzodioxole (6.1 g, 50 mmole) in 60 ml chloroform, stannic chloride (0.3 ml) in 6 ml chloroform was added slowly (ca 20 drops/min.) to the mixture with stirring. After addition of catalyst was completed, it was stirred at room temperature for an additional 4 hours. The reaction was terminated by injection of methanol (2 ml) while stirring until the solution was clear. Filtration, precipitation in methanol (500-600 ml) and drying in vacuo at 40° overnight yielded 2.6 g of the adduct. NMR ($CDCl_3$): δ 4.1, -CH_2-benzodioxole; 4.95, CH_2Cl; 5.8, ArH on benzodioxole subst. backbone; 6.45, ArH of unsubst. PPO; 6.6-6.7, ArH of benzodioxole. Integration of spectra was consistent with 57% benzodioxole substitution (ca 70.1% conversion), 25% residual chloromethyl substituents and 18% unsubstituted oxo-2,6-dimethyl-1,4-phenylene units.

2. Reaction of chloromethylated Poly[oxy-2,6-dimethyl-1,4-phenylene] with o-phenylene carbonate: The reaction was performed in a similar fashion as in the reaction of 1,3-benzodioxole with the chloromethylated PPO described above. However, under identical conditions, only 16%* substitution was observed (based on % oxygen found in the product; Found: C, 73.59; H, 8.63; Cl, 4.91; O, 12.87.

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*This value does not correspond to the value obtained by computation based upon chlorine analysis which may indicate some degree of crosslinking (inter- and intramolecular alkylation).

3. Reaction of chloromethylated Polystyrene resin with 2,2-

dimethyl-1,3-benzodioxole: The chloromethylated polystyrene resin (5 g, 13.2 meq) was swollen in 80 ml dichloromethane in a three-necked resin kettle equipped with a dropping funnel, a condenser, and a mechanical stirrer, 2,2-dimethyl-1,3-benzodioxole (2.0 g, 13.3 meq) was added to the slurry. The flask was then cooled in an ice-bath to 0-5° before injection of stannic chloride (0.2 ml) to the suspension. The slurry was stirred at room temperature for an additional 24 hours. At this point, the beads became purple. The reaction was terminated by injecting 10 ml of methyl alcohol to the reaction mixture while stirring. The beads were removed and wash serially with methanol, water, water/dioxane, dioxane, water, and methanol. Brown colored beads (5.1 g) were obtained after drying in vacuo for 2 days at 60°. Elemental analysis, based on percent oxygen, indicated ca 51.5% substitution; however, the amount of unreacted chlorine found indicated some degree of intermolecular alkylation of the chloromethylated polymer. Found: C, 88.22; H, 7.40; Cl, 0.49; O, 3.67.

(vi) Attempted Reduction of Pendant Chloromethyl Groups with Lithium triethylborohydride (Super Hydride)

1. Chloromethylated PPO: To a dried three-necked flask equipped with a nitrogen inlet, a condenser, and a dropping funnel, flushed with nitrogen, was added chloromethylated PPO (0.5 g, 2.7 meq available chloromethyl group) dissolved in 15 ml dried THF. Lithium triethylborohydride solution in THF (1 M, 4.2 ml) was injected into the dropping funnel through a rubber septum under a positive nitrogen pressure. Lithium triethylborohydride solution was then added slowly into the polymer solution. The mixture was allowed to stir magnetically

at room temperature for 0.5 hour, followed by injection of methanol (1 ml) into the mixture. The polymer was obtained by filtering through glass wool and precipitating in a large amount of methanol. The precipitated polymer was gel-like in appearance and became very brittle and insoluble after drying in vacuo, indicating some degree of degradation.

2. Chloromethylated PPO partially substituted with 1,3-benzodioxole: The reduction method was performed similar to the procedure described above. In this experiment, however, the polymer (1 g, ca 1.2 meq unreacted chloromethyl group) and lithium triethylborohydride (1 M, 4.2 ml) were employed. The reaction time was reduced to 5 min. to avoid degradation. NMR and IR spectra of the polymer indicated no evidence of reduction.

(vii) Preparation of 3,4-Methylenedioxybenzyl chloride (Piperonyl chloride)

1. From 1,3-benzodioxole: A three-necked flask equipped with a mechanical stirrer, a gas inlet tube connected to a HCl tank, and a condenser, was charged with a mixture of paraformaldehyde (7.5 g, 0.25 mole), 1,3-benzodioxole (30 g, 0.246 mole) and anhydrous $ZnCl_2$ (0.5 g). Anhydrous HCl was passed into the stirred mixture at room temperature for 2.6 hours. The mixture was poured into 100 ml ice-water. The solid residue was removed and the solution was extracted with 100 ml ether. The extract was washed with water, followed by saturated Na_2CO_3 solution and finally with water. After drying the extract with anhydrous $MgSO_4$ and concentrating, the residue was fractionally distilled under reduced pressure. The product (11 g)* was

collected at 101-102°/2 mm of Hg. NMR ($CDCl_3$): δ 4.58 (s, 2H, -$\underline{CH_2}$Cl), 6.02 (s, 2H, -O-$\underline{CH_2}$-O-), 6.9 (d, 3H, Ar$\underline{H}$).

*Yield was very low due to the formation of dimers, oligomers, etc., during distillation.

