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Paul V. Grosso
University of Massachusetts Amherst

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POLYMERIC ANTIOXIDANTS FROM 2,6-DI-t-BUTYLPHENOL DERIVATIVES

A Dissertation Presented

By

Paul V. Grosso

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Polymer Science and Engineering

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Approved as to style and content by:

Otto Vogl
O. Vogl, Chairman of Committee

Shaw Ling Hsu
S. L. Hsu, Member

C. Peter Lillya
C. P. Lillya, Member

W J MacKnight
W. J. MacKnight, Department Head
Polymer Science and Engineering

To my parents,

who were always there

"Well, I must endure the presence of. . . caterpillars if I wish to become acquainted with the butterflies."

- Antoine de Saint Exupery

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ABSTRACT

Polymeric Antioxidants from 2,6-Di-*t*-Butylphenol Derivatives

(May 1983)

Paul V. Grosso

B.S., University of Connecticut

M.S., University of Massachusetts

Directed by: Professor Otto Vogl

Two polymerizable derivatives of 2,6-di-*t*-butylphenol were synthesized and copolymerized with 1,3-butadiene and isoprene. The copolymer backbones were hydrogenated and both the diene and saturated copolymer were tested for effectiveness as polymeric antioxidants.

2,6-Di-*t*-butyl-4-vinylphenol and *O*-acetyl-2,6-di-*t*-butyl-4-vinylphenol were synthesized in yields of 47 percent and 79 percent, respectively, starting with 2,6-di-*t*-butylphenol. The former monomer was successfully copolymerized with butadiene and isoprene by radical emulsion, forming polymeric antioxidants. Copolymerization of the latter monomer with styrene and methyl methacrylate was also investigated.

2,6-Di-*t*-butyl-4-isopropenylphenol was synthesized in an overall yield of 43 percent. The monomer was copolymerized in solution with styrene and *n*-butyl acrylate, and in radical emulsion with butadiene and isoprene.

Monomer preparations involving aklylation of 2,6-di-*t*-butylphenol and a Wittig reaction on 2,6-di-*t*-butylphenol-4-formylphenol were investigated, but these procedures were unsuccessful.

Copolymers of 2,6-di-*t*-butyl-4-vinylphenol and 2,6-di-*t*-butyl-4-isopropenylphenol with butadiene and isoprene were hydrogenated using an aluminum/cobalt catalyst under mild conditions to yield hindered phenol-ethylene-copolymers and hindered phenol-ethylene-propylene terpolymers in yields of up to 60 percent.

The phenol-diene copolymers were blended with commercial polydienes and the hydrogenated phenol-diene copolymers were blended with commercial polyolefins. The stabilized blends were tested via oxygen uptake for protection against thermooxidative degradation, which was provided by the polymeric antioxidants.

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CHAPTER I

INTRODUCTION

This dissertation, dealing with the synthesis and testing of polymeric, hindered-phenol antioxidants, is an extension of the functional-polymer research done by Bailey[1] and Tirrell,[2] which was in the area of polymeric ultraviolet stabilizers.

The present work builds on some of the same principles, namely the synthesis of functional polymers and the polymerization of phenols. The first topic was reviewed by the earlier workers, and this chapter will summarize that survey in Section A.

However, since only unhindered phenols were discussed by Tirrell, an extensive review of the reactivity of hindered phenols, especially 2,6-di-_t_-butylphenols, appears in Section B.

Section C is an account of methods used to date for the synthesis of hindered-phenol monomers and polymers and the applications of these polymers.

Finally, Section D will outline the factors which affect antioxidant activity in use and the methods used to study their activity.

A. Methods of Preparation of Functional Polymers

Three synthetic approaches to the problem of preparing polymers containing functional groups have been employed in this laboratory:[1,2] oligomer endcapping; functionalization of an existing polymer; and direct homo- or copolymerization of functional monomers.

Endcapping of oligomers provides a low- or moderate-molecular-weight polymer which is terminated by a functional group. Both polymeric substrate and endcapping material are purified separately, leading to a pure product, but the method is clearly limited as to the amount of functional group which can be incorporated.

Performing reactions on polymers provides versatility regarding the type of functionality able to be included, but difficulties with limiting conversion and removal of side products (which may be polymer-bound) from the product polymer complicate this method.

Direct homo- or copolymerization of functional monomers offers perhaps the greatest flexibility with respect to the amount of functional moiety in the final product. In some cases, however, the polymerization itself may be made more difficult by the choice of functional group. For example, the polymerization of hindered-phenol antioxidants in the present work requires the use of techniques for the rigorous exclusion of oxygen in order to succeed.

B. The Effects of Hindered Phenols on Radical-Chain Processes

Hindered phenols participate in and alter the course of two important radical-chain processes: autoxidation and free-radical polymerization.

It has been conclusively proven that the first reaction which takes place when such molecules enter into these chain processes is abstraction of the phenolic hydrogen atom.[3,4] Thus, the details of how hindered phenols influence the pathways is determined to a great extent by the thermodynamics and kinetics of this reaction.[3]

An understanding of a number of definitions is required before beginning a discussion of radical reactions.

First, as pointed out in a cogent paper by Griller and Ingold,[5] a distinction needs to be made between radical stability (or stabilization) and persistence. Over many years the word "stable" as applied to radicals has been used to denote many things,[6] but the clearest perception of the field is afforded when "stabilization" is used to refer only to thermodynamic stability, i.e., the strength of the bond broken in forming a radical. Thus, on the basis of bond-dissociation energies,[5,7] the benzyl radical is stabilized with respect to an ethyl radical by 13 kcal/mol ($D(CH_3CH_2{-}H) - D(C_6H_5CH_2{-}H) = 13$ kcal/mol). Steric effects are minimized in this definition.[5]

In contrast, steric factors play a major role in the "persistence" of a radical, which is quantified by the rate constant for the decay of the radical.[5] Griller and Ingold have collected numerous interesting examples of destabilized radicals made persistent by substitution with bulky groups.

It is the persistence of hindered phenoxy radicals, as well as their stabilization through delocalization of the unpaired electron, which makes them of particular interest here.

"Hindered" is also a loosely applied term. For the purposes of this work, a phenol having a bulky group, such as *t*-butyl, in at least one ortho position can be called hindered. The substitution imposes certain constraints upon the reactivity of a phenol, as well as the related persistence and reaction pathways of the phenoxyl derived from it.

1. Antioxidant activity. Polymer autoxidation is a thermodegradative chain reaction in which hydrocarbon polymers, among others, are oxidized through reactions with molecular oxygen and the resulting peroxy and hydroxyl

radicals and hydroperoxides. The contributions of many have characterized the elementary reactions comprising autoxidation as follows.[8]

Initiation: $$ROOH \xrightarrow{k_i} RO\cdot,\ RO_2\cdot \qquad (1)$$

Propagation: $$RO_2\cdot + RH \xrightarrow{k_p} ROOH + R\cdot \qquad (2)$$

$$R\cdot + O_2 \xrightarrow[\text{fast}]{k_3} RO_2\cdot \qquad (3)$$

Termination: $$2RO_2\cdot \xrightarrow{k_t} \text{nonradical products} \qquad (4)$$

$$2R\cdot \xrightarrow{k_t'} R\text{-}R \qquad (5)$$

$$RO_2\cdot + R\cdot \xrightarrow{k_t''} RO_2R \qquad (6)$$

The chain-reaction portion of the overall scheme is reactions 2 and 3. The results of autoxidation can be crosslinking, cleavage of macromolecular chains and deterioration of mechanical properties.

Several classes of compounds are capable of delaying the onset and/or slowing the rate of autoxidation by terminating the kinetic chain, and these are collectively referred to as chain-breaking antioxidants. The period of protection they provide is called the induction period.

Chain-breaking antioxidants include[8] hindered phenols, of course, as well as aromatic amines and nitroxides. The remainder of this subsection is concerned exclusively with the antioxidant activity of hindered phenols.

The early studies of the inhibitory effects of hindered phenols and other species on autoxidation involved low-molecular-weight substrates[9] such as aldehydes and aliphatic or aromatic hydrocarbons. These studies pointed toward a sacrificial role of the antioxidant.[9] Also, since inhibition might be caused by interference with either Reaction 2 or 3, an effort was made to distinguish these possibilities on kinetic grounds.[9]

If, under atmospheric oxygen concentrations, an antioxidant were to react with alkylperoxy radicals according to Equation 7,

$$RO_2\cdot + InH \xrightarrow{k_{IN}} \text{Inactive products} \qquad (7)$$

the overall expression for the relative rates of inhibited and uninhibited reaction would show no oxygen dependence (Equation 8,[9] where

$$R/R_o{}^2 = 2k_t/nk_pk_{IN}\ [RH][InH] \qquad (8)$$

R and R_o are the inhibited and uninhibited rates, respectively, n is a stoichiometric factor indicating the number of kinetic chains terminated by each antioxidant molecule, [RH] is the substrate concentration and [InH] is inhibitor concentration).

For the case where antioxidants would exert their effect by reaction with alky radicals (Reaction 9),

$$R\cdot + InH \xrightarrow{k_{IN}'} \text{Inactive products} \tag{9}$$

the parallel relative rate expression is

$$R/R_o = 2k_3k_t[O_2]/nk_p{}^2k_{IN}'[RH]^2[InH] \tag{10}$$

which contains $[O_2]$, the oxygen concentration.

It was experimentally determined that the rate of inhibited autoxidation is independent of oxygen pressure,[9,10] and it was concluded that antioxidants inhibit autoxidation by reacting with the alkylperoxy chain carrier. This is also reasonable in the light of later studies which directly measured the rate of reaction between molecular oxygen and alkyl radicals. The rate is extremely fast, on the order of 10^9 $\underline{M}^{-1}$ s^{-1},[4] so that, under atmospheric oxygen pressures, any alkyl radicals which are formed are nearly instantaneously converted to peroxy radicals.

The mechanism by which hindered phenols react to terminate autoxidative chains was in question for some time. While ten Have[10] held the view that the first step in phenol-mediated inhibition was attack of the chain-carrying radical on the hydroxyl group with abstraction of a hydrogen atom,

$$RO_2\cdot + HO\text{-}In \longrightarrow RO_2H + \cdot O\text{-}In \qquad (11)$$

Hammond and his coworkers disagreed and pointed to several pieces of experimental evidence as proof.[11] Most prominent among these was the observed lack of a kinetic isotope effect.

If the rate-determining step in the reaction were hydrogen abstraction by the peroxy radical as maintained by ten Have, substitution of deuterium for hydrogen in the hydroxyl group of a series of hindered phenols should give rise to a large isotope effect because of the high selectivity of the peroxy radical.[12] The absence of an observable isotope effect in Hammond's experiments[11] led him to conclude that hydrogen transfer was not involved in the rate-determining step.

To account for these observations he proposed the formation of an intermediate "loose" complex between a peroxy radical and an antioxidant molecule[11] (Equation 12),

$$RO_2\cdot + InH \rightleftharpoons [RO_2\cdot \longrightarrow InH] \xrightarrow{RO_2\cdot} \text{Products} \qquad (12)$$

which subsequently reacted with a second peroxy radical to yield oxidized inhibitor. In so doing, Hammond obviated the need for hydrogen abstraction as the rate-determining step.

Further evidence cited in support of this intermediate complex was the excellent correlation of antioxidant activity with Hammett σ values,[3,11] despite the presence of one or two bulky ortho substituents which normally lead to deviations from Hammett correlations.[13] Hammond claimed that, due to the large degree of separation in the complex, steric factors would be of little importance.[11]

Gradually the mechanism which is now generally accepted came to light. In an important paper, Howard and Ingold[14] reported the first deuterium isotope effects in inhibited autoxidation. They had discovered that the phenolic proton is unexpectedly labile and that traces of moisture in even carefully dried solvents could effect exchange with a deuterated phenol. It was found that reproducible results in these isotope-substitution experiments could be secured by addition of a small amount of D_2O directly to the solution under study in order to saturate the medium.

The isotope effect, k_H/k_D, first measured by these workers, was 10.6 for the AIBN-initiated oxidation of styrene.[14] Since then, many groups have performed isotope-effect studies, and these have been reviewed.[4] The values of k_H/k_D for 2,6-di- and 2,4,6-trialkylphenols generally fall between 10 and 12.

While no conclusive answer yet exists for the correlation of inhibitory effectiveness of hindered phenols with σ values, one possible explanation is bending of the hydroxyl group out of the plane of the phenyl ring, thus lessening the effect of the substituents on reactivity.[4]

In the currently accepted mechanism for antioxidant inhibition of autoxidation then, the first step is rate-determining and consists of abstraction of the hydroxyl hydrogen by an alkylperoxy radical to give a phenoxy radical which is stabilized by delocalization of the unpaired electron throughout the aromatic ring.[5,15]

The phenoxy radical is capable of reacting with a second chain carrier, most commonly by coupling in the 4-position, to satisfy the stoichiometric requirements of two terminations per molecule.[16]

The presence of substituents in the 4-position leads to two effects. First, alkyl substituents having hydrogen at the position α to the ring, such as methyl or isopropyl, will contribute to stabilization of the radical via hyperconjugation. Second, a bulky substituent, such as <u>t</u>-butyl (or a polymer backbone) will provide steric hindrance to dimerization of the aroxyl radicals, resulting in a more persistent radical[17,18,19,20] for which reaction with a second peroxy radical becomes preferred. Both of these effects will lead to an antioxidant with greater intrinsic activity.

The rates of reactions of hindered phenols with several oxy radicals (alkoxy, alkylperoxy and peroxy-terminated macroradicals) have been studied and the activation energies, Arrhenius parameters and Hammett ρ values have been determined.

Howard and Furimsky[21] calculated the activation energies and preexponential factors for a group of hindered phenols in the reaction with t-butylperoxy radicals. Reaction rates were determined by direct observation of the change in peroxy-radical concentration with time in an ESR spectrometer. The rate, k_{IN}, for 2,6-di-t-butyl-4-methylphenol was found to be 5×10^3 $\underline{M}^{-1}$ s^{-1} at -37°C. The A factor was a "relatively small"[21] $10^{4.6}$ $\underline{M}^{-1}$ s^{-1}, and the activation energy was 0.8 Kcal/mol^{-1}. Confirming earlier work, a deuterium isotope effect of 11 was found.

Several workers have noted that inhibitor efficiency correlates with σ^+ values as well as σ values.[22,23,24,25,26,27] This is reasonable if one considers that there is a small polar contribution to the transition state of the radical abstraction[4,26,27] (Equation 15),

$$[\mathrm{ArO{:}H{\cdot}OOR}] \longleftrightarrow \mathrm{ArO}\overset{+}{\cdot}\mathrm{H}\overset{-}{:}\mathrm{OOR} \longleftrightarrow \mathrm{ArO{\cdot}H{:}OOR}] \qquad (15)$$

suggesting that electron transfer is more rapid than movement of the hydrogen nucleus.[4] The positive charge in the transition state would be stabilized by electron-donating substituents in the ortho and para positions.

Howard and Furimsky[21] extrapolated ρ^+ values to 65°C to obtain a value of -0.8 for the reaction with t-butylperoxy, -1.12 for polyperoxystyrylperoxy, and -1.36 for tetralylperoxy. It was stated that the variation in ρ^+ values was due to differences in electronegativity among the radicals.

The low activation energies found for hydrogen abstraction by peroxy radicals has been rationalized on the basis of the reversible formation of a hydrogen-bonded complex between the radical and the hindered phenol[21] (Equation 16).

$$\begin{array}{ccccc} RO_2\cdot + HOAr & \rightleftharpoons & RO_2\cdot \text{ --- } HOAr & \rightleftharpoons & RO_2H \text{ ---- }\cdot OAr \\ & & & \swarrow\!\!\!\nearrow & \\ & & RO_2H + \cdot OAr & & \end{array} \qquad (16)$$

The work of Gilchrist[28] tends to support the existence of this kind of complex. While he provides a caveat that his data not be interpreted too broadly, he found that 2,6-di-t-butyl-4-methylphenol tends to associate with polar groups in hydrocarbon media. Using low-temperature, dielectric-loss measurements in hydrocarbon glasses, he determined that the hindered phenol tended to associate "fairly strongly" with carbonyls and less strongly with ethers. Although Gilchrist stopped short of calling this interaction hydrogen bonding, he allowed that this affinity may have some bearing on the antioxidant activity of such molecules.

While the $^{+}$I effects of alkyl substituents can lead to enhanced antioxidant activity versus an unsubstituted phenol, the steric effects introduced by bulky alkyl substituents may actually decrease it. The abstraction of phenolic hydrogen becomes progressively endothermic, and the rate of the reaction decreases, in the series phenol, 2,6-dimethylphenol, and 2,6-di-_t_-butylphenol.[12] The data which exist show that the best balance between inductive and steric effects may be obtained in the 4-alkyl-2-_t_-butylphenols.[4]

A small steric effect may also be observed in the attacking peroxy radical. A decrease in k_{IN} is observed in the series cyclohexenyl (3.0×10^{4} $\underline{M}^{-1}$ s^{-1}), tetralyl (2.85×10^{4} $\underline{M}^{-1}$ s^{-1}), 9,10-dihydroanthryl (1.19×10^{4} $\underline{M}^{-1}$ s^{-1}) and cumyl (1.20×10^{4} $\underline{M}^{-1}$ s^{-1})[29] in the reaction with 2,4,6-tri-_t_-butylphenol. This is not a large range of values considering the varying degrees of steric bulk surrounding the peroxy group in these radicals, and Ingold has stated that the k_{IN} value for a particular phenol is more or less characteristic of that phenol.[30] A natural assumption would then be that, for the reaction of 2,6-di-_t_-butyl-4-methylphenol and related phenols with macroperoxy radicals encountered in polymer autoxidation, k_{IN} would again be about 10^{4} M^{-1} s^{-1}.

This assumption has in fact been borne out. Of 20 hindered phenols studied in the reaction with polyperoxystyrylperoxy radical, the values of k_{IN} fall between 1.5×10^4 and 8.6×10^4 $\underline{M}^{-1}\ s^{-1}$.

On the basis of these data, one might expect a similar value for the reaction between peroxy radicals and polymers containing 2,6-di-t-butylphenyl pendant groups. No rate constants for this reaction have yet appeared.

In this subsection, the detailed mechanism of antioxidant inhibition of autoxidation was established. It incorporates hydrogen-bonded complexes between peroxy radicals and phenols and abstraction of the phenolic hydrogen atom in the rate-determining step.

The next subsection will compare the just-discussed behavior of hindered phenols in reactions under atmospheric oxygen pressures with phenolic activity in polymerizing systems in the absence of oxygen, i.e., the reactions of hindered phenols with carbon radicals.

2. Inhibition and retardation of radical polymerization.

Before launching into a discussion of the differences between the reactions of hindered phenols in the inhibition of autoxidation and their reactions in the inhibition and retardation of free-radical polymerization, the similarities between these two kinds of reactions deserves a measure of consideration.

First, radical polymerization is also a chain process.[31] As such, it is comprised of the same three stages of initiation, propagation and termination.

Initiation: $A_2 \longrightarrow 2A\cdot$ (17)

Propagation: $A\cdot + M \longrightarrow A\text{-}M\cdot$ (18)

$A\text{-}M\cdot + M \longrightarrow A\text{-}M_2\cdot$ (19)

Termination: $A\text{-}M_n\cdot + A\text{-}M_m\cdot \longrightarrow A\text{-}M_{n+m}\text{-}A$ (20)

If oxygen is present in the polymerization medium it can rapidly add to the end of the growing polymer chain, as it adds to the carbon-centered radicals produced during autoxidation (Equation 21).

$$A\text{-}M_n\cdot \xrightarrow{O_2} A\text{-}M_n\text{-}O_2\cdot \quad (21)$$

As already noted, the rate constant for this reaction is on the order of 10^9 $\underline{M}^{-1}$ s^{-1},[4] so that any carbon radicals produced will almost immediately be "capped" with a peroxy endgroup. The result is a peroxy macroradical.

Some monomers, such as styrene and methyl methacrylate, can readily undergo copolymerization with oxygen. Studies have shown that such a polymerization proceeds at a rate slower than the related homopolymerization,[32] and thus molecular oxygen by itself can interfere in radical polymerization by retardation.

In the presence of antioxidants, the peroxy macroradicals formed from oxygen and carbon-centered chain radicals can react in a manner exactly analogous to Reaction 4 above (P· is a macroradical).

$$P\cdot + O_2 \xrightarrow{\text{fast}} PO_2\cdot + HO\text{-}In \longrightarrow PO_2H + \cdot O\text{-}In \qquad (22)$$

As in the autoxidation case, this persistent phenoxyl can form an adduct, with another alkylperoxy radical, in the 4-position. The products are two terminated polymer chains and an oxidized phenol.

Because of this ability, hindered phenols (and other classes of compounds) have been employed as polymerization inhibitors for vinyl monomers such as styrene and methyl methacrylate to avoid losses of monomer to polymerization[32] during storage or distillation and as short-stops in emulsion polymerizations.

In the absence of oxygen similar reactions still occur. The carbon macroradicals, which are sometimes stabilized[5] secondary or tertiary species, and often persistent[5] as well, will survive long enough to react with a phenol, if one is present in the medium, by abstracting the hydroxyl hydrogen (degradative transfer) (Reaction 23)

$$P\cdot + HOAr \longrightarrow PH + \cdot OAr \qquad (23)$$

and by subsequent addition of another carbon radical to the 4-position of the phenol[32] (termination).

The rate of hydrogen abstraction by an alkyl radical is generally slower than that by an alkylperoxy radical, and this is an important difference. The discovery of this difference and the disparity between the two rates is discussed in the remainder of this subsection. The polyvinyl acetate radical has been especially well studied in this regard, and the polystyryl and polymethyl methacrylyl radicals have been examined to a lesser extent.

Breitenbach and coworkers[34] were among the first to recognize that carbon radicals could react with phenols as a result of their investigations of the thermal polymerization of styrene. They noticed that the reaction proceeded almost completely normally in the presence of 0.001 M hydroquinone if oxygen was excluded. The polymerization also proceeded in the presence of 0.01 M and 0.03 M hydroquinone albeit at a rate diminished by several orders of magnitude and with reduced yields. Breitenbach described this observation as remarkable ("auffällige"), since even in 1938 it had long been known that hydroquinone was capable of inhibiting radical polymerization.

At the time it was thought that carbon radicals were incapable of reacting with phenols,[35] and that oxygen's role was to convert phenols to quinones, which then performed the actual inhibition.[35]

The choice of styrene for this early work was somewhat unfortunate because the polystyryl radical is relatively unreactive[35] and many phenols first studied were only sparingly soluble in the monomer.[35] This combination of circumstances conspired to minimize the observed effects.

Later studies with the somewhat more polar polyvinyl acetate radical led to the realization that degradative chain transfer was occurring in these systems, as well as termination; just as in autoxidation, the stoichiometric factor for the phenols was found to be close to 2.0.[35]

Furthermore, kinetic isotope effects, k_H/k_D, determined by Simonyi et al.,[36] are in the range of 10 ± 3 for a group of monohydric phenols, confirming that the same rate-determining step was occurring as in inhibited autoxidation.

Tudos[35] empirically derived an equation relating the rate of reaction with carbon radicals to σ^+ values for a series of monohydric phenols,

$$\log \beta = 0.34 - 1.52\ \Sigma\sigma^+ \qquad (24)$$

where β is a dimensionless constant proportional to the rate of abstraction for a particular phenol. According to Tudos, the most reactive compound (of those he studied) toward abstraction was durohydroquinone ($\beta = 1300$).

2,6-Di-*t*-butylphenol and 2,4,6-tri-*t*-butylphenol, far less reactive, showed β values of 2.5 and 4.1, respectively.

Interestingly, a steric effect is displayed in this mode of phenol reactivity as well. For example, 2,6-dimethylphenol has $\Sigma\sigma^+ = -0.62$ and $\beta = 26$,[35] while for 2,6-di-*t*-butylphenol, having a similar $\Sigma\sigma^+$ of -0.51, the reactivity is reduced an order of magnitude to $\beta = 2.5$.[35]

Absolute rate constants have also been determined for the reactions of carbon-centered radicals with phenols. For the case of the polyvinyl acetate radical,[36] the reaction with durohydroquinone proceeds with a rate of 3.3×10^3 $\underline{M}^{-1}$ s^{-1}, while reaction with *o*,*o*'-di-*t*-butyl-2,2-bis-*p*-hydroxyphenylpropane gave a value of 66 $\underline{M}^{-1}$ s^{-1}. This latter value is several powers of ten slower than the equivalent hydrogen abstraction by an alkylperoxy radical[4] and slower also than the rate of propagation for the homopolymerization, which is 2.3×10^3 $\underline{M}^{-1}$ s^{-1}.[31]

Research done by several groups of Russian workers using ethylbenzene radicals[37] and polypropylene macroradicals[38] tends to corroborate the figures obtained from the study of the polyvinyl acetate radical. It was found that the maximum rates for reaction of the former radicals with various phenols were approximately 10^4 $\underline{M}^{-1}$ s^{-1}, but the majority of the values were roughly 100 times slower than the analogous reactions of peroxy radicals.

A thorough study of chain-transfer constants, C, for phenols which affect polymerization has been performed by Russell and his colleagues.[39] They studied the polymerization of styrene, degassed on a high-vacuum line, at 60°C. They found that the phenols could be divided into two groups: those which cause chain transfer and so lower the molecular weight of polymer produced, but do not retard the polymerization; and those which give rise to chain transfer and retardation. Phenols with chain-transfer constants less than 8×10^{-3} do not retard while those with chain-transfer constants greater than 8×10^{-3} show significant retardation.

2,6-Di-t-butylphenol, a member of the former group, had $C = 4.9 \times 10^{-3}$; 2,6-dimethylphenol, from the latter group, had $C = 1.1 \times 10^{-2}$.

A similar study by Barton and Russell[40] yielded C values of 5.8×10^{-2} for 2,3,4,6-tetramethylphenol in styrene at 60°C, and 1.1×10^{-3} for the same compound in methyl methacrylate at 45°C. Transfer constants for deuterated phenols were found to be lower.

The basis of the measurable but reduced reactivity of carbon radicals versus peroxy radicals toward phenols seems to reside primarily in the Arrhenius preexponential factor. A factors for the reactions of carbon-centered radicals with hindered phenols are smaller than those for the reaction involving peroxyls.[35] This is sensible when the approach of the reactants to form the transition state is considered.

The space surrounding the peroxy group is relatively uncluttered since the terminal oxygen is bonded to only one other atom. The carbon centers of alkyl radicals, be they primary, secondary or tertiary, are more hindered, limiting the possible angles of approach for a successful abstraction reaction.

The foregoing discussion suggests that by proper choice of phenolic inhibitor and by exclusion of oxygen, a reasonable degree of polymerization would be attainable despite the presence of the phenol. Alternately the polymerization of a vinyl-substituted hindered phenol, as described in the final two chapters of this dissertation, would be practical provided the phenolic moiety was not too reactive.

The final subjects of this subsection are a preview of the topic to be discussed in Section C and serve to point out the difficulties inherent in attempting to polymerize phenols.

Work performed by Kato[41] on the polymerization of the unhindered _p_-hydroxystyrene and _m_-hydroxystyrene is instructive. AIBN was used as initiator in THF at 60°C, in the absence of oxygen. Polymers with inherent viscosities of at most 0.32 dL/g were obtained, and polymer conversion was only 52% after two days' reaction time. Control polymerizations involving acetylated monomers afforded products with inherent viscosities up to 0.65 dL/g.

Kato later polymerized other phenolic monomers,[42] including this time the hindered N-(4-hydroxy-3,5-di-t-butylphenyl)acrylamide. The best results obtained for AIBN-initiated homopolymerization of this monomer (at 30°C in THF) gave a product with an inherent viscosity of 0.10.

While polymerizations can be conducted in the presence of hindered phenols and polymerization of vinyl-substituted hindered phenols does occur, because carbon-centered macroradicals are capable of abstracting phenolic hydrogen atoms, rates will be slow due to retardation and degree of polymerization will be low due to degradative chain transfer.

C. Preparation of Hindered-phenol Polymers

Polymers containing hindered-phenol moieties have been synthesized in the past largely for two reasons: use as high-molecular-weight antioxidants and the study of polyradicals derived from them.

The amount of work in this area is not insignificant and a review of the literature begins with methods for the synthesis of hindered-phenol monomers. To keep the task tractable, only 2,6-di-t-butyl derivatives have been considered, although many of the methods apply equally well to other 2,6-di-t-alkylphenols.

Polymeric antioxidants discussed later are only those which have been applied to the stabilization of rubbers and polyolefins, and again are only 2,6-di-t-butylphenol derivatives.

1. Synthetic routes to hindered-phenol monomers. Since the majority of syntheses of hindered-phenol monomers begin with 2,6-di-t-butylphenol (or another 2,6-di-t-alkyl derivative), this discussion begins with a consideration of the industrial syntheses of this important compound.

A process dating from 1949, developed by Stillson and Sawyer,[43] for the synthesis of 2,6-di-t-butylphenol involved dialkylation of a 4-halophenol with isobutylene in the presence of an unspecified catalyst. The intermediate dibutylhalophenol was then reduced by reaction with an alkali metal in liquid ammonia to give the end product.

The Czechoslovak group of Mravec and coworkers[44] in 1974 provided another example of this alkylation by using aluminum phenolate as catalyst. The reaction proceeds at 130°C for 210 minutes at a phenol:isobutylene ratio of 1:4. Of the 100% conversion in the reaction, 73% was ortho-dialkylated product.

Mitsui Petrochemical Industries filed patent application[45] in 1982 for a very similar process. In it, a 1:5 ratio of isobutylene:phenol was heated to 135-40°C in the presence of 0.35 mol of aluminum phenoxide to yield 74% of 2,6-di-t-butylphenol.

A route outlined in a patent issued to Yamada and Taniide[46] provides a one-step synthesis of a polymerizable hindered phenol. Alkenylation of 2,6-di-t-butylphenol, presumably in the presence of a basic catalyst, with allylic halides gave products such as 3-(4-hydroxy-3,5-di-t-butylphenyl)-1-propene. The compounds are reported to be useful as rubber antioxidants and resin stabilizers.

Goodyear Tire and Rubber Company is the holder of a patent[47] for a process in which an α-haloalkyl hindered phenol is dehydrohalogenated in the presence of base to yield a polymerizable antioxidant, 2-(4-hydroxy-3,5-di-t-butylphenyl)-1-t-alkylethylene.

A number of descriptions of routes to hindered-phenol monomers have also appeared in the journals, mostly within the last decade.

2,6-Di-t-butyl-4-isopropenylphenol was synthesized by Pospisil and coworkers[48] by base-catalysed cleavage of 4,4'-isopropylidene(2,6-di-t-butylphenol). Using 1.75% butyllithium at a pressure of 30-50 mm, reaction at 250°C gave the isopropenylphenol in 75% yield. The other product of the reaction was phenol. The products were isolated by distillation.

The group also described[48] a second synthesis of the same material via Grignard reaction of 4-hydroxy-3,5-

di-t-butylacetophenone and methyl iodide. In this case, a 95% yield was obtained after distillation of the intermediate 2-(4-hydroxy-3,5-di-t-butylphenyl)-2-propanol with simultaneous dehydration.

Pospisek et al.[49] explored the kinetics of the base-catalysed isomerization of a group of 4-isopropylidene-2,5-cyclohexadienones (quinone methides) to phenols, and activation parameters were determined. For the isomerization of 4-isopropylidene-2,6-di-t-butyl-2,5-cyclohexadienone (with triethylamine) to 2,6-di-t-butyl-4-isopropenylphenol in 1,2-dichloroethane solution, the ΔH of activation was calculated to be 6.8 kcal mol^{-1}, and ΔS of activation was -45.0 cal $°C^{-1}$.

Braun and Meier[50] had earlier performed the same isomerization by refluxing a solution of the quinone methide in light petroleum ether for 15 minutes in the presence of anhydrous, neutral alumina. Yields reported were 95-100%.

Braun and Meier[51] have also described their synthesis of a vinyl-substituted hindered phenol, as well as a monomer with a blocked hydroxyl group.

The procedure for 2,6-di-t-butyl-4-vinylphenol began with a Knoevenagel condensation between acetic acid and 2,6-di-t-butyl-4-formylphenol. The intermediate 3-(4-hydroxy-3,5-di-t-butylphenyl)acrylic acid was decarboxylated at 210°C and 12 mm. When higher vacuum was employed, a substantial part of the starting material sublimed before decarboxylation. Yield of the vinylphenol, which was distilled at 146-8°C and 12 mm after its formation, was 69-84%. Braun stated that the reason for the high yields was the inability of the compound to polymerize. At 12 mm pressure, this interpretation may be correct.

Synthesis of 2,6-di-t-butyl-4-isopropenylphenol by Braun and Meier,[51] in addition to the quinone methide isomerization already recounted, was accomplished by a Grignard reaction similar to that employed by Pospisil, described above. In the former's procedure, however, dehydration was afforded by use of a phosphoric acid catalyst.

A polymerizable hindered phenol with a blocked hydroxyl group was synthesized by Braun and Meier in a three-step procedure.[51] Because they were unable to radically polymerize free phenols, they felt a blocked monomer was a necessity.[52] The starting material, 4-methoxy-3,5-di-t-butylbenzonitrile, underwent a Grignard reaction with methylmagnesium iodide to yield 4-methoxy-3,5-di-t-butylphenylmethylketone (55%). A second Grignard reaction yielded 2-(4-methoxy-3,5-di-t-butylphenyl)-2-propanol (90%) which was subsequently dehydrated with phosphoric acid to yield 55% of methyl(4-isopropenyl-2,6-di-t-butylphenyl)ether.

A route to an acetylated phenol was described by

Hewgill and Smith[54] in 1976. It was developed after these workers read of Braun's reports of the inability of free-phenol monomers to undergo free-radical polymerization.

Their procedure involved diacylation of 2,6-di-t-butylphenol with aluminum chloride catalyst at -5°C in acetyl chloride solvent. Yield of O,4-diacetyl-2,6-di-t-butylphenol was 93%. A 5:1 aluminum chloride:phenol ratio was needed to effect diacylation exclusively. Reduction of the intermediate with sodium borohydride in ethanol at 0°C gave 88% of O-acetyl-2,6-di-t-butyl-4-(1-hydroxyethyl)-phenol, which was dehydrated at 140-70°C using fused potassium hydrogen sulfate and powdered copper. The final product, O-acetyl-3,5-di-t-butyl-4-vinylphenol, was isolated in 87% yield by evaporative distillation at 160-80°C and 15 mm.

Two interesting postscripts to this last publication have appeared in the literature.

In 1980, Braun and Wittig[53] published substantially the same procedure as Hewgill but made no reference to the earlier work.

In 1982 a Japanese group related[55] a synthesis of O,4-diacetyl-3,5-di-t-butylphenol which matched that of Hewgill except for the reaction temperature--20°C--and the yield--100%.

The synthesis of polymerizable antioxidants of the substituted 3-phenylpropionic ester type has been disclosed in a patent[56] assigned to the Goodyear Tire and Rubber Company. It is claimed that the process can be carried out either batchwise or continuously. The method consists in part of reacting 4-hydroxy-3,5-di-t-butylbenzyl chloride with isobutyraldehyde in the presence of base. The product of this condensation, 3-(4-hydroxy-3,5-di-t-butylphenyl)-2,2-dimethylpropionaldehyde, was reduced via sodium borohydride in ethanol to give the propanol. In the last step of the sequence, methyl methacrylate was transesterified with this alcohol and the byproduct methanol was removed, along with excess methyl methacrylate, by azeotropic distillation to yield 3-(4-hydroxy-3,5-di-t-butylphenyl)-2,2-dimethylpropyl methacrylate.

A similar scheme appeared in other patents assigned to Goodyear.[57,58] In these, in part, the same substituted benzyl chloride starting material was alkylated with acetylacetone (base catalyst) to give 2-(4-hydroxy-3,5-di-t-butylphenyl)-1-acetylethylmethyl ketone, which was decarbonylated by heating for 10 hours. Borohydride reduction of the resulting monoketone provided 4-(4-hydroxy-3,5-di-t-butylphenyl)-2-butanol, which underwent a transesterification reaction with methyl methacrylate in the presence of a tetraalkyl titanate catalyst. After hydrolysis of the catalyst with water, the product, isolated by hexane extraction, was 4-(4-hydroxyphenyl-3,5-di-t-butylphenyl)-2-butyl methacrylate.

Kline[59] describes a synthesis of 2,6-di-alkyl-4-alkenylphenols in another patent assigned to Goodyear. A starting material such as 2-(4-hydroxy-3,5-di-*t*-butylphenyl)-2-hydroxyethane (or the 2-hydroxy-2-propane) is chlorinated in an excess of concentrated hydrochloric acid at room temperature. The intermediate is then dehydrochlorinated in refluxing pyridine to yield 2,6-di-*t*-butyl-4-vinylphenol.