2. From 3,4-methylenedioxyphenylmethanol (piperonyl alcohol)

Method A: Piperonyl alcohol (15.3 g, 0.099 mole) was placed in a 250 ml Erlenmeyer flask and 25ml of conc. HCl was added carefully. The mixture was stirred until all the solid dissolved. The solution was poured into a separatory funnel, and a phase separation occurred. The lower organic layer was separated and washed serially with H_2O, twice with 10% Na_2CO_3 and finally with H_2O, then dried with anhydrous $MgSO_4$ to give a nearly quantitative yield of crude product. It was then distilled under reduced pressure through a short-path column to yield about 14.0 g (83%) of the product (b.p.112.5°/5 mm of Hg).

Method B: Piperonyl alcohol (15.3 g, 0.1 mole) and pyridine (8 g, 0.1 mole) were added to a three-necked round flask equipped with a pressure-equalized dropping funnel, a mechanical stirrer, and a condenser connected to a 10% NaOH trap. The stirred mixture was placed in an ice-bath while thionyl chloride (12 g, 0.1 mole) was added gradually; the temperature was kept below 30°. The reaction mixture was stirred for 0.5 hour after the addition was complete and then poured on ice and stirred for thirty minutes. The product was separated, washed until neutral with saturated Na_2CO_3 solution, dried with anhydrous $CaCl_2$ and fractionally distilled under reduced pressure to yield 15.5 g of the product (b.p.112.5°/5 mm of Hg).

(viii) Friedel-Crafts Reactions of the Preformed Polymers and 3,4-Methylenedioxybenzyl chloride (Piperonyl chloride)

1. Reaction of polystyrene with piperonyl chloride: A three-necked resin kettle equipped with a pressure-equalized dropping funnel, a condenser, and a mechanical stirrer, was charged with a solution of polystyrene (1.04 g, 10 mmole) in dichloromethane (30 ml). The vessel was cooled to 0-5° before injecting $SnCl_4$ (0.05 ml) into the stirred solution. Piperonyl chloride (0.85 g, ca 5.0 mmole) was then added through the funnel at such a rate that the addition was complete in 0.25 hour. After addition was complete, the solution was stirred in an ice-bath for an additional 5 minutes and then at room temperature for an additional 1.25 hours. The reaction was terminated by injecting 1 ml CH_3OH containing a few drops of NH_4OH. At this point, the mixture turned from intense blue to light grey. The reaction mixture was centrifuged and the supernatant, a clear solution, was poured into methanol. A precipitate formed and was isolated and dried in vacuo at 60° for 24 hours to yield ca 0.8 g of the polymer; the grey colored residue was dried in vacuo at 60° to constant weight. Elemental analysis indicated that only ca 40.6% of the available piperonyl chloride attached to the polymer substrate; the residue was actually a polymer obtained by condensation polymerization via Friedel-Crafts alkylation of piperonyl chloride. Found: For the substituted polymer; C, 87.75; H, 7.28; O (by diff.), 4.97. For the residue; C, 74.39; H, 5.47.

2. Reaction of Poly[oxy-2,6-dimethyl-1,4-phenylene] with piperonyl chloride: The reaction was performed in a similar fashion as above. However, under identical conditions, a crosslinked polymer formed and precipitated from the solution. Only trace amounts of the expected soluble polymeric adduct was obtained.

C. CHEMICAL MODIFICATION OF POLYMERIC MATRICES: NUCLEOPHILIC APPROACH

1. Preparation of 3,4-methylenedioxyphenylmethanol (piperonyl alcohol) from piperonal: The PtO_2 used as a catalyst for hydrogenation was prepared by reaction of $H_2PtCl_6.6H_2O$ and sodium nitrite in a molten state. A solution of piperonal (30 g, 0.2 mole) in 95% ethanol (200 ml, 0.5 ml of 0.2 M $FeCl_2$ and 0.2 g of PtO_2 were added to a medium pressure hydrogenation bottle. Hydrogenation was initiated at 44-45 psi gauge pressure by agitating the bottle. Hydrogen uptake ceased at 30 psi. The mixture was filtered to remove the catalyst suspension and the filtrate was concentrated by flash distillation. Decolorizing carbon was employed at this point to remove the color. The clear liquid crystallized from a mixture of ethyl ether and petroleum ether to yield 26.8 g (88%) of piperonyl alcohol, m.p.53-54° (lit.[127] m.p.52-53°).

2. Reaction of Poly(vinylbenzyl chloride) with piperonyl alcohol: Poly(vinylbenzyl chloride) (2.08 g, 0.02 meq) and a piperonyl alcohol (3.8 g, 0.025 mole) dissolved in a 4:1 v/v mixture of dioxane and ethanol were stirred under nitrogen in a 100 ml round flask equipped with a condenser. Potassium hydroxide pellets (1.5 g, 0.025 mole) were added through the condensor to the solution. The slurry was refluxed under nitrogen for 18 hours, then cooled and the inorganic salts removed by centrifugation. The supernatant was precipitated in 1% aqueous potassium hydroxide and reprecipitated from dioxane into water. After drying in vacuo for 48 hours, 2.0g of adduct was obtained. NMR ($CDCl_3$): δ 1-2, -C<u>H</u>-C<u>H</u>$_2$-; 3.7, -C<u>H</u>$_2$-O-C<u>H</u>$_2$-; 4.4, -C<u>H</u>$_2$Cl; 6.0-7.5, Ar<u>H</u>. Elemental analysis indicated an 84% substitution; Found: C, 74.72; H, 7.00; Cl, 2.22.