Layer and Tenney[60] submitted a European patent application in which 2,6-di-*t*-butylphenol was converted to the sodium phenoxide salt by reaction with sodium methoxide in DMF. The anion was then reacted with allyl bromide for one hour at 50°C. The product was 3-(4-hydroxy-3,5-di-*t*-butylphenyl)-1-propene, a result of C-alkylation and rearomatization.

2. Polymerization of hindered-phenol monomers and applications of the polymers.

At this juncture, a definition of the types of high-molecular-weight antioxidants is appropriate.

High-molecular-weight antioxidants (and high-molecular-weight additives in general) may be classified as either polymeric or polymer-bound. Polymeric antioxidants are polymer chains incorporating stabilizer in definite, regular locations along their length. The antioxidant function can be written as a part of the repeat unit of the polymer. Additives of this type may be made either by direct homo- or copolymerization of functional monomers or by reactions on polymers.

Polymer-bound antioxidants, on the other hand, are polymers which contain stabilizer introduced at random locations along a chain, or as a part of a network. A repeat unit for the polymer which includes the antioxidant cannot be written. For convenience, polymers endcapped with stabilizers are placed in the latter class.

Polymer-bound antioxidants will be covered first in this subsection, followed by polymeric antioxidants.

Perhaps the most exemplary method of forming a polymer-bound antioxidant is the carbene-insertion reaction developed by de Jonge et al.[61] A carbene was generated, through the agency of heat or ultraviolet light, from an azoquinone precursor. When the carbene, 4-oxo-3,5-di-t-butyl-2,5-cyclohexadieneylidene, was formed in the presence of polypropylene, insertion took place into various bonds in the polymer. The polymers were tested, and those containing approximately 0.1 wt % of bound stabilizer, after a 24-hour extraction with methanol, displayed a four-hour induction period in an oven-aging test at 140°C. A control containing 2,6-di-t-butyl-4-methylphenol (BHT) gave an induction period of 0.5 hours after extraction.

Scott[62,63] has synthesized an antioxidant bound to polypropylene by irradiating a film of the polymer with

250 nm light while in contact with a solution of 4-hydroxy-3,5-di-t-butylbenzyl acrylate and benzophenone sensitizer. The film was then extracted with acetone for 48 hours and oxidized in a closed system at 120°C. The induction period was 550 hours for a stabilizer concentration of 0.1%. 0.1% of the same antioxidant was incorporated by a conventional compounding technique, extracted and found to exhibit an induction period of only 2 hours.

Parks, in a patent assigned to the Goodyear Tire and Rubber Company,[64,65] described a method by which a polymerizable antioxidant was bound to an unsaturated rubber during vulcanization. Thus, 4-(4-hydroxy-3,5-di-t-butylphenyl)-2-butyl methacrylate was added to a bottle containing a 67:33 butadiene-acrylonitrile latex. The bottle was flushed with nitrogen, tumbled overnight, then AIBN (1 pphm) was added, and the bottle was tumbled for 16 hours at 70°C. The dried, stabilized NBR was evaluated via oxygen uptake after extraction with methanol and a methanol-toluene azeotrope. Time required to absorb 1% oxygen at 100°C was 78 hours.

The Russian group of Spasskova and Egorova has synthesized a polymer-bound antioxidant for rubbers[66] by endcapping an amino-terminated polydiene (MW 1500) with 4-hydroxy-3,5-di-t-butylbenzyl bromide.

A similar strategy is seen in the work of Domnina and coworkers,[67] who reacted 2-(4-hydroxy-3,5-di-t-butylphenyl)propionic acid with isocyanate-terminated polybutadiene or polyisoprene. Elimination of carbon dioxide from the intermediate imino anhydride at 130°C yielded antioxidant bound via an amide group. Evaluation of the stability of this polymer, it was reported, showed results superior to the use of 2,6-di-t-butyl-4-methylphenol (BHT).

Scott[68] has also produced polymer-bound antioxidants by reacting 4-hydroxy-3,5-di-t-butylbenzyl mercaptan and a radical initiator with natural rubber. The reaction took place under an inert atmosphere and could be run in a solution or latex. The grafted polymer showed only a slight decrease in activity versus direct addition of the stabilizer, which acts as an autosynergist. Furthermore, Scott reports that the economics of the process make it "commercially viable."

As a final example of a polymer-bound stabilizer, the work of Russell and Vail[70] is presented. In this application styrene, isobutylene, or a combination of the two were polymerized cationically using Lewis acids. The macrocations thus produced terminate by addition to the 4-position of 2,6-di-t-butylphenol, also present in the medium. A hindered-phenol antioxidant with a tail of 1,000 to 1,500 MW was formed. The additives were shown to delay crosslinking in SBR at 120°C in air.

Many methods have been employed to produce polymeric antioxidants. Reactions on existing polymers and direct polymerization of the antioxidant by free-radical, anionic, cationic and coordination means are treated below.

Tomatsu and coworkers have explored the transesterification reaction as a method of creating polymeric antioxidants.[70,71] They reacted a propylene-10-undecene-1-ol copolymer (1.02 mmol OH/g) with ethyl 3-(4-hydroxy-phenyl-3,5-di-_t_-butylphenyl)propionate and sodium methoxide in ethanol. The product, claimed to be useful as a stabilizer for polyolefins, was a white powder with an antioxidant content of 2×10^{-4} g/g of polymer.

Minagawa et al.[72] have synthesized a polymeric t-butylated phenol by treating a poly-_p_-vinylphenol ($\bar{M}_n = 500$) with isobutylene and toluenesulfonic acid in toluene. The additive was used to stabilize polypropylene when present in the amount of 0.001 to 5% by weight.

Direct copolymerization of polymerizable antioxidants has led to many materials, some of which were studied for reasons unrelated to stabilization of polymers.

Kato et al.[73,74] have developed a system involving copolymerization of 2-vinyloxyethyl 4-hydroxy-3,5-di-_t_-butylbenzoate with styrene or methyl methacrylate. A copolymer containing 3 wt % of the benzoate, made by AIBN-initiated polymerization in toluene, first at 60°C and 2,000 atmospheres for 30 minutes, then at 70°C and 8,000 atmospheres for 24 hours, showed no change in intrinsic viscosity after 200 hours at 150°C. The composition of the gas under which the degradations were run was not specified, nor was the degree to which the polymerization medium was oxygen-free.

Radical-emulsion polymerization was used by Kline[75] to polymerize 2 wt % N-(4-hydroxy-3,5-di-t-butylphenyl)-methacrylamide with butadiene and styrene. The initiator was paramenthane hydroperoxide promoted by a mixture of ferrous sulfate, tetrasodium EDTA and sodium formaldehyde sulfoxylate. The polymer was worked up after 18 hours of reaction, and at that point the conversion was 37%. The slow rate of reaction is undoubtedly due to the presence of the hindered phenol. Again, no specific data was given regarding oxygen content of the medium. The polymer produced by this procedure required 420 hours to absorb 1% oxygen at 100°C. No control value was given.

Kline also copolymerized 2,6-di-t-butyl-4-vinylphenol and 2,6-di-t-butyl-4-isopropenylphenol, as well as other hindered phenols,[59] with styrene and butadiene in emulsion. SBR rubbers incorporating 1.5 wt % phenolic monomer, as well as NBR polymers, required 258-309 hours and 88-96 hours, respectively, to absorb 1% oxygen at 100°C, proving their usefulness as "self-stabilizing" polymers.

Braun and several colleagues have done considerable research over the past 15 years in the area of polyradicals: carbon-centered,[76] nitrogen-centered[77] and oxygen-centered.[52,76,77,78] The oxygen-centered radicals, polyphenoxyls, are of interest here. These were synthesized by polymerization of 2,6-di-t-butyl-4-vinylphenol and 2,6-di-t-butyl-4-isopropenylphenol cationically, or by radical polymerization of blocked monomers, followed by oxidation of the polyphenol to the polyphenoxyl with lead dioxide.

A point made in several of Braun's contributions[52,53,77,78] was that unblocked, hindered-phenol monomers such as these would not polymerize in free-radical systems due to the inhibitory effect of the phenol. It was further stated that only cationic polymerization could succeed. It is probable that oxygen was not properly removed from solutions used for polymerization. Braun's results stand in sharp contrast to the large body of data from other, oxygen-free polymerizations of hindered phenols.

However, Braun's studies of the polyradicals he synthesized are of value. They showed that polyradicals' ESR spectra were of lower resolution[78] than those of low-molecular-weight analogs. Also, the spectral resolution became poorer as the amount of phenoxyl moiety was increased relative to styrene in a copolymer. This was attributed to extensive spin-spin interaction in the coiled polymers and the reduced mobility afforded by the chain.

The lifetimes of the radicals were also measured and compared to those of the analogous low-molecular-weight compounds.[78] Polyisopropenylphenoxyls are "stable" (persistent) for weeks, and the model 2,4,6-tri-t-butylphenoxyl is also a persistent species. The half-life of the polyvinylphenoxyls, 2 hours for a 6 mol % copolymer, is quite different than that of the low-molecular-weight analog's several-second half-life. Although no investigation of the cause of this difference was undertaken, it seems clear that incorporation of a phenoxyl into a polymer chain results in greater persistence[5] as a result of steric shielding of the radical site by the polymer chain and reduced mobility.

Recently Braun has examined the effectiveness of his polyphenols as stabilizers against photooxidative degradation.

Hewgill and Smith[54] chose to block the phenolic function of their monomer, O-acetyl-2,6-di-t-butyl-4-vinylphenol, by esterification, based on Braun's reports of unsuccessful radical polymerizations. Radical polymerization of the blocked phenol proceeded to high molecular weight, and the acetate group was cleaved from the polymer by lithium aluminum hydride in refluxing THF. Hewgill and Smith went on to produce a polyradical by oxidation of the polymer with aqueous, alkaline potassium ferricyanide. A g value of 2.0046 was measured for the polyradical, almost identical to the g value of 2.0045 for 2,4,6-tri-t-butylphenol.

The antioxidant properties of this polyphenol were not explored in detail.[79]

Following Braun's monomer synthesis scheme and his cationic-polymerization approach, Okamoto et al. synthesized homopolymers and styrene copolymers of 2,6-di-t-butyl-4-vinylphenol.[80,81] The copolymers were then employed to selectively hydrogen-bond with and thus separate non-hindered amines from a mixture also containing hindered amines. For example, a 17:83 mixture of 4-ethylpyridine and 2,6-dimethylpyridine became enriched to 99% 2,6-dimethylpyridine after stirring with the homopolymer to remove the less hindered amine. A similar separation of n-butylamine and tri-n-butylamine was also effected.

Braun has stated that anionic polymerization of 2,6-di-t-butyl-4-vinylphenol was not possible,[52] but Toyomoto and Fukawa[82] have succeeded. The phenol is first allowed to react with one equivalent of n-butyllithium to form the lithium phenoxide. The phenoxide can then be copolymerized with butadiene (in hexane solution for two hours) after a further addition of n-butyllithium to serve as initiator.

It is also not impossible to synthesize polymeric antioxidants by Ziegler-Natta techniques, although this seems surprising in view of the haptophilicity of phenols.

In 1972, a Japanese patent issued to Mitsui Petrochemical Industries[83] outlined the polymerization of ethylene, propylene, isoprene or 4-methyl-1-pentene with a hindered phenol. A complex of 2,6-di-t-butyl-4-vinylphenoxide with diethylaluminum chloride was combined with titanium trichloride and an olefin monomer. After reaction at 70°C for one hour, the polymer was worked up by addition of hydrochloric acid and methanol.

5-(4-hydroxy-3,5-di-t-butylbenzyl)-2-norbornene, synthesized via Diels-Alder reaction of dicyclopentadiene and 3-(4-hydroxy-3,5-di-t-butylphenyl)-1-propene at 240°C and 50 psi, was also polymerized using coordination catalysts, according to Layer and Tenney.[60] This monomer was copolymerized with dicyclopentadiene, methylnorbornene or 1-hexene. The researchers claim that the copolymers required 11 days to develop a "fair" amount of carbonyl functionality, as opposed to five days for "common" antioxidants.

D. Factors Affecting Antioxidant Activity

1. Intrinsic activity versus functional activity. In the controlled world of the laboratory, quantities such as the rate of reaction between an alkylperoxy radical and a hindered-phenol antioxidant can be readily measured.[4] Such

a quantity can be related to the "intrinsic activity"[84] of an antioxidant and is a fundamental property related to the kinetics and thermodynamics of the reaction between the two molecules in solution.

In actual service, conditions are quite different. The intrinsic activity is modified, nearly always attenuated, by environmental and physical influences.[85] The polymer matrix itself will have a great effect on the rate of the abstraction reaction, imposing a limit on the rate of diffusion of the reactants.[86] The molecular weight of the stabilizer and its solubility in the polymer, as well as any solvent with which the polymer is in contact, conspire to affect the retention of the stabilizer. The reduced effectiveness of an antioxidant under in-use conditions such as these can be termed its "functional activity."

The accelerated testing methods outlined in the last subsection of this chapter are designed to measure functional activity, and what follows immediately is a more in-depth, though qualitative, discussion of those factors which serve to separate the two kinds of activity.

An antioxidant must be soluble in a polymer matrix in order to be effective, and it has been pointed out that this is <u>the</u> most important consideration.[87] Unlike an ultraviolet absorber, which is able to act efficiently by a screening action alone, an antioxidant must be present at the site where oxidative attack is occurring. Since oxygen has a high permeability in the amorphous phase of most polymers,[88,89,90] mobility and solubility of the stabilizer are clearly necessary. Insolubility would lead to segregation of the additive, leaving large areas of the polymer unprotected and causing exudation (blooming).

For most commercial phenolic antioxidants, however, this is not a problem because while their solubilities are in the neighborhood of 15 wt %,[91] they are customarily employed in amounts less than 1 wt %.

On the negative side, high solubility in hydrocarbon polymers for low-molecular-weight additives implies high solubility in organic solvents as well.[8] For instance, 2,6-di-*t*-butyl-4-methylphenol (BHT) is soluble up to 50 wt % in isopentane.[91]

It is well established also that extraction of stabilized polymer samples over prolonged periods with methanol or acetone is capable of removing essentially all of the stabilizer.[85] Thus, a use environment which involves frequent or protracted contact with organic solvents or aqueous detergent solutions will remove low-molecular-weight stabilizers.[85,92,93]

Volatility is also an important modifier of intrinsic activity.[85] An appreciable body of work demonstrates conclusively that an increase in additive molecular weight results in an increase of functional effectiveness.[85,92]

For instance, as the length of alkyl groups of 3-(4-hydroxy-2,6-di-t-butylphenyl)propionic esters was varied from methyl to stearyl, the functional antioxidant activity was observed to increase. (The antioxidant became more permanent but there was actually little change in the intrinsic activity of the phenol.) The study was done using polypropylene films which were aged in an air oven. Determination of induction periods by torsion-braid analysis gave a value of 25 hours for BHT and nearly 10,000 hours for 4-octadecyl-2,6-di-t-butylphenol.[94]

Holcik[95,96] is another author who has examined the volatility of antioxidants. During mixing of polypropylene with various antioxidants in a Brabender plastograph (190°C for five minutes), he found that while 43% of BHT was lost, less than 1% of a C_{21}-substituted 2,6-di-t-butylphenol was volatilized.[96]

Polymeric and polymer-bound antioxidants offer several advantages over conventional antioxidants, and while some of these are obvious, some are more subtle.

As discussed above, it is apparent that losses of stabilizer due to volatilization can be neglected for a truly high-molecular-weight additive. In most cases, leaching of the stabilizer from the polymer matrix is also negligible provided the molecular weight is sufficiently high, for to dissolve most polymeric or polymer-bound additives would require a solvent which also would dissolve the host. One frequently overlooked advantage of stabilization with a polymer system is that uniform, molecular dispersal of the functional moieties can be readily accomplished[84] provided the percentage of stabilizer units in any copolymer or graft is insufficient to cause incompatibility and phase separation.

There are several potential drawbacks to the use of polymeric stabilizers and incompatibility is certainly one of them. Because as the molecular weight of a solute polymer increases the allowable difference in solubility parameter between solute and host decreases, it is not possible to create one general-purpose[92,97] polymeric antioxidant which would be compatible with several important classes of commercial polymers.

Another liability is that the decreased mobility of the polymeric additive may hamper the ability of the stabilizer to reach sites of attack by oxygen,[86,92] decreasing the functional activity somewhat.

It has been suggested[92] that a molecular weight of 3,000 to 20,000 would be optimum for polymeric antioxidants, striking a balance between volatility, compatibility and mobility.

2. Effect of polymer morphology on polymer oxidation. It is now well known that autoxidation of polyethylene and polypropylene occurs exclusively in the amorphous

phase.[90,98,99] The linear relationship between polymer oxidation rate and X-ray-determined crystallinity was elucidated by Walker and coworkers.[98] The limiting oxygen uptake is also directly proportional to amorphous content in most polyolefins.[89]

These phenomena are the results of density differences between crystalline and amorphous regions. Crystalline regions, being of greater density, are relatively impermeable to oxygen.[90,98]

Confirming this interpretation is the example of poly(4-methyl-1-pentene). The crystalline phase of this polymer is unusual in that its density, 0.83 g/mL, is less than that of the amorphous phase, 0.84 g/mL.[98] Thus, the oxygen permeability of the crystalline phase is higher than that of the amorphous phase and the former is preferentially oxidized.[90,98]

It has been shown by UV fluorescence microscopy[100,101] that antioxidants and probably other noncrystallizable impurities (atactic polymer or a polymeric additive) are concentrated in the interlamellar amorphous regions and/or are pushed ahead of the growth front of crystallites in a crystallizing polymer. Hence, the majority of the antioxidant in a semicrystalline polymer will be concentrated where it can be most beneficial--in the amorphous phase, which is accessible to oxygen.

3. Oxygen uptake as an assay of functional antioxidant activity. The progress of thermooxidative degradation may be followed in several ways, each corresponding to a different change occurring in the degrading polymer during accelerated testing. All of these methods yield information about the induction period of a stabilized polymer.

The induction period is the time required to exhaust added antioxidant. The longer the induction period for a fixed amount of stabilizer, the higher the functional activity (effectiveness) of that stabilizer. The end of the induction period is marked by a sharp increase in the rate of oxidation.

Infrared spectrophotometry is a sensitive, quantitative method for following the buildup of carbonyl and other oxygen-containing functionality in an oxidizing polymer sample.

Alternately, portions of a degrading polymer may be taken at intervals and the viscosity determined. The decrease in molecular weight could also be followed by repeated GPC analyses.

A good simulation of processing conditions may be achieved by using differential thermal analysis (DTA). In this technique, a stabilized polymer sample is heated over a range of several hundred degrees and loss of stabilizer by volatilization as well as the rate of oxidation are indicated by endotherms and exotherms, respectively, recorded by the instrument.[96]

Oxygen-uptake experiments, which provide direct volumetric or manometric determination[102,103] of the amount of oxygen reacting with a degrading virgin or stabilized polymer, are an uncomplicated, inexpensive way to measure induction period. The results of these experiments correlate well with polymer lifetimes in actual use.[104]

An apparatus can easily be built which allows for multiple, simultaneous determinations. The equipment designed for the present work is diagrammed in Figure 3, Chapter II.

From the rate of oxygen uptake measured at a range of temperatures, the activation energy for autoxidation may be calculated. A value of 35 kcal/mol was obtained by Wilson[103] for unstabilized polyethylene.

Finally, it should be noted that the conditions under which oxygen-uptake experiments are conducted, i.e., in a small, closed vessel, do not reflect the effects of additive volatility to the extent that DTA or circulating-air oven tests would. Instead, according to Scott,[85] stabilizer compatibility is emphasized.

E. Summary

This chapter has addressed those matters which have a direct bearing on the work described in the remainder of this dissertation.

The chemical reactivity of hindered phenols, which makes them valuable additives, was shown to be the same activity which must be overcome in order to succeed in polymerizing hindered-phenol monomers.

Synthetic routes to hindered-phenol monomers, their polymers, and the applications of these materials were also treated, as were the general methods employed for synthesis of functional polymers.

Finally, the physical and chemical determinants of the activity of low-molecular-weight and macromolecular antioxidants were discussed, and the difference between intrinsic and functional activity was explained. This last dichotomy was related to the use of polymeric antioxidants.

CHAPTER II

EXPERIMENTAL SECTION

A. Materials

The following chemicals were obtained from the indicated sources.

Acetic anhydride (MCB)
Acetonitrile (MCB)
Aluminum trichloride (A)
Ammonium chloride (F)
Argon (L)
4,4'-Azobis(cyanovaleric acid) (A)
Azobisisobutyronitrile (A)
Benzene (MCB)
Bistrimethylsilylacetamide (P)
Boron trifluoride etherate (A)
BTS catalyst (B)
1,3-Butadiene (L)
n-Butyl acrylate (A)
Calcium oxide (F)
Chloroform (MCB)
Chloroform-d_1 (A)
Chlorotrimethylsilane (A)
Cobalt 2-ethylhexanoate (PB)
Copper powder (F)
Cyclohexane (A)
2,6-Di-*t*-butyl-4-formylphenol (A)
2,6-Di-*t*-butylphenol (E)
Dimethyl sulfoxide (MCB)
Ethanol (MCB)
Ethyl acetate (MCB)
Ethyl ether (MCB)
Hexane (MCB)
High-density polyethylene (D)
Hydrochloric acid (MCB)
Hydrogen, research grade (MCB)
Iodomethane (A)

Isoprene (A)

Linear, low-density polyethylene (D)

Lithium aluminum hydride (ALFA)

Lithium chloride (F)

Low-boiling petroleum ether (MCB)

Low-density polyethylene (D)

Magnesium sulfate (MCB)

Magnesium turnings (F)

Methanol (MCB)

Methyl methacrylate (A)

Polybutadiene, cis (S)

Polybutadiene, random cis, trans (S)

Polyethylene glycol (F)

Polyisoprene, cis (S)

Polyisoprene, trans (S)

Polypropylene, atactic (D)

Potassium hydrogen sulfate (M)

Potassium persulfate (F)

Propylene oxide (A)

Sodium carbonate (F)

Sodium dodecyl sulfate (F)

Sodium hydride (F)

Sodium hydroxide (F)

Styrene (A)

Styrene-butadiene rubber (PS)

Toluene (MCB)

Triethylaluminum (ET)

Triethylamine (A)

Triphenylmethyl phosphonium bromide (A)

o-xylene (A)

Sources: A = Aldrich Chemical Co.; ALFA = Alfa Products; B = BASF Colors and Chemicals, Inc.; D = Dow Chemical Co.; E = Eastman Organic Chemicals; ET = Ethyl corp.; F = Fisher Scientific Co.; L = Linde Division, Union Carbide Corp.; M = Mallinckrodt Chemical Works; MCB = MCB Manufacturing Chemists, Inc.; P = Petrarch Systems, Inc.; PB = Pfaltz and Bauer, Inc.; PS = Polysciences, Inc.; S = Scientific Polymer Products, Inc.

B. Purification of Reagents and Solvents

Acetonitrile was refluxed over calcium hydride and distilled. The fraction boiling between 81°C and 82°C was collected and stored under argon until use.

Argon was purified by passage through a column (40 cm long and 5 cm in diameter) packed with BTS catalyst and heated to 150°C, yielding gas less than 1 ppm in oxygen. Argon thus purified is referred to as "oxygen-free" throughout.

Azobisisobutyronitrile (AIBN) was recrystallized twice from methanol and dried for 12 hours at room temperature and 0.1 mm.

Benzene was refluxed over sodium-potassium amalgam and distilled. The fraction boiling between 79.5°C and 80.5°C was collected and stored under argon until use.

1,3-Butadiene (CP Grade) was freed of CO_2 inhibitor by passage through a column containing sodium hydroxide, but otherwise used as received.

n-Butyl acrylate was washed with aqueous sodium hydroxide to remove inhibitors.

Cyclohexane was refluxed over calcium hydride for 24 hours and distilled. The fraction boiling between 80°C and 81°C was collected and stored under argon until use.

Dimethyl sulfoxide was stirred with calcium hydride and distilled (42°C/1 mm) immediately before use.

Isoprene (Gold Label) was distilled at 34.5°C to 35°C and 1 atmosphere pressure and stored under argon in the cold until use.

Methyl methacrylate was distilled at 100°C and 1 atmosphere pressure to remove inhibitors and stored under argon in the cold until use.

Styrene was distilled at 44-45°C under aspirator vacuum to remove inhibitors, then stored under argon in the cold until use.

Triethylamine was refluxed over calcium hydride and distilled. The fraction boiling between 89°C and 90°C was collected.

All other reagents and solvents were used as received.

C. Preparation and Polymerization of 2,6-Di-t-butyl-4-vinylphenol and O-Acetyl-2,6-di-t-butyl-4-vinylphenol

1. O,4-Diacetyl-2,6-di-t-butylphenol. Prepared according to Hewgill.[54] See pp. 165, 175, and 186.

2. O-Acetyl-2,6-di-t-butyl-4-(1-hydroxyethyl)phenol. Prepared according to Hewgill.[54] See pp. 165, 176, and 186.

3. O-Acetyl-2,6-di-t-butyl-4-vinylphenol. Prepared according to Hewgill.[54]

The product was purified by distillation through a very short column at reduced pressure. Yield of O-acetyl-2,6-di-t-butyl-4-vinylphenol, collected at 138-40°C and 0.01 mm, was 90%. The colorless, viscous liquid slowly crystallized while stored at -5°C. See pp. 166, 176, and 187.

4. 2,6-Di-t-butyl-4-vinylphenol. O-Acetyl-2,6-di-t-butyl-4-vinylphenol (41.0 g, 150 mmol) was dissolved in 250 mL of dry toluene. The solution was added to a 500 mL, round-bottomed flask, followed by lithium aluminum hydride (5.8 g, 15 mmole). The grey solution was heated to reflux over a period of several hours, and reflux was maintained, under an argon atmosphere, for 3 days. Excess lithium aluminum hydride was consumed by reaction with 30 mL of ethyl acetate. The intermediate aluminum complex was then hydrolyzed by addition of 100 mL of concentrated hydrochloric acid. The grey aqueous layer was drained away from the colorless organic layer in a separatory funnel. The organic layer was washed with three 70 mL portions of saturated aqueous sodium carbonate until neutral, followed by water. During these washings the organic layer became yellow. The toluene solution was dried over magnesium sulfate, and the solvent was removed on a rotary evaporator to give a yellow oil. With the aid of a mineral-oil chaser, distillation of the oil at 86-90°C and 0.4 mm Hg yielded 21.0 g (60%) of liquid 2,6-di-t-butyl-4-vinylphenol.

The monomer was stored under argon at -5°C, slowly crystallizing in the cold. Analytical and spectral data are given by Braun.[51] See pp. 166, 177, and 187.

5. Polymerization of O-Acetyl-2,6-di-*t*-butyl-4-vinylphenol in solution. A polymerization tube was charged with *O*-acetyl-2,6-di-*t*-butyl-4-vinylphenol (0.96 g, 3.5 mmol), dry benzene (3 mL) and AIBN (30 mg, 0.18 mmol, 5 mol%). The tube was degassed by the freeze-thaw technique and sealed at 0.01 mm. After 36 hours at 70°C, the polymer was precipitated by adding the tube's contents to 250 mL of methanol. The product was collected on a sintered-glass funnel and dried at 80°C and 0.025 mm to yield 0.89 g (93%) of a fine, white powder. The inherent viscosity of the polymer (0.5% in benzene, 30°C) was 0.29 dL/g. The infrared spectrum (film) showed bands at 1769 cm^{-1} (C=O stretch) and 1596 cm^{-1} (aromatic C=C stretch). See p. 188. The ^{13}C NMR spectrum ($CDCl_3$) showed peaks at: 22.63 ppm ($CO\underline{C}H_3$); 31.73 ppm ($C(\underline{C}H_3)_3$); 35.12 ppm ($\underline{C}(CH_3)_3$); 124.8 to 145.6 ppm (aromatic); and 170.10 ($O\underline{C}OCH_3$). See p. 177. ^1H NMR showed peaks at δ: 1.1 ($C(C\underline{H}_3)_3$); 2.2 ($COC\underline{H}_3$); and 6.4 (aromatic). See p. 167.

ANAL. Calcd. for $(C_{18}H_{26}O_2)_n$: C, 78.79%; H, 9.55%. Found: C, 78.25%; H, 9.19%.

6. Copolymerization of O-Acetyl-2,6-di-t-butyl-4-vinylphenol with methyl methacrylate in solution. A polymerization tube was charged with *O*-acetyl-2,6-di-*t*-butyl-4-vinylphenol (0.64 g, 2.3 mmol), methyl methacrylate (0.70 g, 7.0 mmol), dry benzene (4.8 mL) and AIBN (30 mg, 0.18 mmol, 2 mol%). The tube was degassed by the freeze-thaw technique and sealed at 0.01 mm. After 36 hours at 70°C, the contents of the tube had formed a solid plug. The plug was dissolved in benzene (20 mL) and the polymer was precipitated by slow addition of this benzene solution to 250 mL of methanol. The product was collected on a sintered-glass funnel and dried at 80°C and 0.025 mm for 12 hours to yield 1.13 g (84%) of white material. The inherent viscosity of the polymer (0.5% in benzene, 30°C) was 0.35 dL/g. The infrared spectrum (film) showed bands at 1597 cm^{-1} (aromatic C=C stretch), 1738 cm^{-1} (methacrylate C=O stretch) and 1768 cm^{-1} (acetate C=O stretch). See p. 188. The ^{13}C NMR spectrum ($CDCl_3$) showed peaks at: 17.99 ppm $(-\overset{CO}{\overset{|}{C}}-\underline{C}H_3)$; 50.93 ppm $(-O\underline{C}H_3)$; 126-145 ppm (aromatic); 171.3 ppm $(O\underline{C}OCH_3)$; and 177.5 ppm $(\underline{C}O_2CH_3)$. See p. 178.

The ^1H NMR spectrum showed δ: 0.4-2.0 (backbone $C\underline{H}_2$, $C\underline{H}$); 1.2 $(C(C\underline{H}_3)_3)$; 2.2 $(OCOC\underline{H}_3)$; 2.8 $(CH-C\underline{H}_3)$; 3.5 $(OC\underline{H}_3)$; and 6.7 (aromatic). See p. 168.

ANAL. Calc. for $-\!(C_{18}H_{26}O_2)\!-_{0.46}\ -\!(C_5H_8O_2)\!-_{0.54}$: C, 68.63%; H, 8.74%. Found: C, 68.82%; H, 8.66%.

7. Copolymerization of 2,6-Di-t-butyl-4-vinylphenol with 1,3-butadiene in emulsion. 1,3-Butadiene was condensed into a 360 mL capacity polymerization tube using the apparatus shown in Figure 1. The amount of liquid collected was determined by weighing the tube before and after filling with diene. A slight excess was collected, and the liquid was allowed to warm slightly in order to vaporize some of the condensate until the correct net weight (40.0 g, 740 mmol, 80 parts by weight) had been reached. The collection tube was then capped with a septum and the liquid 1,3-butadiene was transferred via double-tipped needle (under pressure of oxygen-free argon) to a 100 mL, round-bottomed flask, also capped with a septum, containing 2,6-di-t-butyl-4-vinylphenol (10.0 g, 43 mmol, 20 parts, 5 mol%). The vinyl monomer was dissolved, by shaking, in the butadiene. The solution was kept below the boiling point of butadiene (-4°C) at all times using powdered, solid carbon dioxide. The solution was deoxygenated by bubbling oxygen-free argon through it for one-half hour. It was then transferred via double-tipped needle to a second 360 mL polymerization tube containing the remainder of the emulsion recipe: 4,4'-azobis(cyanovaleric acid) initiator (1.2 g, 2.4 parts); sodium dodecyl sulfate emulsifier (2.5 g, 5 parts); and distilled water (90 g, 180 parts). This second tube had been fitted with a high-vacuum, three-way stopcock, one take-off of which had been

Figure 1. Apparatus for collection of liquid butadiene. The components are: A, cylinder of inhibited butadiene; B, regulator; C, tygon tubing; D, drying tube containing potassium hydroxide or Ascarite; E, syringe needle; F, open neck of G, 360-mL polymerization tube; H, dry ice or dry ice-isopropanol bath.

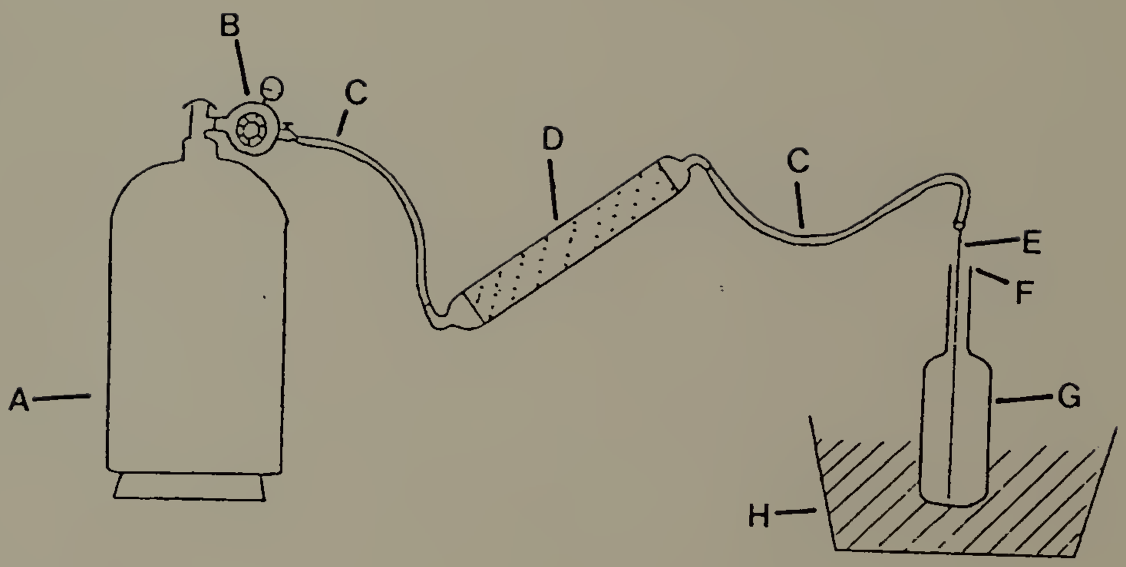

Figure 1.

sealed with a small septum to facilitate double-tipped-needle transfers. This second tube was kept in a rock salt-ice bath at -5°C. (-5°C is cold enough to maintain 1,3-butadiene below its boiling point as it is being added to the emulsion matrix, but at this temperature the matrix itself will not readily freeze.) Immediately after the transfer was complete, the aqueous phase was remelted by hand-warming, with occasional venting of butadiene pressure in the tube. The tube was rapidly and vigorously shaken to emulsify the contents and frozen in liquid nitrogen while emulsified. (Freezing of a non-emulsified aqueous phase will cause expansion which can shatter the polymerization tube.) The time between completion of the comonomer transfer and freezing in liquid nitrogen did not exceed one minute, which minimized the need to vent butadiene. The polymerization tube was evacuated and sealed at 0.01 mm. Annealing of the seal was carefully done, since the tube was expected to experience considerable internal pressure (see p. 110). The tube was thawed slowly, placed in a 65°C water bath and shaken to keep the contents of the tube emulsified (see Fig. 2). After one week, the tube, now containing a light yellow, stable latex, was removed from the water bath, chilled thoroughly in ice and carefully broken open at the neck. Escaping butadiene gas tended to force frothy latex out of the neck of the tube. Firm finger pressure over the hole, relieved periodically,

Figure 2. Emulsion polymerization apparatus. Components are: A, jackstand; B, wrist-action shaker; C, thermometer; D, polymerization tube; E, cylindrical, glass water bath; F, stirring hotplate; G, polystyrene-foam "peanuts."