D. MONOMER SYNTHESIS

Preparation of 5-vinyl-1,3-benzodioxole (49)

Method A: From 1,3-benzodioxole

1. Preparation of 5-bromo-1,3-benzodioxole: Dioxane dibromide was used as a brominating agent and was prepared following the method of L.A. Yanovskaya, et al.[76] A solution of dioxane dibromide (10.9 g, 0.444 mole) in chloroform (30 ml) was added slowly with stirring to 4.9 g (0.04 mole) of 1,3-benzodioxole dissolved in 10 ml of chloroform. After the addition was complete, the reaction mixture was stirred at room temperature for 14 hours. The mixture was transferred to a separatory funnel and washed twice with 10% sodium hydroxide solution, then with water, until neutral to pH. The organic layer was dried with anhydrous $MgSO_4$, flash evaporated and the residue was distilled under vacuum to yield 5.2 g (60%) of the monobromo adduct, b.p.101°/6 mm of Hg (uncorrected). NMR (neat): δ 5.9 (s, 2H, -O-CH_2-O-), ca 6.98 (m, 3H, ArH).

2. Preparation of 5-vinyl-1,3-benzodioxole: In a dry three-necked round-bottom flask equipped with a mercury sealed stirrer, a dropping funnel, and an efficient reflux condenser topped with a calcium chloride tube, was placed 9.7 g (0.4 gram atoms) of magnesium turnings and about 25 ml of absolute ether. A solution of 80.4 g (0.4 mole) of 5-bromo-1,3-benzodioxole in 250 ml of absolute ether was added with stirring at a rate which maintained rapid refluxing (the reaction was initiated by placing the flask briefly in a warm-bath after 20 ml of the ether solution was added). After the addition was completed and the reaction subsided, the mixture was stirred and heated on the steam bath under reflux for an additional 0.5 hour. A cooled solution of 20 g (0.46

mole) of freshly distilled acetaldehyde in 75 ml of absolute ether was then added through the dropping funnel as rapidly as the condenser capacity permitted. The mixture was then cooled in ice, and the addition compound was decomposed by adding 100ml of a 25% aqueous solution of ammonium chloride. The ether solution was separated and dried over anhydrous magnesium sulfate followed by removal of the ether via flash distillation. The crude 5-(1-hydroxyethyl)-1,3-benzodioxole* was used without further purification. A drop of conc. H_2SO_4 was added to the crude alcohol; fractional distillation (using 1.2 x 20 cm Vigreux column) under reduced pressure using nitrogen ebulator afforded 5-vinyl-1,3-benzodioxole (47 g), b.p.122-124°/25 mm of Hg (uncorrected). IR (neat): 3080, 3000, 2975, 2885, and 2675 cm^{-1} (C-H stretch), 1625, 975 cm^{-1} ($CH=CH_2$), 1185, 1120, 1100 ($-O-CH_2-O$); NMR ($CDCl_3$): δ 5.07 (1H, cis $-CH=C\underline{H}_2$), 5.50 (1H, Trans $-CH=C\underline{H}_2$), 5.82 (2H, $-O-C\underline{H}_2-O-$), 6.60 (1H, $-C\underline{H}=CH_2$), 6.73 (2H, Ar$\underline{H}$), 6.90 (1H, Ar$\underline{H}$).

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*A small portion of crude alcohol was separated for identification purpose; it solidified upon prolonged-standing and was recrystallized from petroleum ether; NMR ($CDCl_3$): δ 1.35 (d, 3H, $-CH-C\underline{H}_3$), 2.5-2.85 (bs, 1H, $O\underline{H}$), 4.7 (q, 1H, $-C\underline{H}-CH_3$), 5.75 (s, 2H, $-O-C\underline{H}_2-O-$), 6.7 (d, 3H, Ar$\underline{H}$).

Method B: From piperonal

Magnesium turnings (14.58 g, 0.6 gram atom) were placed in a dry 1-liter round-bottom flask equipped with a dropping funnel and an efficient condenser. A solution (50 ml) of methyl iodide (38 ml) in absolute ether (300 ml) was then added to the flask. When the reaction commenced, the ether solution was added with stirring (magnetically) at

a rate which maintained rapid refluxing. After the addition was completed and the reaction subsided, the mixture was stirred and heated under reflux for 0.5 hour. It was then allowed to come to room temperature. A solution of piperonal (60 g, 0.4 mole) in 300 ml of absolute ether was added as rapidly as the exotherm would permit. After the exotherm had subsided, the mixture was heated to reflux for 1 hour. The Grignard complex was hydrolyzed with 300 ml 10% hydrochloric acid, and the supernatant ether solution was washed with 5% aqueous sodium bicarbonate, then water, then dried over anhydrous magnesium sulfate and the ether evaporated to yield 62.5 g (94%) crude 5-(1-hydroxyethyl)-1,3-benzodioxole. The crude alcohol was then fractionally distilled in the presence of a trace conc. of H_2SO_4 in a similar fashion as described in method A to afford 5-vinyl-1,3-benzodioxole, b.p.122-124°/25 mm of Hg (uncorrected). Passage of the crude product through a silica gel column (hexane eluant) and fractional distillation yielded 43.8 g (78.5%) of colorless oil, b.p.91°/0.5 mm of Hg. IR and NMR spectra were identical to the spectra obtained from the vinyl monomer prepared by method A.

E. POLYMERIZATION REACTIONS OF 5-VINYL-1,3-BENZODIOXOLE (49)

1. Homopolymerization of 49

a. Radical polymerization: A dried polymerization ampoule was charged with ca 3.3 g of 49 and 10 mg of AIBN. After three freeze-thaw degassing cycles, the tube was sealed under vaccum and immersed in a constant temperature bath at 65° for 1.5 hours. The mixture was then diluted with $CHCl_3$ and precipitated in methanol. After reprecipitation and drying at 40° in vacuo for 24 hours, 0.5 g (15.2% conv.) of white amorphous polymer was obtained. Molecular weight based upon polystyrene standards: $\overline{M}_w$ = 168,982; $\overline{M}_n$ = 104,139; MWD = 1.62. The spectra data include: IR (film): 3065, 3005, 2940, 2675 cm^{-1} (C-H stretch), 1185, 1120 cm^{-1} (-O-CH_2-O-); NMR ($CDCl_3$): δ 1.36 (2H, -CH-CH_2-), 1.78 (1H, -CH-CH_2-), 5.88 (2H, -O-CH_2-O-), 6.06 (3.8H, ArH), 6.55 (1.2H, ArH). The ultraviolet spectrum showed maxima at 289 nm.