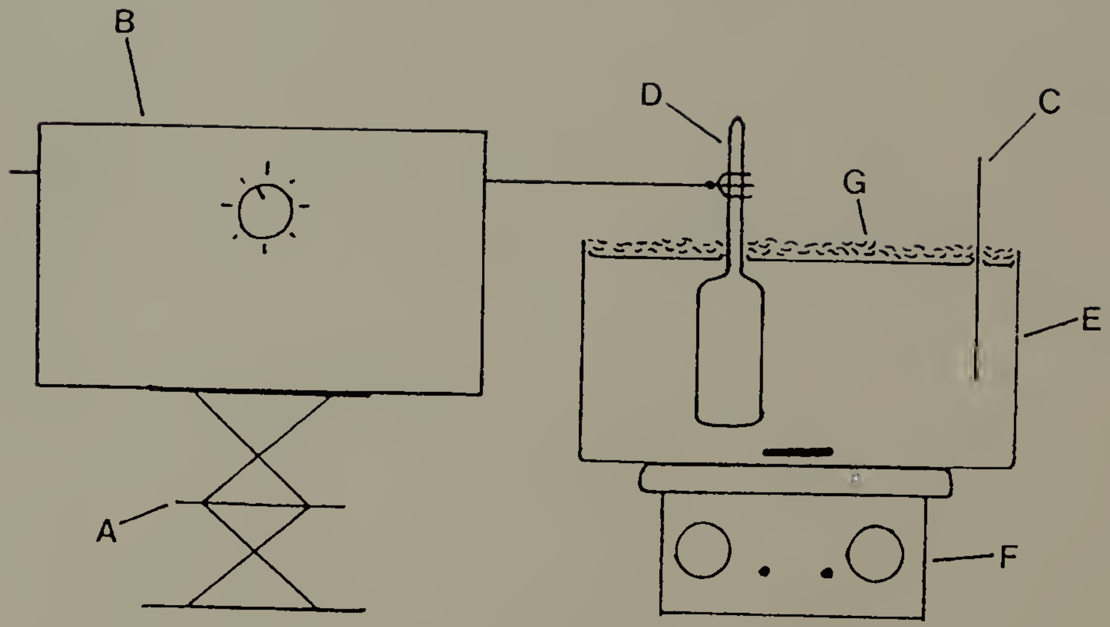

Figure 2.

contained the latex and vented the gas. 10 mL of 10% aqueous lithium chloride solution were added to the tube and it was shaken. Pressure built up during this operation as well. Next, 5 mL of concentrated hydrochloric acid was added and the shaking repeated. At this point, coagulated polymer particles could be discerned. The coagulated latex was added slowly to 700 mL of rapidly stirred methanol, and large white clumps of polymer soon coalesced from the initially formed, hazy suspension. The precipitated polymer was stored under methanol in the freezer until all polymer had settled to the bottom of the storage vessel. The methanol was then poured off and the polymer transferred to a 100 mL beaker, where it was dissolved in cyclohexane at room temperature. Reprecipitation into 500 mL of methanol, followed by cooling in the freezer and decantation of the methanol, gave a gelatinous product. The material was placed in a 2 oz. sample vial and dried, first in a bell jar under aspirator vacuum and then in a vacuum dessicator at 0.1 mm, with heating from an infrared lamp, for 24 hours. (The analytical sample was dried for three days at 160°C and 0.005 mm.) The yield of clear, slightly amber and viscous polymer was 10.6 g (21%). The molecular weight values for the polymer, obtained from gel permeation chromatography, were $\bar{M}_n$ = 16,300 and $\bar{M}_w$ = 45,000. Infrared analysis (film) showed bands at 3650 cm^{-1} (hindered phenol O-H stretch), 1640 cm^{-1} and 1670 cm^{-1}

(cis and trans C=C stretch) and 1596 cm^{-1} (aromatic C=C stretch). See p. 191. The ^{13}C NMR spectrum ($CDCl_3$) showed peaks at: 30.55 ppm (*t*-butyl $\underline{C}H_3$); 27.49, 30.18, 32.77, 34.09, 38.22 and 43.57 (butadiene $-\underline{C}H_2-$); 114.21, 128.41, 129.51, 129.66, 130.08, 130.51, 131.30, and 142.76 ppm (=$\underline{C}$H of polybutadiene with random cis, trans geometry). See p. 181. ^1H NMR analysis ($CDCl_3$) showed peaks at δ: 1.4 ($C(C\underline{H}_3)_3$); 2.0 ($C\underline{H}_2$ of polybutadiene); 5.3 ($C\underline{H}$ of 1,4 butadiene unit); 4.9 ($-C\underline{H}=C\underline{H}_2$ of 1,2 butadiene units); and 6.7 (aromatic). See p. 171. A comparison of integrated areas of the peaks at δ 1.4 ($C(C\underline{H}_3)_3$) and 4.6-5.6 δ ($C\underline{H}$) indicated a copolymer composition of 6% 2,6-di-*t*-butyl-4-vinylphenol and 94% 1,3-butadiene.

ANAL. Calcd. for $-(C_{16}H_{24}O)-_{0.06}$ $-(C_4H_6)-_{0.94}$: C, 88.45%; H, 11.13%. Found: C, 88.24%; H, 11.14%.

8. Copolymerization of 2,5-di-t-butyl-4-vinylphenol with isoprene in emulsion. Freshly distilled isoprene (4.8 g, 70 mmol, 96 parts by weight) was pipetted into a 50 mL, pear-shaped flask containing 2,6-di-*t*-butyl-4-vinylphenol (0.2 g, 0.9 mmol, 1 mol%, 4 parts). The flask was capped with a septum and shaken to dissolve the phenolic monomer. A stream of oxygen-free argon was bubbled through the solution, which was maintained at 0°C. After one-half hour the solution was transferred via double-tipped needle to a polymerization tube containing the rest of the emulsion recipe: 4,4'-azobis(cyanovaleric acid) initiator (0.06 g, 1.2 parts); sodium dodecyl sulfate emulsifier (0.25 g, 5 parts); and distilled water (9 g, 180 parts). The tube had been fitted with a high-vacuum, three-way stopcock, one take-off of which was sealed with a small septum to facilitate double-tipped-needle transfers. This tube was also deoxygenated by bubbling a stream of oxygen-free argon through it. After filling, the tube was shaken to emulsify the contents and immersed in liquid nitrogen. The tube was evacuated and sealed at 0.01 mm. It was shaken in a 65°C water bath (Figure 2). After 72 hours the tube was opened and the latex coagulated by addition of first 1 mL of 10% aqueous lithium chloride solution followed by 0.5 mL of concentrated hydrochloric acid. The tube was shaken and the contents took on a blue cast. The mixture was poured into 250 mL of stirred methanol. The white suspension which formed quickly coalesced into a white clump of polymer. The product was dissolved in cyclohexane and reprecipitated into methanol, then dried at 60°C and 0.1 mm for 24 hours to yield 1.13 g (23%) of clear, rubbery polymer. (The analytical sample was dried for three days at 160°C and 0.005 mm.) Molecular weights of the material, as determined by gel permeation chromatography, were $\bar{M}_n = 23{,}500$ and $\bar{M}_w = 121{,}000$. The infrared spectrum (film) showed absorbances at 3650 cm^{-1} (hindered phenol O-H stretch), 1640 cm^{-1} (trisubstituted C=C stretch) and 1597 cm^{-1}

(aromatic C=C stretch). The bands at 3650 and 1597 cm^{-1} were weak. See p. 192. ^{13}C NMR analysis ($CDCl_3$) showed peaks at: 16-40 ppm (alkane absorptions of polyisoprene); and 110-135 ppm (alkene absorptions of polyisoprene). See p. 182. Peaks due to phenolic monomer were too small to be visible. ^{1}H NMR showed these peaks at δ: 1.4 ($C(C\underline{H}_3)_3$); 1.6 and 1.7 ($-C\underline{H}_3$ of cis, trans polyisoprene); 2.0 and 2.1 ($C\underline{H}_2$ of polyisoprene); 4.6 and 5.0 ($=C\underline{H}_2$ of 3,4 and $=C\underline{H}-$ of 1,4 isoprene units, respectively). See p. 171.

ANAL. Calcd. for $-\!(C_{16}H_{24}O)\!-_{0.08}$ $-\!(C_5H_8)\!-_{0.92}$: C, 87.72%; H, 11.71%. Found: C, 87.42%; H, 11.32%.

9. Copolymerization of 2,6-di-t-butyl-4-vinylphenol with isoprene in bulk. A polymerization tube was charged with 2,6-di-*t*-butyl-4-vinylphenol (0.4 g, 1.7 mmol, 1 mol%) dissolved in freshly distilled isoprene (9.6 g, 140 mmol) and AIBN (0.23 g, 1.7 mmol, 1 mol%). The tube was fitted with a high-vacuum, three-way stopcock, one take-off of which was sealed with a septum. Oxygen-free argon was bubbled through the solution, by means of a long syringe needle, for one-half hour while the tube was kept in an ice bath at 0°C. The tube was degassed further by the freeze-thaw technique and sealed at 0.01 mm. It was then placed in a 65°C water bath. After 110 hours the polymer was isolated by pouring the contents of the tube into 500 mL of stirred methanol. The white, globular precipitate was dried at 60°C and 0.1 mm for 24 hours to yield 2.06 g (21%) of a nearly clear, viscous liquid. (The analytical sample was dried for three days at 160°C and 0.005 mm.) Molecular weights of the polymer were $\bar{M}_n = 6,300$ and $\bar{M}_w = 9,000$, determined by gel permeation chromatography. The infrared spectrum showed absorption peaks at 3650 cm^{-1} (hindered phenol O-H stretch), 1665 cm^{-1} (trisubstituted C=C stretch) and 1640 cm^{-1} (vinylidene C=C stretch from 3,4 addition).

ANAL. Calcd. for $-(C_{16}H_{24}O)-_{0.01}\ -(C_5H_8)-_{0.99}$: C, 88.10%; H, 11.82%. Found: C, 88.01%; H, 11.82%.

D. Preparation and Polymerization of 2,6-Di-t-butyl-4-isopropenylphenol and O-Acetyl-2,6-di-t-butyl-4-isopropenylphenol

1. *O,4-Diacetyl-2,6-di-t-butylphenol*. Prepared according to Hewgill.[54]

2. *O-Acetyl-2,6-di-t-butyl-4-(2-hydroxy-2-propyl)phenol*. Into a 2 liter, three-neck, round-bottomed flask (fitted with a mechanical stirrer, a Claisen adapter carrying an argon inlet and a one liter addition funnel, and a 25 mL, septum-capped addition funnel) were placed magnesium turnings (5.60 g, 230 mmol) which had been further ground in a mortar and pestle. Adsorbed atmospheric water was removed from the interior glass surfaces and the magnesium by heating the setup with a heat gun while flushing the apparatus with argon. Iodomethane (32.6 g, 230 mmol) was

added by syringe to the 25 mL addition funnel, and a crystal of iodine was placed in the flask. Enough dry ethyl ether was poured into the reaction flask to cover the metal turnings, a few drops of iodomethane were added and the stirrer was started. The ether, brown from the iodine, rapidly turned white and turbid due to a suspended precipitate. The Grignard reaction started almost immediately, as indicated by bubbles which formed at the ether-magnesium interface. The argon inlet was replaced by a water-cooled condenser, and the remaining iodomethane was added sufficiently fast to maintain a gentle reflux. After one-half hour, all of the magnesium had dissolved. The 25 mL addition funnel was replaced by the argon inlet and *O*,4-di-acetyl-2,6-di-*t*-butylphenol (60.0 g, 210 mmol) dissolved in one liter of dry ether was added dropwise, again at a rate fast enough to ensure gentle refluxing. After the addition was complete, the reaction was heated to reflux and stirred rapidly for four hours. The intermediate magnesium complex was hydrolysed by dropwise addition of ammonium chloride (32 g in 100 mL of water). The amber-colored organic layer was separated from the aqueous layer and ether was removed on a rotary evaporator to yield a tan solid. The product was not purified further before dehydration to *O*-acetyl-2,6-di-*t*-butyl-4-isopropenylphenol. However, a ^{1}H NMR ($CDCl_3$) of the crude product showed peaks at δ: 1.5 ($C(C\underline{H}_3)_3$); 1.7 ($HO\text{-}\overset{|}{C}(C\underline{H}_3)_2$); 2.2 ($COC\underline{H}_3$); 3.5

(O$\underline{H}$); and 7.5 (aromatic). Infrared analysis (neat) showed peaks at 3440 cm^{-1} (broad; hydrogen-bonded O-H stretch); 1770 cm^{-1} (acetate C=O stretch); and 1603 cm^{-1} (aromatic C=C stretch).

3. *O-Acetyl-2,6-di-t-butyl-4-isopropenylphenol*. Crude *O*-acetyl-2,6-di-*t*-butyl-4-(2-hydroxy-2-propyl)phenol (58 g) was placed in a 250 mL, round-bottomed flask. Potassium hydrogen sulfate (1.5 g, freshly fused and ground) and powdered copper (0.1 g) were added as well as 60 mL of a mineral-oil chaser. The alcohol was melted and stirred at 60°C and 0.2 mm pressure until the end of dehydration was signaled by the absence of violent bubbling in the reaction vessel. The dehydration product was then distilled from the same flask through a very short column. The product, a clear viscous liquid, was collected between 130 and 140°C at 0.05 mm. The yield over two steps (Grignard reaction and dehydration) was 40.4 g (63%). The infrared spectrum (neat) showed peaks at: 1770 cm^{-1} (acetate C=O stretch); 1632 cm^{-1} (vinylidene C=C stretch); and 1597 (aromatic C=C stretch). See p. 189. ^{13}C NMR analysis ($CDCl_3$) showed peaks at: 21.90 ppm ($OCO\underline{C}H_3$); 22.47 ppm ($CH_2=\overset{|}{C}-\underline{C}H_3$); 31.45 ppm ($C(\underline{C}H_3)_3$); 35.37 ppm ($\underline{C}(CH_3)_3$); 112.12 ppm ($\underline{C}H_2=\overset{|}{C}-CH_3$); 123.59, 138.14, 143.37 and 147.46 ppm (aromatic); 141.85 ppm ($CH_2=\overset{|}{\underline{C}}-CH_3$); and 170.69 ppm ($\underline{C}=O$). See p. 179. The ^{1}H NMR ($CDCl_3$) spectrum displayed peaks at δ: 1.3 ($C(C\underline{H}_3)$,

18H); 2.0 ($CH_2{=}\overset{|}{C}{-}\underline{C}H_3$, 3H); 2.2 ($COC\underline{H}_3$, 3H); 4.8 and 5.1 ($C\underline{H}_2{=}\overset{|}{C}{-}CH_3$, 2H); and 7.2 (aromatic, 2H). See p. .

ANAL. Calcd. for $C_{19}H_{28}O_2$: C, 79.12%; H, 9.78%. Found: C, 79.32%; H, 10.74%.

4. 2,6-Di-t-butyl-4-isopropenylphenol. *O*-Acetyl-2,6-di-*t*-butyl-4-isopropenylphenol (20.2 g, 70 mmol) was dissolved in 125 mL of dry toluene. The solution was added to a 500 mL, round-bottomed flask, followed by lithium aluminum hydride (2.7 g, 70 mmol). The grey solution was heated to reflux over a period of several hours, and reflux was maintained, under an argon atmosphere, for three days. Excess lithium aluminum hydride was consumed by reaction with 15 mL of ethyl acetate. The intermediate aluminum complex was then hydrolyzed by addition of 50 mL of concentrated hydrochloric acid. The grey aqueous layer was drained away from the colorless organic layer in a separatory funnel. The organic layer was washed with three 40 mL portions of saturated aqueous sodium carbonate followed by water until neutral. During these washings the organic layer became a faint yellow. The toluene solution was dried over magnesium sulfate and the solvent was removed on a rotary evaporator to give a light yellow oil. With the aid of a mineral-oil chaser, distillation of the oil at 92-94°C and 0.05 mmHg yielded 11.2 g (74%) of liquid 2,6-di-*t*-butyl-4-isopropenylphenol. The monomer was stored under argon at -5°C, slowly crystallizing in the cold. Analytical and spectral data for this compound are given by Braun.[51]

5. Copolymerization of 2,6-di-*t*-butyl-4-isopropenylphenol with *n*-butyl acrylate in solution. A polymerization tube was fitted with a high-vacuum, three-way stopcock and one take-off of the stopcock was capped with a septum. The tube was flushed with argon and 2,6-di-*t*-butyl-4-isopropenylphenol (0.25 g, 1 mmol) dissolved in dry benzene (1.0 mL) was added by syringe. *n*-Butyl acrylate (1.30 g, 10 mmol) was added in the same manner, as was AIBN (3.2 mg, 0.02 mmol, 0.2 mol%) dissolved in benzene (1 mL). The tube was degassed by the freeze-thaw technique and sealed at 0.01 mm. It was placed in an oil bath at 70°C. After three days the polymer was isolated by pouring the contents of the tube into 250 mL of methanol. The suspension which resulted was allowed to coalesce on the walls of the vessel. The supernatant methanol was decanted and the sticky polymer which remained was redissolved in benzene. Freeze-drying gave a tacky, water-white film of polymer, which was dried further at room temperature and 0.05 mm for 18 hours. Yield was 0.62 g (40%). (The analytical sample was dried for three days at 160°C and 0.005 mm.) The inherent viscosity of the polymer (0.5% in benzene, 30°C) was 0.04 dL/g. The infrared spectrum (neat)

displayed peaks at 3450 cm^{-1} (O-H stretch) and 1745 cm^{-1} (ester C=O stretch). See p. 190. ^{1}H NMR ($CDCl_3$) showed peaks at δ: 0.8-1.6 ($O\text{-}CH_2\text{-}C_3\underline{H}_7$ and backbone protons); 1.5 ($C(C\underline{H}_3)_3$); 2.2 ($-C\underline{H}_3$ pendant group); 4.1 ($O\text{-}C\underline{H}_2\text{-}$); 5.0 ($-O\underline{H}$); and 7.0 (aromatic). See p. 170. Comparison of peak areas at 4.1 and 7.0 δ indicated a copolymer composition of 40% 2,6-di-*t*-butyl-4-isopropenylphenol and 60% *n*-butyl acrylate.

ANAL. Calcd. for $-\!(C_{17}H_{26}O)\!-_{0.48}$ $-\!(C_{7}H_{12}O_{2})\!-_{0.52}$: C, 73.89%; H, 10.02%. Found: C, 73.84%; H, 11.03%.

6. Copolymerization of 2,6-di-t-butyl-4-isopropenylphenol with styrene in solution. A polymerization tube was fitted with a high-vacuum, three-way stopcock, one take-off of which was capped with a septum. The tube was flushed with argon. It was then charged, by syringe, with 2,6-di-*t*-butyl-4-isopropenylphenol (0.25 g, 1 mmol) dissolved in freshly distilled styrene (1.2 g, 10 mmol). AIBN (3.2 mg, 0.02 mmol, 0.2 mol%) dissolved in dry benzene (1.0 mL), was added next. The tube was degassed by the freeze-thaw technique and sealed at 0.01 mm. After three days in a 70°C oil bath, the tube was opened and the polymer was precipitated in 200 mL of methanol. The white flakes of product were collected by filtration and dried for 12 hours at 60°C and 0.1 mm to yield 0.32 g (22%). The inherent viscosity of the polymer (0.5% in benzene, 30°C) was

0.23 dL/g. Infrared analysis of the copolymer (film) showed bands at 3640 cm^{-1} (hindered phenol O-H stretch), 3100-3000 cm^{-1} (aromatic C-H stretch), 2980-2840 cm^{-1} (aliphatic C-H stretch), 1950-1740 cm^{-1} (styrene overtone and combination bands), 1601 cm^{-1} (styrene C=C stretch), and 1595 cm^{-1} (C=C stretch of 2,6-di-t-butylphenyl group). See p. 191. ^1H NMR ($CDCl_3$) showed peaks at δ: 0.8-2.2 (backbone protons); 1.4 ($C(C\underline{H}_3)_3$); 5.0 ($-O\underline{H}$); 7.1 (aromatic protons of styrene); and 6.6 (aromatic protons of 2,6-di-t-butyl-4-isopropenylphenol). See p. 170.

ANAL. Calcd. for $-\!\!(C_{17}H_{26}O)\!\!-_{0.18}\ -\!\!(C_8H_8)\!\!-_{0.82}$: C, 90.56%; H, 8.26%. Found: C, 90.56%; H, 8.23%.

7. Copolymerization of 2,6-di-t-butyl-4-isopropenylphenol with styrene in emulsion. A polymerization tube was charged with distilled water (6 mL), polyethylene glycol (MW = 1000) emulsifier (0.1 mL), sodium dodecyl sulfate emulsifier (10 mg) and sodium hydroxide (3 mg). Argon, deoxygenated by passing through a commercially available Oxy-Trap, was bubbled into the solution for one-half hour. The tube was then charged with 2,6-di-t-butyl-4-isopropenylphenol (0.25 g, 1 mmol) which had been dissolved in freshly distilled styrene (2.4 g, 20 mmol). Potassium persulfate initiator (70 mg, 0.2 mmol, 1 mol%) and a micro stir bar were added last. The tube was sealed with a septum and an argon atmosphere was maintained using a

syringe needle as a gas inlet. The contents of the tube were stirred rapidly at 50°C for 48 hours. The latex in the tube was coagulated by addition of 10% aqueous lithium chloride solution (1 mL) and concentrated hydrochloric acid (2 mL). On shaking the tube, clumps of polymer were formed and these were collected by filtration. The polymer was reprecipitated from benzene into methanol. The fine flakes of polymer were collected by filtration. Yield was 0.12 g (5%). The spectral properties of this copolymer were identical to those of the copolymer described in section D6.

8. Copolymerization of 2,6-di-t-butyl-4-isopropenylphenol with 1,3-butadiene in emulsion. 1,3-Butadiene was condensed into a 360 mL capacity polymerization tube using the apparatus shown in Figure 1. The amount of liquid collected was determined by weighing the tube before and after filling with diene. A slight excess was collected, and the liquid was allowed to warm slightly in order to vaporize some of the condensate until the correct net weight (40.0 g, 740 mmol, 80 parts by weight) had been reached. The collection tube was then capped with a septum and the liquid butadiene was transferred via double-tipped needle, under pressure of oxygen-free argon, to a 100 mL, round-bottomed flask, also capped by a septum, containing 2,6-di-t-butyl-4-isopropenylphenol (10.0 g, 41 mmol, 20 parts,

5 mol%). The isopropenyl monomer was dissolved by shaking in the butadiene. The solution was kept below the boiling point of butadiene (-4°C) at all times using powdered, solid carbon dioxide. The solution was deoxygenated by bubbling oxygen-free argon through it for one-half hour. It was then transferred via double-tipped needle to a second 360 mL polymerization tube containing the remainder of the emulsion recipe: 4,4'-azobis(cyanovaleric acid) initiator (1.2 g, 2.4 parts); sodium dodecyl sulfate emulsifier (2.5 g, 5 parts); and distilled water (90 g, 180 parts). This second tube had been fitted with a high-vacuum, three-way stopcock, one take-off of which had been sealed with a septum to facilitate double-tipped-needle transfers. This second tube was kept in a rock salt-ice bath at -5°C. (-5°C is cold enough to maintain butadiene below its boiling point as it is being added to the emulsion matrix, but at this temperature the matrix itself will not readily freeze.) Immediately after the transfer was complete, the aqueous phase was remelted by hand-warming, with occasional venting of butadiene pressure in the tube. The tube was rapidly and vigorously shaken to emulsify the contents and frozen in liquid nitrogen while emulsified. (Freezing of a non-emulsified aqueous phase will cause expansion which can shatter the polymerization tube.) The time between completion of the comonomer transfer and freezing in liquid nitrogen did not exceed one minute,

which minimized the need to vent butadiene. The polymerization tube was evacuated and sealed at 0.01 mm. Annealing of the seal was carefully done, since the tube was expected to endure considerable internal pressure (see p. 110). The tube was thawed slowly, placed in a 65°C water bath and shaken to keep the contents of the tube emulsified (see Figure 2). After one week, the tube, now containing a light yellow, stable latex, was removed from the water bath, chilled thoroughly in ice and carefully broken open at the neck. Escaping butadiene gas tended to force frothy latex out of the neck of the tube. Firm finger pressure over the hole, relieved periodically, contained the latex and vented the gas. 10% aqueous lithium chloride solution (10 mL) was added to the tube and it was shaken. Pressure built up during this operation as well. Next, 5 mL of concentrated hydrochloric acid were added and the shaking repeated. The coagulated latex was added slowly to 700 mL of rapidly stirred methanol, and large white clumps of polymer soon coalesced from the initially formed, hazy suspension. The precipitated polymer was stored under methanol in the freezer until all polymer had settled to the bottom of the storage vessel. The methanol was then decanted and the polymer transferred to a 100 mL beaker, where it was dissolved in cyclohexane at room temperature. Reprecipitation into 500 mL of methanol, followed by cooling in the freezer and decantation of the methanol, gave a gelatinous product. The material was placed in a 2 oz. sample vial and dried, first under aspirator vacuum in a bell jar and then in a vacuum dessicator, with heating from an infrared lamp at 0.1 mm for 24 hours. (The analytical sample was dried for three days at 160°C and 0.005 mm.) The yield of clear, light amber, and sticky polymer was 7.9 g (16%). The molecular weight values for the polymer, obtained from gel permeation chromatography, were $\bar{M}_n$ = 13,000 and $\bar{M}_w$ = 25,700. Infrared analysis (film) showed bands at 3650 cm^{-1} (hindered phenol O-H stretch), 1640 cm^{-1} and 1670 cm^{-1} (cis and trans C=C stretch) and 1596 cm^{-1} (aromatic C=C stretch). See p. 191. The ^{13}C NMR spectrum ($CDCl_3$) showed peaks at: 30.22 ($C(\underline{C}H_3)_3$); 27.49, 30.18, 32.77, 34.09, 38.22 and 43.57 ppm ($-\underline{C}H_2-$ of random cis, trans - polybutadiene); 114.21, 128.41, 129.51, 129.66, 130.08, 130.51, 131.30 and 142.76 ppm ($=\underline{C}H-$ of random cis, trans-polybutadiene). See p. 181. ^1H NMR analysis ($CDCl_3$) showed peaks at δ: 1.4 ($C(C\underline{H}_3)_3$); 2.0 ($-C\underline{H}_2-$ of polybutadiene); 5.3 ($=C\underline{H}-$ of 1,4 butadiene unit); 4.9 ($-C\underline{H}=C\underline{H}_2$ of 1,2 unit); and 6.7 (aromatic). See p. 171. A comparison of integrated areas of the peaks at 1.4 δ and 4.9-5.3 δ indicated a copolymer composition of 6% 2,6-di-t-butyl-4-isopropenylphenol and 94% butadiene.

ANAL. Calcd. for $-\!(C_{17}H_{26}O)\!-_{0.06}\ -\!(C_4H_6)\!-_{0.94}$: C, 88.46%; H, 11.15%. Found: C, 88.21%; H, 11.03%.

9. Copolymerization of 2,6-di-*t*-butyl-4-isopropenylphenol with isoprene in emulsion. Freshly distilled isoprene (35.8 g, 525 mmol, 72 parts by weight) was pipetted into a 100 mL, round-bottomed flask containing 2,6-di-*t*-butyl-4-isopropenylphenol (6.5 g, 26 mmol, 13 parts, 5 mol%). The flask was capped with a septum and shaken to dissolve the phenolic monomer. A stream of oxygen-free argon was bubbled through the solution, which was maintained at 0°C. After one-half hour the solution was transferred via double-tipped needle to a polymerization tube containing the rest of the emulsion recipe: 4,4'-azobis(cyanovaleric acid) initiator (1.2 g, 2.4 parts); sodium dodecyl sulfate emulsifier (2.5 g, 5 parts); and distilled water (90 g, 180 parts). The tube had been fitted with a high-vacuum, three-way stopcock, one take-off of which had been sealed with a septum to facilitate double-tipped-needle transfers. This tube was also deoxygenated by bubbling a stream of oxygen-free argon through it. After being filled, the tube was shaken to emulsify the contents and immersed in liquid nitrogen. The tube was evacuated and sealed at 0.01 mm. It was shaken in a 65°C water bath (Figure 2). After one week the tube was opened and the latex coagulated by addition of 10% aqueous lithium chloride solution (10 mL) and concentrated hydrochloric acid (5 mL). The tube was shaken to mix the contents thoroughly. The mixture was poured into 700 mL of stirred methanol. The white suspension

which formed quickly coalesced into a mass of white polymer. After cooling in the freezer to allow all of the product to settle to the bottom of the vessel, the polymer was transferred to a 100 mL beaker and dissolved in cyclohexane at room temperature. It was reprecipitated into methanol, and the methanol was cooled in the freezer, then decanted. The polymer was dried, first in a bell jar under aspirator vacuum, then using an IR lamp at room temperature and 0.1 mm in a vacuum dessicator. (The analytical sample was dried for three days at 160°C and 0.005 mm.) Yield of clear, rubbery polymer was 7.4 g (18%). Molecular weights of the material, as determined by gel permeation chromatography, were $\bar{M}_n = 10,500$ and $\bar{M}_w = 18,500$. The infrared spectrum (film) showed absorbances at 3650 cm^{-1} (hindered phenol O-H stretch), 1665 cm^{-1} (trisubstituted C=C stretch) and 1597 cm^{-1} (aromatic C=C stretch). See p. 192. ^{13}C NMR analysis ($CDCl_3$) showed peaks at 16-40 ppm (alkane absorptions of polyisoprene) and 110-135 ppm (alkene absorptions of polyisoprene). The peak at 30.2 ppm, due to $-\underline{C}H_3$ of the t-butyl group of the phenolic monomer, was covered by isoprene peaks. See p. 182. ^1H NMR ($CDCl_3$) showed peaks at δ: 1.4 ($C(C\underline{H}_3)_3$); 1.6 and 1.7 ($-C\underline{H}_3$ of cis, trans-polyisoprene), 2.0 and 2.1 ($-C\underline{H}_2-$ of polyisoprene); 4.6 and 5.0 ($=C\underline{H}_2$ of 3,4- and $=C\underline{H}-$ of 1,4-isoprene units, respectively). See p. 171. Comparison of integration areas for the peaks at 1.6-1.7 δ and 1.4 δ indicates a copolymer composition of 4% 2,6-di-*t*-butyl-4-isopropenylphenol and 96% isoprene.

ANAL. Calcd. for $-\!(C_{17}H_{26}O)\!-_{0.06}$ $-\!(C_5H_8)\!-_{0.94}$: C, 87.84%; H, 11.75%. Found: C, 86.71%; H, 11.61%.

E. Preparation of 4-Acetyl-2,6-di-*t*-butylphenol

2,6-Di-*t*-butylphenol (52 g, 250 mmol) was placed in a 250 mL Erlenmeyer flask. Acetic anhydride (30 mL, 300 mmol) was added followed by boron trifluoride etherate (40 mL). The flask was tightly stoppered and kept at 5°C for seven days. Workup consisted of pouring the dark brown solution into an ice-filled beaker. (Some pieces of brown solid were also present.) A crust of solid was formed as ether evaporated from the beaker. The crude product was twice decolorized and recrystallized from a 70%-30% ethanol-water mixture to give a faintly orange material which was dried for 12 hours at 0.5 mm and 60°C. Yield was 19.4 g (30%), m.p. 150-151.5. Infrared analysis (KBr) showed peaks at 3595 cm^{-1} (hindered phenol O-H stretch) and 1670 cm^{-1} (methyl phenyl ketone C=O stretch). See p. 193. The ^{13}C NMR spectrum ($CDCl_3$) showed peaks at 26.27 ppm ($-CO\underline{C}H_3$), 30.15 ppm ($C(\underline{C}H_3)_3$), 34.37 ppm ($\underline{C}(CH_3)_3$), 126.09 ppm, 129.17 ppm, 135.82 ppm and 158.43 ppm (aromatic), and 197.53 ppm ($-\underline{C}OCH_3$). See p. 184. ^1H NMR analysis ($CDCl_3$) showed resonances at δ: 1.5

($C(CH_3)_3$, 18H); 2.6 ($COCH_3$, 3H); 2.9 (OH, 1H); and 8.1 (aromatic, 2H). See p. 173.

ANAL. Calcd. for $C_{16}H_{24}O_2$: C, 77.38%; H, 9.74%. Found: C, 77.21%; H, 9.86%.

F. Attempted Alkylation of 2,6-Di-*t*-butylphenol

2,6-Di-*t*-butylphenol (10.0 g, 50 mmol) was dissolved in hexane (150 mL) and added to a 500 mL, three-neck, round-bottomed flask. Propylene oxide (2.9 g, 50 mmol) and aluminum trichloride (7.0 g, 53 mmol) were also added to the flask and the reaction was stirred at 0°C for 12 hours. The reaction mixture was then poured onto ice, and the aqueous layer separated from the organic layer. Hexane was removed on a rotary evaporator. The residue was distilled at 89-91°C and 0.5 mm Hg. The ^{13}C NMR spectrum of the distillate was identical to that of the starting material. See p. 175.

G. Attempted Wittig Reaction With 2,6-Di-*t*-butyl-4-formylphenol

Sodium hydride (1.2 g, 50 mmol) was placed in a 125 mL, round-bottomed flask and triphenylmethyl phosphonium bromide (18.0 g, 50 mmol, previously dried at 3 mm and 50°C for 12 hours) was weighed out and placed in a 250 mL addition funnel, which was then fitted with a septum. These first two operations were performed in a glove bag.

A magnetic stir bar was added to the round-bottomed flask and it was fitted with a condenser, Claisen adapter and an argon inlet. One neck of the Claisen adapter was capped with a septum, argon flow was started through the apparatus, and dry dimethyl sulfoxide (25 mL) was syringed into the flask. The mixture was heated to 80°C for 45 minutes, and hydrogen evolution was observed. Dry dimethyl sulfoxide (50 mL) was added by syringe to the triphenylmethyl phosphonium bromide in the addition funnel and the resulting solution was added dropwise to the solution of methylsulfinyl carbanion in the round-bottomed flask. To this orange mixture was added 2,6-di-t-butyl-4-formylphenol (11.7 g, 50 mmol) via a solids-addition tube inserted in the other neck of the Claisen adapter. On addition of the aldehyde, the solution turned deep green. Not all of the aldehyde dissolved. The reaction was stirred at room temperature for two days. The green dimethyl sulfoxide solution was then distilled to dryness (29-30°C and 0.10 mm). The dark green mass which remained was extracted with ether for 24 hours in a Soxhlet apparatus. The light green solid which remained on evaporation of the ether was identified as starting material on the basis of melting point and infrared spectrum.

H. Attempted Silylation of 2,6-Di-*t*-butyl-4-formylphenol

1. Reaction of 2,6-di-*t*-butyl-4-formylphenol with chlorotrimethylsilane. Dry acetonitrile (125 mL) was added to a 250 mL, round-bottomed flask containing 2,6-di-*t*-butyl-4-formylphenol (2.3 g, 10 mmol). One neck of the flask was sealed with a septum. Under an argon atmosphere, the solvent was brought to reflux and the system became homogeneous. Triethylamine (1.2 g, 12 mmol) was added to the reaction by syringe and a brown color appeared. Next, chlorotrimethylsilane (1.1 g, 10 mmol) was added via syringe, which turned the reaction an amber color. Reflux was continued for a further 12 hours, then the reaction was cooled and acetonitrile removed on the rotary evaporator to yield orange crystals. These were dissolved in benzene (450 mL) and washed with three 125 mL portions of distilled water (to remove triethylammonium chloride). The benzene solution was dried over magnesium sulfate. After removal of the dessicant, the solution was decolorized and benzene was removed on the rotary evaporator to give free-flowing, light yellow crystals. Recrystallization from low-boiling petroleum ether yielded fine, white needles which, according to melting point and ^1H NMR data, were starting material.

2. Reaction of 2,6-di-t-butyl-4-formylphenol with bistrimethylsilylacetamide. 2,6-Di-t-butyl-4-formylphenol (0.5 g, 2 mmol) was weighed into a 50 mL, round-bottomed flask. Under an argon atmosphere, bistrimethylsilylacetamide (8.3 g, 40 mmol) was added by syringe, immediately dissolving the phenol. The reaction was stirred at room temperature for one hour. Then the yellow mixture was diluted with chloroform (30 mL) and transferred to a separatory funnel where it was washed with four 20 mL portions of distilled water. The organic layer was dried over magnesium sulfate and solvent was removed on the rotary evaporator to yield yellow crystals. Trituration with low-boiling petroleum ether removed most of the color. Recrystallization from acetonitrile yielded beige plates which were shown by melting point and ^{1}H NMR to be starting material.

I. Catalytic Hydrogenation of Copolymers of 2,6,-Di-t-butyl-4-vinylphenol and 2,6-Di-t-butyl-4-isopropenylphenol with 1,3-Butadiene and Isoprene

Poly(2,6-di-t-butyl-4-vinylphenol-co-1,3-butadiene) (2.2 g, 40 mmol of unsaturation, 6 mol% phenolic units) was weighed into a 100 mL, round-bottomed flask. The flask was capped with a septum, flushed with oxygen-free argon and charged with dry cyclohexane (100 mL). After the polymer had dissolved, the cyclohexane solution was transferred via double-tipped needle to an assembled 160 mL, stirred, thermostatted reactor. (A septum was conveniently located on the reactor by temporarily removing the thermocouple from its threaded fitting. The thermocouple was replaced before pressurizing the reactor.) Next, triethyl aluminum-cobalt 2-ethylhexanoate catalyst (0.67 mL of a 0.178 M solution in cyclohexane, 7 mol%) was syringed into the reactor. The reactor was flushed with CP Grade hydrogen by charging to 300 psi five times and venting each time. Finally, the reactor was charged to 50 psi and heated to 50°C. These conditions were maintained for one hour with intermittent stirring. The reactor was then cooled, vented and opened. The black solution inside was shaken vigorously with 10% hydrochloric acid (30 mL) until it turned pink, signifying formation of the aquo cobalt complex. The pink emulsion which resulted could not be broken, so it was added directly to 500 mL of stirred methanol to precipitate the polymer. The off-white product was collected on a sintered-glass funnel and purified by dissolution in cyclohexane and reprecipitation into methanol. The polymer was dried at 60°C and 0.1 mm for 12 hours. (The analytical sample was dried for three days at 160°C and 0.005 mm.) Yield of white, spongy solid was 0.3 g (60%). Infrared analysis (film) showed peaks at 3650 cm^{-1} (hindered phenol O-H stretch), 2930-2860 cm^{-1} (alkane C-H stretch), 1465-1450 cm^{-1} (CH_2 and CH_3 deformation) and 720 cm^{-1} (alkane

C-H rocking). See p. 192. ^{13}C NMR (benzene-d_6) showed a major peak at 30.2 ppm ($-\underline{C}H_2-$) and minor peaks at 27.44, 30.71 and 34.02 ppm (alkane branches). See p. 183. ^1H NMR (benzene-d_6) showed one peak at 1.4 δ (broad; alkane protons). See p. 172.