Anal.: Found: C, 72.89; H, 5.59

Calcd.: C, 72.97; H, 5.40

b. Anionic polymerization: Tetrahydrofuran (15-20 ml) was distilled from CaH_2 under argon directly into a carefully dried 100 ml elongated flask equipped with side arm. Freshly distilled 49 (1.6 ml, ca 2 g) was injected and the solution cooled to -70°. Injection of 1.8 ml of 2 M butyl lithium in hexane produced a permanent yellow color. After 20 min. at -70° the polymerization was terminated by injecting 1 ml of methanol. The dried polymer (0.47 g, 23.5% conv.) exhibited spectra similar to those obtained from a free radical polymerization; molecular weights: $\overline{M}_w$ = 57,163, $\overline{M}_n$ = 43,802, MWD = 1.305.

c. Cationic polymerization: 49 (1.5 ml, ca 1.87 g) was polymerized in dichloromthane (20 ml) in the presence of $BF_3.OEt_2$ (0.1

ml, 12.6 mmole) as a catalyst. The solution turned purple as the catalyst was added. After 7 hours at room temperature, the polymerization was terminated by injecting 2 ml of methanol. The dried polymer (1.2 g, 64.2% conv.) exhibited spectra similar to those from the radical and anionic polymerization. However, the average M.W. of the polymer obtained was rather low: $\overline{M}_w$ = 1,493, $\overline{M}_n$ =1,158, MWD =1.29.

2. Dilatometric studies of the homopolymerization of 5-vinyl-1,3-benzodioxole (49)

Monomer, 49, containing AIBN catalyst (ca 0.317 wt%) was carefully introduced into a bulb of a calibrated dilatometer (calibrated by mercury at 30°, $\overline{V}_0$ = 10.0828 ml, $\frac{\Delta V}{\Delta h}$ = 1.762 x 10^{-2} ml/cm). After the capillary had been attached to the bulb and sealed with mercury, polymerization was then initiated by immersing the dialometer in a constant water bath (T = 70 + 0.05°). After following the polymerization for the desired interval, the polymer was isolated by pouring the mixture into methanol, dissolving the polymer in benzene, and reprecipitating in methanol. The conversion was calculated from the weight of the polymer (1.23 g, $\overline{M}_n$ = 104,139, $\overline{M}_w$ = 168,982) after drying for 48 hours, at 40° in vacuo. The initial rate of polymerization (R_p') was calculated from the initial volume by using the following equation:

$$R_p' = \frac{\Delta V}{\Delta T}\frac{(1)}{VK}$$

where the contraction K was estimated from gravimetric conversion data to be 0.31958. The plot of contraction during polymerization of the monomer, 49, is shown in Figure 7; the initial rate of polymerization,

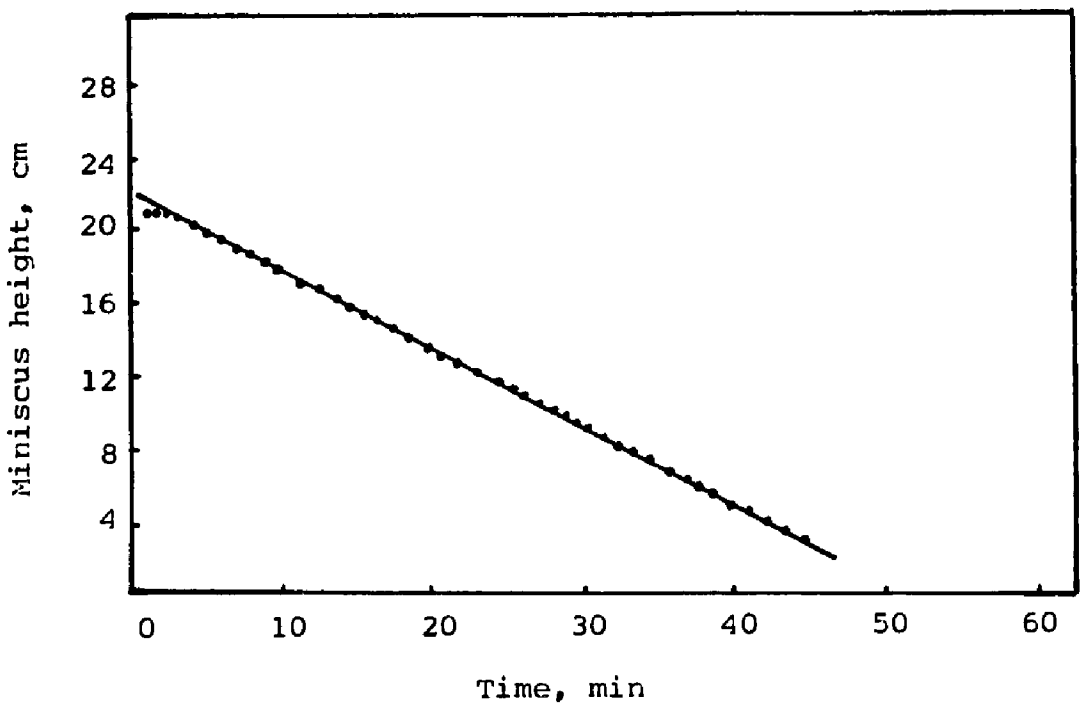

Figure 7: Typical plot of contraction in the dilatometer during polymerization of 5-vinyl-1,3-benzodioxole

1.534×10^{-2} mol.l^{-1}.min^{-1} ($R_p = R_p' [M] = 7.28$ mol.l^{-1}).