ANAL. Calcd. for $-\!(C_{16}H_{24}O)\!-_{0.06}$ $-\!(C_4H_8)\!-_{0.94}$: C, 85.45%; H, 14.13%. Found: C, 83.78%; H, 13.76%; ASH, 2.1%.

The procedure for hydrogenation of poly(2,6-di-*t*-butyl-4-isopropenylphenol-co-1,3-butadiene) was identical to that described above, as were the spectral and physical properties.

Copolymers of 2,6-di-*t*-butyl-4-vinylphenol and 2,6-di-*t*-butyl-4-isopropenylphenol with isoprene were hydrogenated in a similar manner using 10 mol% triethyl aluminum-cobalt 2-ethylhexanoate catalyst. Also, during workup of the product, the pink emulsion separated readily, and the resulting cyclohexane solution was thus added to methanol (500 mL) to isolate the polymer. After reprecipitation and drying, the brown polymer was tough and rubbery. (The analytical sample was dried for three days at 160°C and 0.005 mm.) Infrared analysis (film) of the hydrogenated isoprene copolymers showed peaks at: 3650 cm^{-1} (hindered phenol O-H stretch); 2980-2850 (alkane C-H stretch); 1470-1450 cm^{-1} (CH_2 and CH_3 deformation); and 732 cm^{-1} (alkane C-H rocking). See p. 193. ^{13}C NMR analysis (benzene-d_6) showed peaks at: 20.08, 25.08, 28.05, 33.37, 33.71, 35.01 and 38.06 (branched and linear alkane absorptions). See p. 183. ^1H NMR analysis showed only two broad peaks, one at 1.0 δ ($-\underline{C}H_3$) and 1.3 δ ($-CH_2-$). See p. 172.

ANAL. Calcd. for $-\!(C_{17}H_{26}O)\!-_{0.06}$ $-\!(C_5H_{10})\!-_{0.94}$: C, 85.46%; H, 14.15%. Found: C, 84.24%; H, 14.65%; ASH, 2.2%.

J. Solution Blending of Copolymers

Diene copolymers of 2,6-di-*t*-butyl-4-vinylphenol and 2,6-di-*t*-butyl-4-isopropenylphenol were blended with homopolymers of butadiene and isoprene, and styrene-butadiene rubber, according to Table 1. The blends were made by mixing a cyclohexane solution of the appropriate diene polymer (30 mL of a 2 g/60 mL solution, Table 2) with a cyclohexane solution of the correct polymeric stabilizer (0.6 mL of a 0.015 g/2 mL solution of butadiene copolymers; 1.0 mL of a 0.016 g/2 mL solution of isoprene copolymers). The blend, containing 0.001 g of phenolic stabilizer per gram or 0.1 weight % antioxidant units, was precipitated in methanol (250 mL), dried at 160°C and 0.005 mm for two days, and stored in the cold.

Hydrogenated diene copolymers of 2,6-di-*t*-butyl-4-vinylphenol and 2,6-di-*t*-butyl-4-isopropenylphenol were blended with polyolefins similarly, according to Table 3.

Table 1. Blends Made With Diene Polymers for Oxygen-Uptake Experiments.

	cis-Poly-butadiene	Random *cis*, *trans*-Poly-butadiene	SBR	*cis*-Poly-isoprene	*trans*-Poly-isoprene
Poly)2,6-di-*t*-butyl-4-vinylphenol-co-butadiene)	X	X	X		
Poly(2,6-di-*t*-butyl-4-isopropenylphenol-co-butadiene)	X	X	X		
Poly(2,6-di-*t*-butyl-4-vinylphenol-co-isoprene)				X	X
Poly(2,6-di-*t*-butyl-4-isopropenylphenol-co-isoprene)				X	X

All blends contain 0.1 weight % phenolic moiety.

Table 2. Solutions of Phenol-diene Copolymers Prepared for Blending With Polydienes.

Polymer	Mol % Antioxidant	g of Polymer	Volume* of Solution, mL
Poly(2,6-di-*t*-butyl-4-vinylphenol-co-butadiene)	6	0.015	2.0
Poly(2,6-di-*t*-butyl-4-isopropenylphenol-co-butadiene)	6	0.015	2.0
Poly(2,6-di-*t*-butyl-4-vinylphenol-co-isoprene)	8	0.016	2.0
Poly(2,6-di-*t*-butyl-4-isopropenylphenol-co-isoprene)	6	0.016	2.0
cis-Polybutadiene	-	2.0	60.0
random *cis*, *trans*-Polybutadiene	-	2.0	60.0
cis-Polyisoprene	-	2.0	60.0
trans-Polyisoprene	-	2.0	60.0
Styrene-butadiene copolymer (SBR), 25% styrene	-	2.0	60.0

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*All solutions in cyclohexane, 99+%.

Table 3. Blends Made With Polyolefins for Oxygen-Uptake Experiments.

	HDPE	LDPE	LLDPE	Atactic Polypropylene
Hydrogenated poly(2,6-di-*t*-butyl-4-vinylphenol-co-butadiene)	X	X	X	X
Hydrogenated poly(2,6-di-*t*-butyl-4-isopropenylphenol-co-butadiene)	X	X	X	X
Hydrogenated poly(2,6-di-*t*-butyl-4-vinylphenol-co-butadiene)	X	X	X	X
Hydrogenated poly(2,6-di-*t*-butyl-4-isopropenylphenol-co-isoprene)	X	X	X	X

All blends contain 0.1 weight % phenolic moiety.

The blends were made by mixing a hot o-xylene solution of the appropriate polyolefin (50 mL of a 4 g/200 mL solution, Table 4) with an o-xylene solution of the correct hydrogenated polymeric stabilizer (0.5 mL of a 0.02 g/2 mL solution for hydrogenated butadiene copolymers, 0.5 mL of a 0.03 g/2 mL solution for hydrogenated isoprene copolymers). The blend, containing 0.001 g of phenolic stabilizer per gram or 0.1 weight % antioxidant units, was precipitated in methanol (250 mL), dried at 60°C and 0.005 mm for two days, and stored in the cold.

The same procedure was used in preparing blends of hydrogenated polymeric stabilizers with high-density polyethylene and linear, low-density polyethylene, as shown in Table 5, for use in differential scanning calorimetry studies of compatibility.

K. Measurements

Oxygen-uptake experiments were performed at 150°C and one atmosphere oxygen pressure in the apparatus shown in Figure 3. Up to eight samples were tested simultaneously by employing eight such apparati connected to sources of vacuum and oxygen through a manifold equipped with a Firestone valve. 50 mg of the blend to be tested were placed in a glass tube, which was closed at one end, followed by a plug of glass wool, 2 g of calcium oxide, and another plug of glass wool. The glass tube was then attached to the

Table 4. Solutions of Hydrogenated Phenol-diene Copolymers Prepared for Blending with Polyolefins.

Polymer	Mol % Antioxidant	g of Polymer	Volume* of Solution, mL
Hydrogenated poly(2,6-di-_t_-butyl-4-vinylphenol-co-butadiene)	6	0.02	2.0
Hydrogenated poly(2,6-di-_t_-butyl-4-isopropenylphenol-co-butadiene)	6	0.02	2.0
Hydrogenated poly(2,6-di-_t_-butyl-4-vinylphenol-co-isoprene)	8	0.12	2.0
Hydrogenated poly(2,6-di-_t_-butyl-4-isopropenylphenol-co-isoprene)	6	0.03	2.0
High-density polyethylene (HDPE)	-	4.0	200
Low-density polyethylene (LDPE)	-	4.0	200
Linear-low density polyethylene (LLDPE); poly(ethylene-co-1-butene)	-	4.0	200
Atactic polypropylene	-	4.0	200

*All solutions in _o_-xylene, 97%.

Table 5. Blends Made for Compatibility Studies via Differential Scanning Calorimetry.

Hydrogenated poly(2,6-di-*t*-butyl-4-vinylphenol-co-butadiene) blended with HDPE	0, 33, 67, 100 weight % HDPE
Hydrogenated poly(2,6-di-*t*-butyl-4-vinylphenol-co-butadiene) blended with LLDPE	0, 33, 67, 100 weight % LLDPE
Hydrogenated poly(2,6-di-*t*-butyl-4-isopropenylphenol-co-isoprene) blended with HDPE	0, 33, 67, 100 weight % HDPE
Hydrogenated poly(2,6-di-*t*-butyl-4-isopropenylphenol-co-isoprene) blended with LLDPE	0, 33, 67, 100 weight % LLDPE

All samples annealed at 150°C under vacuum before testing on DSC to duplicate thermal history of samples used in oxygen-uptake experiments.

Figure 3. Oxygen-uptake apparatus. Components are: A, three-way stopcock; B, glass tubing; C, graduated five-mL pipet; D, tygon tubing; E, mercury; F, stopcock; G, mercury reservoir.

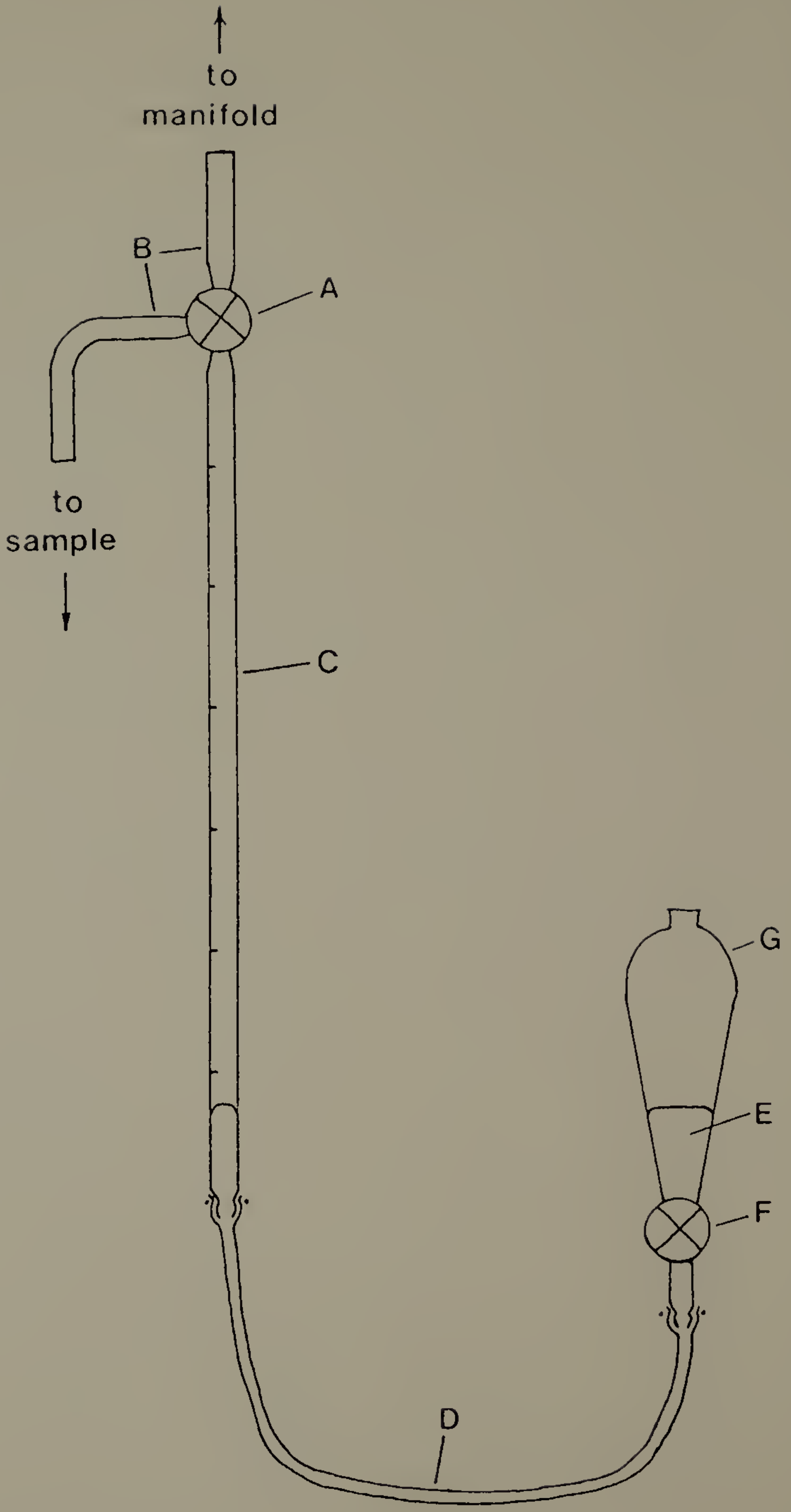


Figure 3.

measurement apparatus by a short length of tygon tubing. The apparatus was alternately evacuated and filled with oxygen three times. After the final filling, the pressure in the apparatus was adjusted to one atmosphere with the aid of the Firestone valve and by raising or lowering the mercury reservoir until the level in the reservoir was the same height as that in the buret of the apparatus. The sample tube was kept in a 150°C bath throughout the experiment and oxygen uptake was determined volumetrically by direct reading of the buret.

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. Low-molecular-weight, crystalline samples were analyzed as potassium bromide pellets, while high-molecular-weight samples and low-molecular-weight oils were analyzed as films deposited from chloroform, cyclohexane, benzene or o-xylene on a sodium chloride plate.

^1H NMR spectra were recorded on a Varian T-60 60 MHz spectrometer.

^{13}C NMR spectra were recorded on a Varian CFT-20 Fourier-transform spectrometer operating at 22.6 MHz. Sample concentrations were typically 20-40 w/v % in $CDCl_3$ or benzene-d_6. Several hundred transients were accumulated for low molecular weight samples, while polymer samples required at least 20,000 transients. Other parameters included a pulse delay of 0 to 15 seconds, a pulse width of

5 to 15 microseconds, and an acquisition time of 1.023 seconds.

Inherent viscosity measurements were made at 30°C using an Ubbelohde-type viscometer. Reported values are the average of three runs. Solution concentrations were 0.5 g/dL in benzene.

Gel permeation chromatography was performed on a Waters Associates Model 201 liquid chromatograph using tetrahydrofuran as solvent. The flow rate was 1.5 mL/min. The instrument was calibrated using a set of four narrow-distribution polystyrenes supplied by Pressure Chemicals and Waters Associates.

Glass transition temperatures of pure polymers and blends were determined on a Perkin-Elmer DSC 2 differential scanning calorimeter at a heating rate of 20 K/min. and a sensitivity of 5 mcal/sec. The instrument was calibrated using a cyclohexane standard exhibiting a crystal-crystal transition at 186.1 K and a melting point of 279.7 K.

Melting points of low-molecular-weight samples were determined on a Mel-Temp capillary melting-point apparatus and are uncorrected.

Microanalyses were performed by the Microanalytical Laboratory at the University of Massachusetts, Amherst, Massachusetts.

CHAPTER III

RESULTS AND DISCUSSION

A. Objectives

The objectives of this work were the synthesis of two polymerizable derivatives of 2,6-di-_t_-butylphenol, copolymerization of the monomers with 1,3-butadiene and isoprene, and the hydrogenation of the backbones of the copolymers. Both the diene and saturated copolymers were tested for effectiveness as polymeric antioxidants.

2,6-Di-_t_-butyl-4-vinylphenol and _O_-acetyl-2,6-di-_t_-butyl-4-vinylphenol were synthesized in yields of 47% and 79%, respectively, starting with 2,6-di-_t_-butylphenol. The former monomer was successfully copolymerized with butadiene and isoprene by radical emulsion, forming polymeric antioxidants. Copolymerization of the latter monomer with styrene and methyl methacrylate was also investigated.

2,6-Di-_t_-butyl-4-isopropenylphenol was synthesized in an overall yield of 43%. The monomer was copolymerized in solution (using AIBN initiator) with styrene and _n_-butyl acrylate, and in radical emulsion with butadiene and isoprene.

Monomer preparations involving alkylation of 2,6-di-t-butylphenol and a Wittig reaction on 2,6-di-t-butyl-4-formylphenol were investigated, but these procedures were unsuccessful.

Copolymers of 2,6-di-t-butyl-4-vinylphenol and 2,6-di-t-butyl-4-isopropenylphenol with butadiene and isoprene were hydrogenated using an aluminum/cobalt catalyst under mild conditions to yield hindered phenol-ethylene copolymers and hindered phenol-ethylene-propylene terpolymers in yields of up to 60%.

The phenol-diene copolymers were blended with commercial polydienes and the hydrogenated phenol-diene copolymers were blended with commercial polyolefins. The stabilized blends were tested via oxygen uptake for protection against thermooxidative degradation, which was provided by the polymeric antioxidants.

B. Preparation and Polymerization of 2,6-Di-t-butyl-4-vinylphenol and O-Acetyl-2,6-di-t-butyl-4-vinylphenol

1. Introduction. 2,6-Di-t-butyl-4-vinylphenol and O-acetyl-2,6-di-t-butyl-4-vinylphenol were synthesized in yields of 47% and 79%, respectively, starting with 2,6-di-t-butylphenol. The former monomer was successfully copolymerized with 1,3-butadiene and isoprene by radical emulsion, forming polymeric antioxidants. Homopolymerization of the latter monomer and its copolymerization with methyl

methacrylate were also investigated.

2. Preparation of 2,6-di-*t*-butyl-4-vinylphenol and *O*-acetyl-2,6-di-*t*-butyl-4-vinylphenol. The first three steps of the synthesis were those developed by Hewgill[54] in his synthesis of *O*-acetyl-2,6-di-*t*-butyl-4-vinylphenol (see Figure 4).