3. Determination of reactivity ratio in copolymerization of 5-vinyl-1,3-benzodioxole (49)

a. With styrene (M_2): Styrene was purified before use by extracting three times with 10% aqueous NaOH to remove the inhibitor, washed three times with distilled water, dried over anhydrous $CaCl_2$ and distilled under dry nitrogen at 20 mm of Hg and 40-42° immediately prior to the polymerization experiment.

Styrene (M_2) and 5-vinyl-1,3-benzodioxole (M_1) were weighed into 10 ml hydrolysis tubes containing ca 0.01 g (0.06 mmole) AIBN. The total molar composition of the monomer mixture was maintained at ca 0.028 mole, but the feed ratio was varied. The tubes were degassed in vacuum by three alternate freeze-thaw cycles and then sealed in vacuo. The tubes were immersed in a 70° oil bath until a noticeable increase in viscosity indicated the formation of copolymer. The copolymers were diluted with 10 ml of chloroform and precipitated in methanol. The copolymers were reprecipitated twice from benzene into methanol. The precipitates were dried in vacuo at 60° for 48 hours and weighed to determine the extent of conversion. The composition of the copolymers was calculated from their elemental analysis. Results are shown in Table 12.

The reactivity ratios were estimated by the method of intercepts (Figure 8) or the Fineman-Ross method (Figure 9). Values of $r_1 = 1.02$ and $r_2 = 0.6$ were obtained.

b. With methyl methacrylate (M_2): Methyl methacrylate (MMA) was extracted twice with equal parts of 10% aqueous NaOH and subsequent washings with distilled water until litmus paper indicated the absence

Table 12

Copolymerization of 5-Vinyl-1,3-benzodioxole (M_1) with Styrene (M_2)

Feed		Mole fraction in feed			Initiator	Polymerization copolymer[b]			Mole fraction in	
wt_1(g)	wt_2(g)	M_1	M_2	M_1/M_2 (=F)	(mg) time[a] (h)	m_1	m_2	% conv.	(=f)	m_1/m_2
3.682	0.295	0.897	0.10	8.692	11.6	1.20	5.78	0.902	0.098	9.204
3.274	0.588	0.794	0.206	3.861	9.93	1.20	4.66	0.810	0.189	4.272
1.259	2.014	0.302	0.698	0.434	10.77	0.75	3.97	0.377	0.623	0.606
0.408	2.583	0.099	0.901	0.109	9.61	0.75	3.67	0.146	0.854	0.172

[a]Polymerization temperature, 70°.

[b]Calculated from elemental analyses.

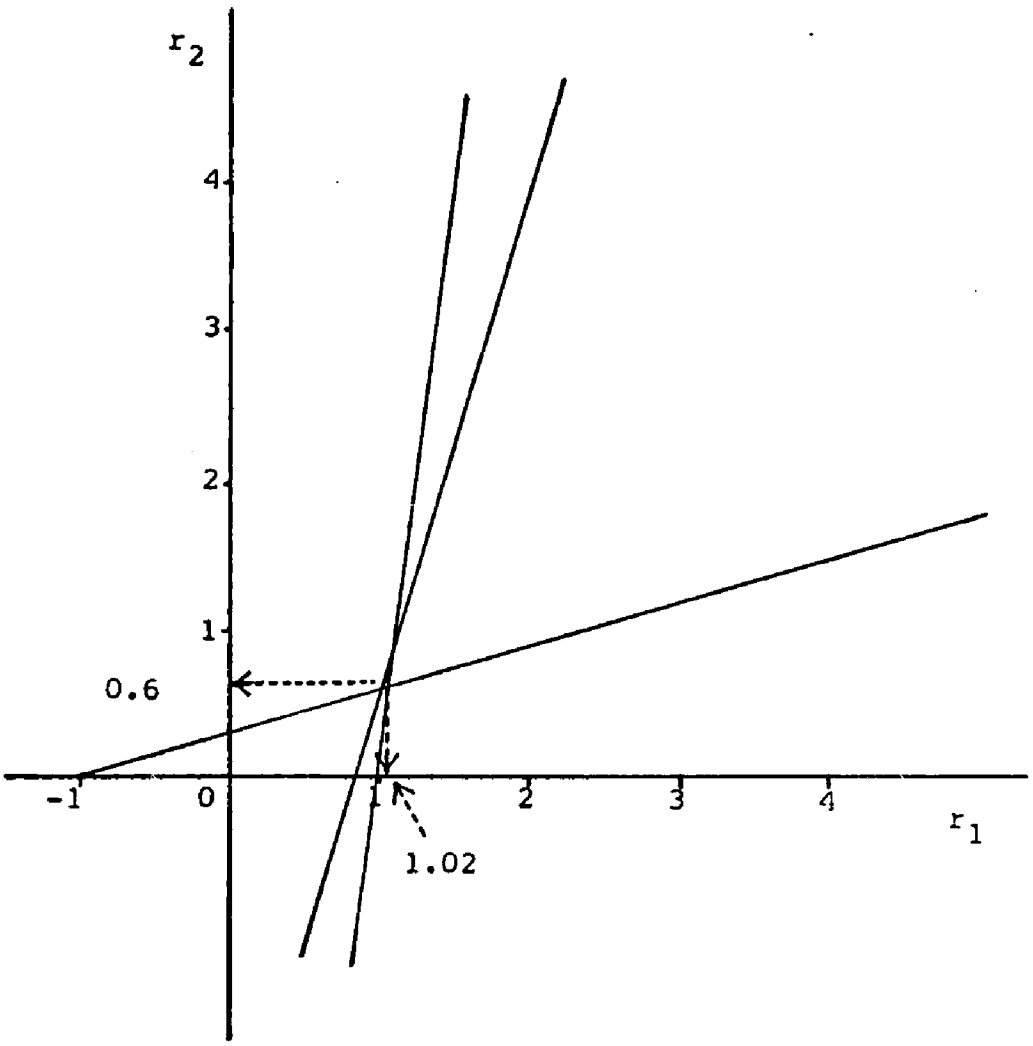

Figure 8: Method of intersection plot for 5-vinyl-1,3-benzodioxole (M_1) - styrene (M_2) copolymerization.

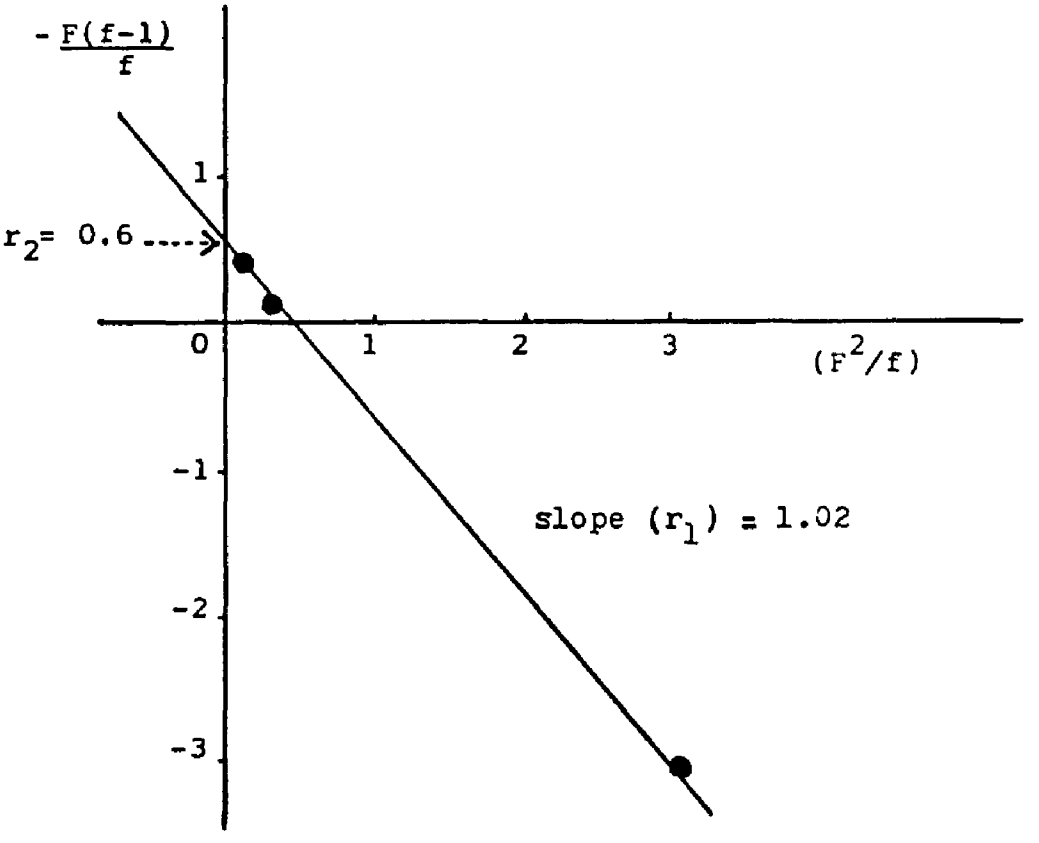

Figure 9: Fineman-Ross plot for 5-vinyl-1,3-benzodioxole (M_1) - styrene (M_2) copolymerizations

of the base. The monomer was dried with anhydrous $MgSO_4$ and was distilled under dry nitrogen, b.p.33-35° (60 mm of Hg).

Methyl methacrylate (M_2) and 5-vinyl-1,3-benzodioxole (M_1) were copolymerized in bulk at 60° using AIBN (1% from the monomers) as initiator. The copolymerizations were carried out in an NMR sample tube. Three feed compositions were used:

$x_o = 0.5415$; where

$x_o = 0.9265$; $x_o = M_1/M_2$

$x_o = 2.2304$;

The instantaneous monomer concentration as a function of time (Figure 3, p. 71) was followed by the ratio of two signal areas in the ^1N NMR spectrum. The signals were those from the unsaturated region for the monomer and the signal of the reference substance, hexamethyldisiloxane. The reactivity ratios were estimated by the method of intercepts (Figure 4, p. 74). Values of $r_1 = 1.1$ and $r_2 = 0.45$ were obtained.

F. SUSPENSION TERPOLYMERIZATION OF 5-VINYL-1,3-BENZODIOXOLE (49), STYRENE, AND DIVINYLBENZENE

A 250 ml resin kettle equipped with an efficient mechanical stirrer was charged with 150 ml distilled water containing 0.45 g barium sulfate and 0.25 g of polyvinyl alcohol (85% hydrolyzed). The solution was deaerated by sparging with nitrogen while heating the vessel to 60°. A solution of azo-bis-isobutyronitrile (0.5 g, 1 mole%) in a mixture of 49 (27.94 g, 0.189 mole), styrene (19.63 g, 0.189 mole), and divinylbenzene (0.98 g, 0.0075 mole) was injected into the vigorously stirred aqueous solution. The suspension was stirred at 75-80° for 18 hours before it was allowed to cool to room temperature. The beads were isolated by filtration and washed serially with methanol, benzene, methanol, tetrahydrofuran and methanol. After drying at 60° *in vacuo* to a constant weight of 46.6 g, 98% conversion, the beads could be subjected to further modifications.

Anal: Found: C, 80.51; H, 6.40.

G. REMOVAL OF FORMAL BLOCKING GROUPS

1. With 48% hydrobromic acid. A 100 ml three-necked flask was charged with a slurry of 1.1 g of poly(5-vinyl-1,3-benzodioxole) resin (4.54 meq of active site) in 25 ml glacial acetic acid and 5 ml 48% hydrobromic acid was added dropwise while refluxing and stirring. The mixuture was refluxed for 18 hours. The black polymer resin was isolated by filtration and washed several times with hot water until the washing media was neutral, then washed with hot methanol. It was dried at room temperature in vacuo to constant weight. The degree of swelling of the beads was decreased to a great extent; this indicated some degree of oxidation and further crosslinking.

2. With dil. sulfuric acid in the presence of 5,5-dimethyl-1,3-cyclohexanedione (Dimedone): To the terpolymer beads (1 g, 4.13 meq of active site) suspended in 50 ml of a mixture of water and ethanol (50/50: v/v) were added 1 g of dimedone and 5 ml of conc. H_2SO_4. It was refluxed under a nitrogen atmosphere for ca 34 hours. The white polymer resin was then filtered and washed serially with H_2O, dioxane, H_2O and several times with MeOH. It was dried in vacuo to constant weight. An elemental analysis of the treated resin was identical to that of the untreated beads, which indicated no breaking of formal linkage.

3. With toluene sulfonic acid and 1-butanethiol: A stirred solution of 1 g poly(5-vinyl-1,3-benzodioxole) (7 meq) in 30 ml DMF was treated with toluene sulfonic acid monohydrate (1.33 g, 7 meq) and 1-butanethiol (1.5 ml). The mixture was raised to ca 70° in an oil bath and was kept at that temperature for 20 hours under a positive nitrogen atmosphere. White polymer was isolated by precipitating the reaction mixture in methanol and drying in vacuo at room temperature to constant

weight.

NMR ($CDCl_3$) and elemental analysis were, however, identical to that of the starting polymer.

4. With conc. sulfuric acid and 1-butanethiol: The set-up and procedure was the same as in (3), except that toluene sulfonic acid was replaced by conc. sulfuric acid. Nevertheless, an elemental analysis indicated no breaking of formal linkage.

5. With boron trichloride

Method A: Terpolymer beads, 12.16 g (4.122 meq/g of the available active site) were swollen in 160 ml of dichloromethane and the suspension was cooled under nitrogen in a dry-ice acetone bath while 100 ml of 1 M boron trichloride in dichloromethane was injected. The mixture was allowed to warm to room temperature and stirred for 30 hours before hydrolysis of the borate complex was effected by adding 8 ml of methanol. The hydrolyzed beads were washed serially with methanol, and dried at 40° in vacuo. The yellowish brown colored resin (11.5 g) turned to purple upon exposure to heat and air, IR (KBr pellet) 3600-3100 cm^{-1} (broad) and disappearance of formal bands at 2780 and 1035 cm^{-1}.

Anal: Found C, 79.11; H, 6.85; Cl, 1.63; B, 0.02.

Method B: An alternative procedure involved addition of 20ml of 1 M boron trichloride in dichloromethane to a slurry of terpolymer beads (2 g, 8.244 meq) in 50 ml DCM. The mixture was stirred at room temperature under nitrogen for 18 hours before 3 ml of 1-butanethiol was injected. The suspension was stirred at room temperature for an additional 6 hours. The beads were removed and washed serially with hot methanol, hot water, hot methanol, hot water, and finally with methanol.

The purple resin (1.91 g) was obtained after drying in vacuo at room temperature for 3 days.

Anal: Found: C, 78.03; H, 6.86; B, 0.014; S, 1.04. IR: the same as above

Method C: The best result was obtained by first swelling the terpolymer (15 g, 64.5 meq) by refluxing with dichloromethane (200 ml) for 0.5 hour. The slurry then was allowed to cool to room temperature and then in a dry-ice acetone bath while 130 ml of 1 M boron trichloride was injected. The mixture was stirred at room temperature under nitrogen for about 24 hours before methanol (20 ml) was injected. The deactivated mixture was heated to reflux for 2 hours and stirred at room temperature overnight. The beads were removed and washed several times with hot methanol, followed by hot water, until the filtrate was neutral to pH. Purple beads (14.3 g) were obtained after drying in vacuo at room temperature to constant weight. IR (KBr pellet): the same as above.

H. OXIDATION OF CATECHOL RESIN TO THE CORRESPONDING o-BENZOQUINONE

1. With hydrogen peroxide: In a 100 ml round bottomed flask, a mixture of 1.0 g free-catechol resin (terpolystyrene-4-vinyl-1,2-dihydroxybenzene--2% DVB) (ca 4.31 meq catechol moieties available) and 30 ml 3% hydrogen peroxide aqueous solution was stirred overnight at room temperature. The resin was filtered, washed several times with 20 ml each of hot water, and dried at room temperature in vacuo to yield brown colored beads. IR (KBr pellet) 1730 cm^{-1} (s) reveals presence of carbonyls.

Anal: Found: C, 76.34; H, 6.56.

2. With potassium nitrosodisulfonate (Fremy's Radical): To a stirred suspension of 0.5 g free-catechol resin (terpolystyrene--4-vinyl-1,2-dihydroxybenzene--2% DVB) (ca 2.2 meq. catechol moieties available) in 10 ml DMF was added a solution of 1.2 g (4.44 mmole) potassium nitrosodisulfonate and 0.3 g Na_2HPO_4 in 10 ml water. The suspension was stirred at room temperature for 3 hours and was then filtered and washed with DMF, and 1:1, DMF: water, several times with hot water, 2-3 times with CH_3OH, and CH_2Cl_2 and dried in vacuo at 60° to constant weight to yield ca 0.5 g resin; IR* (KBr pellet) 1730 cm^{-1} (s), indicative of extensive oxidation to the o-benzoquinone.

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*The pellet was partially opaque.

I. PREPARATION AND USE OF POLYMER REAGENTS

1. Preparation of catecholborane resin: Poly(5-vinyl-catechol) resin (2 g, 8.62 meq of the available active site) in benzene (50 ml) was distilled until most of the liquid was gone and the distillate was clear. Freshly distilled (from CaH_2) tetrahydrofuran (ca 30 ml) was distilled into the slurry and the suspension was refluxed for 15 min.. The slurry was allowed to come to room temperature and then to ca -60° in a dry-ice acetone bath. While maintaining a positive nitrogen pressure, borane-tetrahydrofuran complex (1M) (13 ml) was injected into the mixture. The bath was then removed and was allowed to come to room temperature under nitrogen for an additional 40 hours. The beads were then removed by filtration under a blanket of nitrogen and washed several times with dried tetrahydrofuran and finally dried in vacuo at room temperature to constant weight.* IR (KBr pellet): 3700-3020 cm^{-1} (broad, unreacted OH), 2360, 2260 cm^{-1} (B-H stretch), 1420-1370 cm^{-1} (B-O stretch). Elemental analysis indicated that more than 50% of the available active site (catechol moiety) was converted to catecholborane.

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*The white beads were obtained at first but turned slightly purple upon prolonged storing.

a. Reduction of carbonyl function with catecholborane resin: The GLC analysis in this work was carried out on a Hewlett-Packard Model HP 5700A GC equipped with a Model 3373 B Digital Integrator using SE 30 (5% on 80/100 Chromosorb W, 0.25 in. x 6 ft.).

The substrate (i.e., benzaldehyde, cyclohexanone) (ca 1.2 mmole) was placed into a flame-dried 25 ml pear-shaped flask, fitted with

stirring bar and septum, and connected to a mercury bubbler to maintain a nitrogen atmosphere. Dried THF (10 ml) was added along with an internal standard (i.e., toluene) for GLC analysis. Catecholborane resin (1 g, ca 2.1 meq catecholborane moiety) was then added to the reaction mixture with constant stirring. In the next 30 min., the evolution of gas was noticeable and the beads turned gradually to blue; this indicated the commencement of the reaction. The results were summarized in Table 10, page 88.

When the GLC analysis indicated no further reaction, the beads were removed and quenched with water in tetrahydrofuran. At this point the color of the beads turned from blue to tan or brown.*

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*Only trace amounts of the correspondig alcohols were detected by GLC analysis.

b. Selective reduction of benzaldehyde in the presence of various substrates: Reductions were carried out similar to the procedure described above, except the mixture of substrates (ca 1.2 mmole of each) was used. The reaction mixture was stirred at room temperature for 120 hours before the reaction was terminated. GLC analysis was performed on the liquid to determine the extent of the reaction for each substrate. The results wre summarized in Table 11, page 88.

2. Preparation of o-phenylene phosphorochloridate resin: Catechol resin was treated prior to use with a 10% sodium thiosulfite solution in water saturated with THF and was dried in vacuo at room temperature to constant weight. The treated resin (0.5 g, ca 2.13 meq available catechol) was placed in a 100 ml round flask followed by adding 30 ml dry benzene. Most of benzene was then distilled from the mixture and

the remaining benzene was decanted under a blanket of nitrogen. Freshly distilled THF (from CaH_2) (12 ml) was introduced into the flask. The slurry was stirred (magnetically) for a while; then 0.33 g (4.17 mmole) dry pyridine and 0.327 g (2.13 mmole) $POCl_3$ was added. The reaction was terminated after it was stirred at room temperature under nitrogen for 18 hours. The beads were transferred under nitrogen to a flame dried Schlenck tube and washed several times with dry THF and dry benzene. The entire apparatus with lower stopcock open was placed in vacuo, first at room temperature for overnight, then at 60° for an additional 48 hours. Elemental analysis indicated pendent phosphorochloridate on the resin to be 1.431 meq/g; Found: C, 61.69; H, 6.17; P, 5.29; Cl, 6.70; O, 17.41.

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VITA

Supon Chotiwana was born in Cheingmai, Thailand on February 10, 1949. He graduated from Trium Udom Suksa School in 1966 and received a Diploma in Analytical Chemistry from Chulalongkorn University in 1971 and began employment in the Department of Science, Ministry of Industry. He went to the Phillipines the following year and was enrolled at Silliman University from which he received a Bachelor of Science degree in Chemistry in 1973. He entered a Graduate School at Lamar University in Beaumont, Texas in 1974, where he received the Master of Science degree in Chemistry in 1975. Currently he is a candidate for the degree of Doctor of Philosophy with a major in organic polymer chemistry and a minor in analytical chemistry.

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EXAMINATION AND THESIS REPORT

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Title of Thesis: Polymeric Catechols

Approved:

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Date of Examination:

April 5, 1983