2,6-Di-*t*-butylphenol underwent simultaneous Freidel-Crafts O-acylation and C-acylation at the 4-position, using five equivalents of aluminum chloride and acetyl chloride as solvent. Reduction of the methyl ketone followed using sodium borohydride in ethanol. Dehydration of the resulting alcohol gave *O*-acetyl-2,6-di-*t*-butyl-4-vinylphenol in 79% yield.

The dehydration procedure was faithful to that of Hewgill,[54] but the product was isolated in a different manner. In place of evaporative distillation, the material was vacuum distilled through a very short column at 138-40°C and 0.01 mm. The product remained liquid until an aliquot was removed for analysis via disposable pipet or until it was cooled to -5°C. Further purification of *O*-acetyl-2,6-di-*t*-butyl-4-vinylphenol prior to polymerization was achieved by evaporative distillation at 90-100°C and 0.025 mm.

Lithium aluminum hydride (LAH) was employed, as it was by Hewgill,[54] to cleave the acetate ester. However,

Figure 4. Synthesis of 2,6-di-_t_-butyl-4-vinylphenol and _O_-acetyl-2,6-di-_t_-butyl-4-vinylphenol.

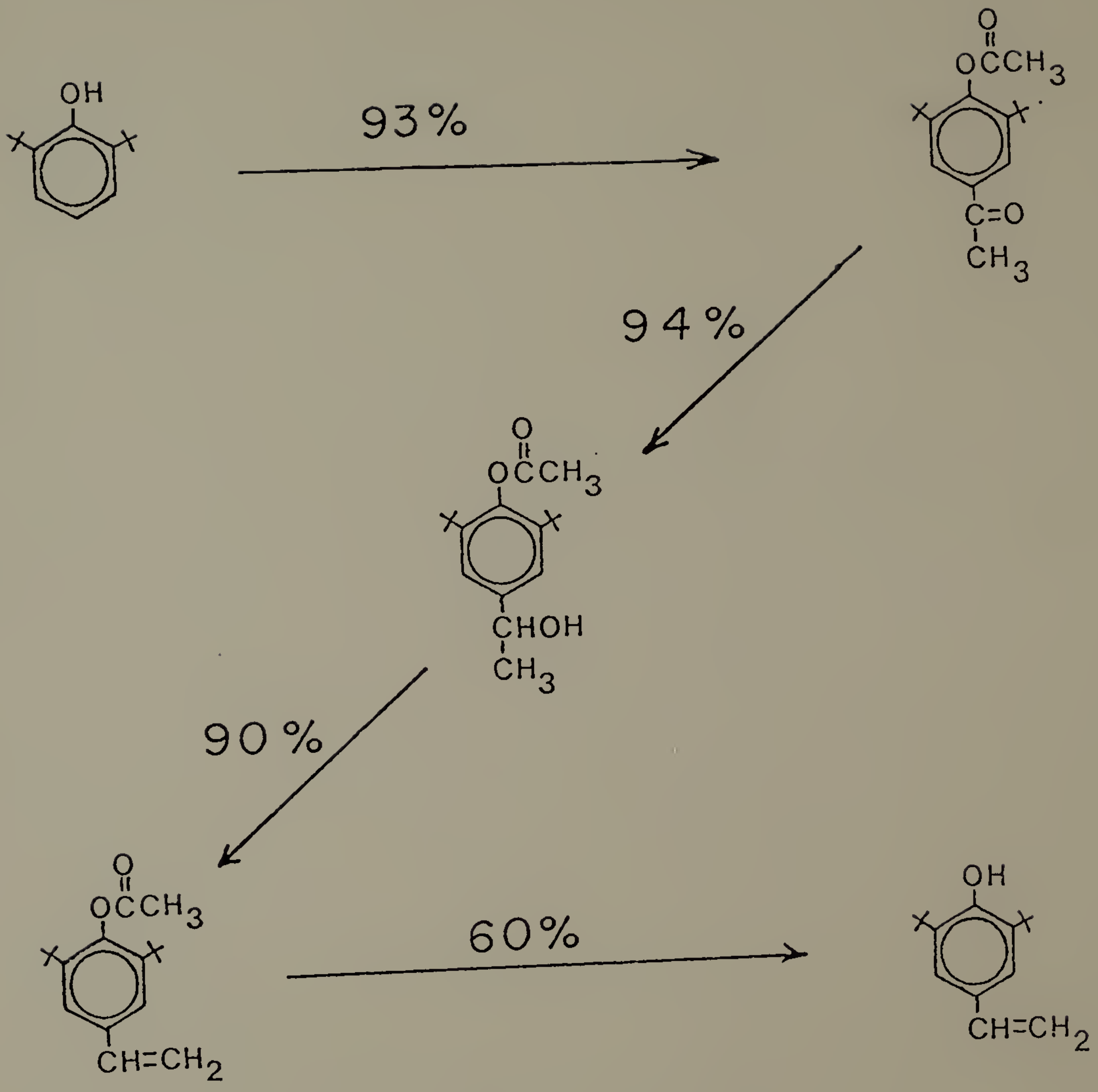


Figure 4.

whereas Hewgill performed this reaction on a polymer containing blocked phenol groups, in this case the monomer was the substrate. The reaction was conducted in toluene, a high-boiling solvent which readily dissolved O-acetyl-2,6-di-t-butyl-4-vinylphenol.

The reaction mixture was brought to reflux extremely slowly (over a period of several hours) to reduce the possibility of a runaway reaction between LAH and moisture in the nominally dry, spectral-grade solvent.

Use of a mineral-oil chaser during the distillation of 2,6-di-t-butyl-4-vinylphenol reduced losses of monomer due to overheating and provided yields of up to 60%. The liquid product was collected at 86-90°C and 0.4 mm. It, too, solidified when stored at -5°C.

3. Preparation of polymers of 2,6-di-t-butyl-4-vinylphenol and O-acetyl-2,6-di-t-butyl-4-vinylphenol. The polymerizations of O-acetyl-2,6-di-t-butyl-4-vinylphenol proceeded at a reasonable rate and in good yield, but it was apparent from the existence of an induction period in these radical polymerizations that the acetylated monomer was contaminated with a small amount of free phenol.

A series of copolymerizations with methyl methacrylate was carried out, and yield of polymer was determined as a function of time. The data are plotted in Figure 5. The polymerization is inhibited for approximately

Figure 5. Plot of conversion vs. time for the copolymerization of O-acetyl-2,6-di-t-butyl-4-vinylphenol with methyl methacrylate at 75°C. Initiator was AIBN (0.5 mol %).

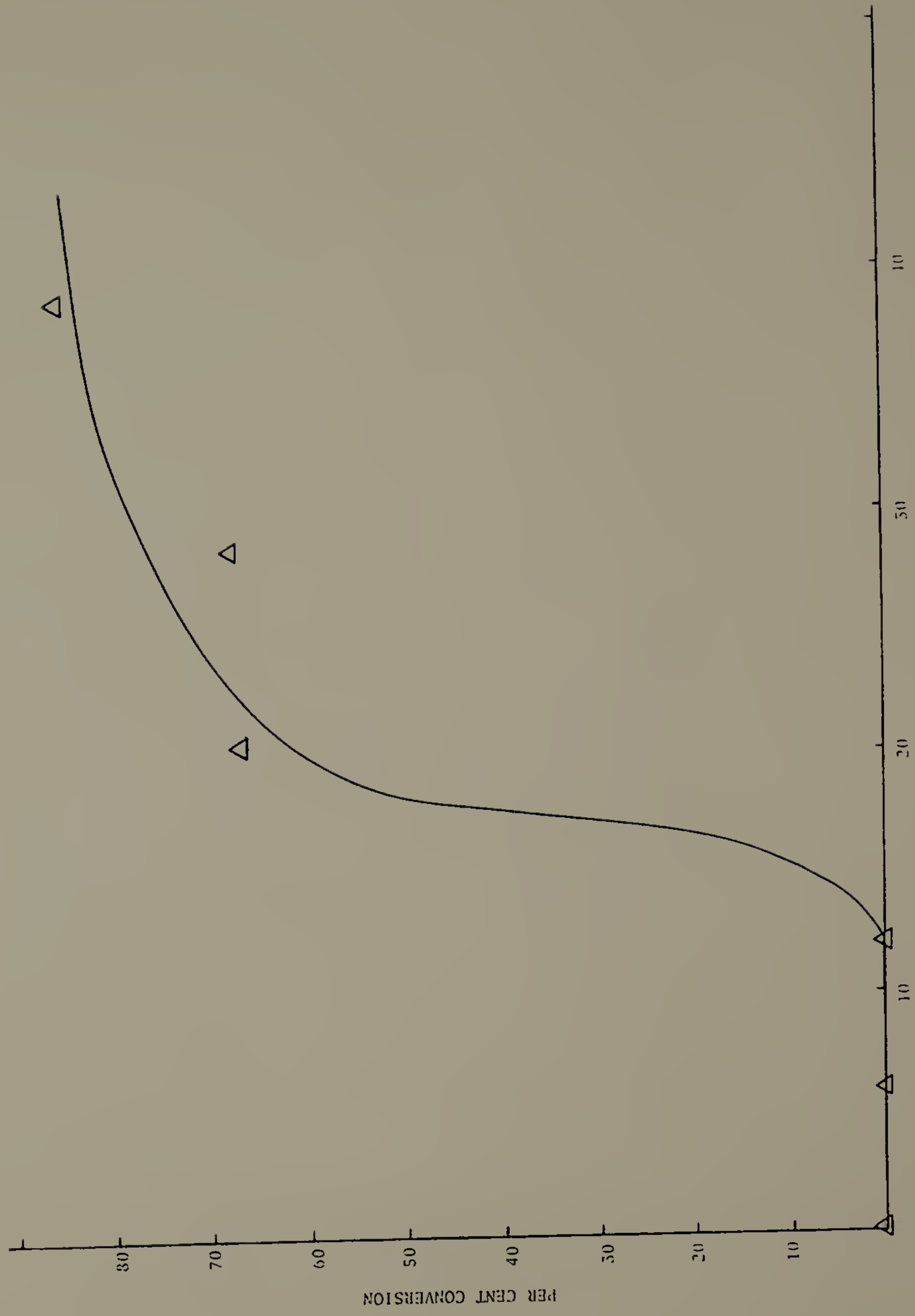


Figure 5.

12 hours, and afterward the reaction proceeds rapidly. Presumably, during the first 12 hours any free phenol which is present is consumed by incipient macroradicals.

Homopolymerization of O-acetyl-2,6-di-t-butylphenol gave 93% conversion after 36 hours at 70°C. An unusually large 5 mol % AIBN initiator was used to offset the loss of growing chains to reaction with chain-terminating free-phenol monomer, and this is no doubt partly responsible for the fairly low inherent viscosity of 0.29 dL/g.

Copolymerization of the same monomer with methyl methacrylate for 36 hours (70°C) with 2 mol % AIBN yielded 84% of copolymer with inherent viscosity of 0.35 dL/g.

The chain-transfer constant for the acetylated monomer, C, was determined, using the equation developed by Mayo,[105]

$$\frac{1}{\bar{M}_n} = \frac{1}{\bar{M}_{n_o}} + C_x \frac{[x]}{[M]} \qquad (25)$$

where $\bar{M}_n$ is the number-average molecular weight obtained in the presence of transfer agent, $\bar{M}_{n_o}$ is the number-average molecular weight obtained in the absence of transfer agent and [x] and [M] are concentrations of transfer agent and monomer, respectively. X in this case is the acetylated monomer and M is methyl methacrylate.

The polymerization runs employed in the determination of the chain-transfer constant are listed in Table 6.

Table 6. Copolymerizations of *O*-acetyl-2,6-di-*t*-butyl-4-vinylphenol with Methyl Methacrylate.

Tube	Methyl Methacrylate, M		*O*-acetyl-2,6-di-*t*-butyl-4-vinylphenol, X		[x]/[M]	$\bar{M}_n$	$1/\bar{M}_n$ ($\times 10^5$)
	g	mmol	g	mmol			
A	0.80	8.0	0.55	2.0	0.25	46,900	2.1
B	0.60	6.0	1.10	4.0	0.67	36,200	2.8
C	0.40	4.0	1.64	6.0	1.5	37,400	2.7
D	0.20	2.0	2.19	8.0	4.0	28,200	3.6

Polymerizations carried out at 70°C for 16 h, using 0.5 mol % AIBN.

Number-average molecular weights ($\bar{M}_n$) were determined by gel-permeation chromatography (GPC). A plot of $1/\bar{M}_n$ vs. [x]/[M] appears in Figure 6, and the slope of this line, 3.4×10^{-6}, equals C for transfer to acetylated monomer. This value is close to that measured for methyl acrylate.[31]

It should be noted that this value can only be regarded as approximate since it is probably affected by the low concentration of free-phenol monomer present and the small amount of chain-transfer due to solvent.[31]

Also, the efficiency of reinitiation by the radical formed from the acetylated monomer (probably a carbon radical centered on the α-carbon of the acetyl group, by analogy with vinyl acetate) is not known, introducing a further complication.[106]

Polymerization of the free-phenol monomer 2,6-di-t-butyl-4-vinylphenol was not as straightforward. Numerous methods of removing oxygen from the polymerization medium were explored before success was achieved. While repeated freeze-thaw cycles proved barely adequate for free-phenol polymerizations in solution, this method was unsuitable for emulsion systems because of its adverse effect on emulsion stability.

Purging a system by bubbling oxygen-free gas through it seemed attractive, but an oxygen remover with a large capacity was necessary. A device called an Oxy-Trap, sold by Alltech Associates, which is a coil of 1/4"

Figure 6. Plot of $1/\bar{M}_n$ vs. [x]/[M] for x = O-acetyl-2,6-di-t-butyl-4-vinylphenol. Slope = 3.4×10^{-6}. Correlation coefficient = 0.93.

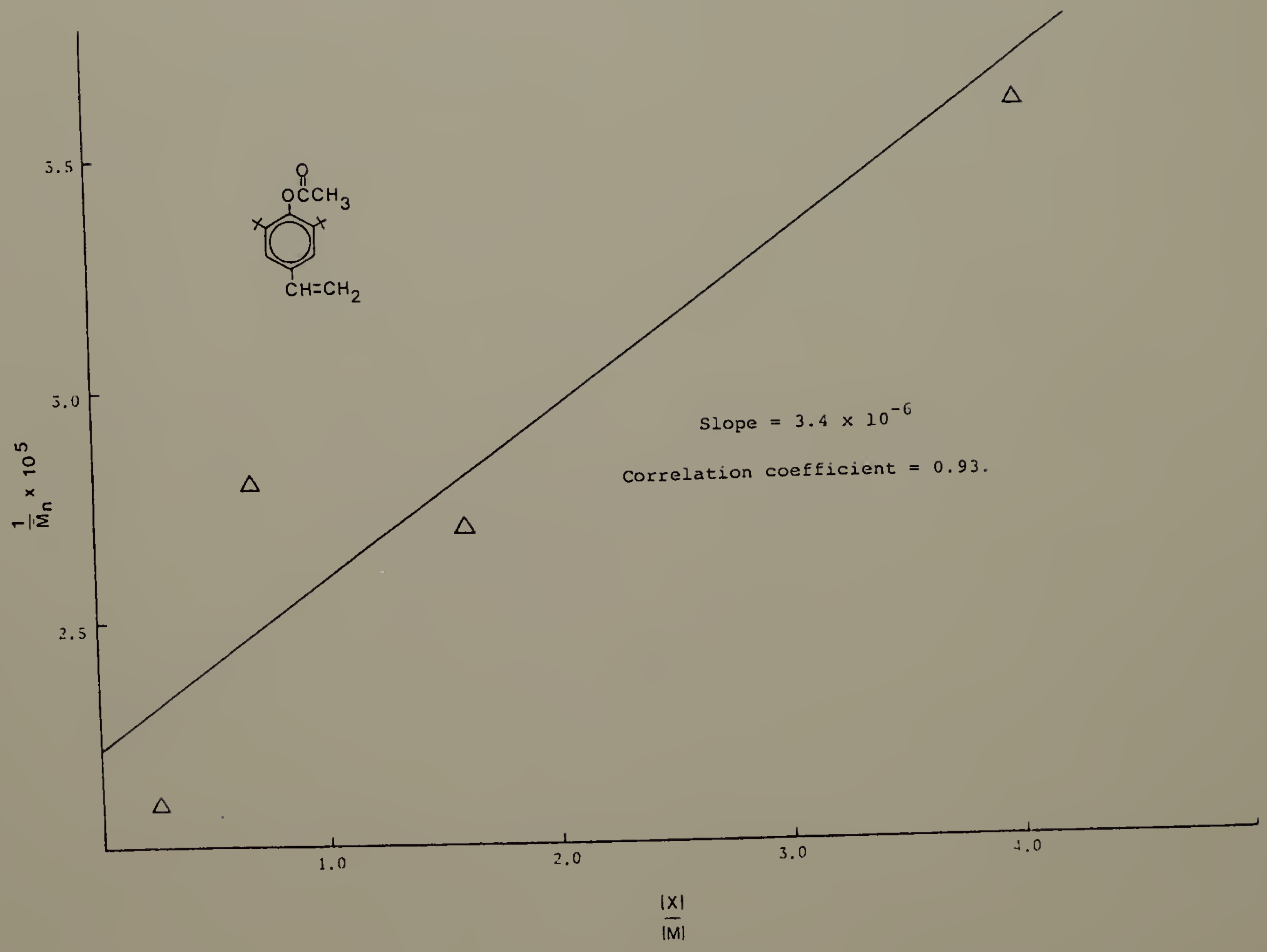

$\frac{1}{\bar{M}_n} \times 10^5$
3.5
3.0
2.5
1.0
2.0
3.0
4.0
$\frac{[X]}{[M]}$
$OCCH_3$
O
$CH=CH_2$
Slope = 3.4×10^{-6}
Correlation coefficient = 0.93.

Figure 6.

aluminum tubing fitted with a copper-based oxygen absorbent, was of limited utility due to its short lifetime at the flow rates used. The device is recommended by the manufacturer as a carrier-gas purifier for gas chromatography.

The best results were obtained using a large (40 x 5 cm) heated column containing BTS catalyst. This efficient, supported-copper catalyst, produced by BASF, is effective at space velocities of 1,000 hr^{-1}[107] and visible inspection of the regenerable catalyst is facilitated by the use of a glass column. At 150°C the material has an oxygen capacity six times that at room temperature,[107] and this was the temperature employed.

A similar amount of effort went into the choice of initiator for the emulsion copolymerization of free-phenol monomers.

Use of potassium persulfate, a common dissociative initiator, led to yields of isoprene-free phenol copolymers of 5% or less after as much as 11 days. The cause is a side reaction of the initiator with water, forming oxygen as a product.[108] The reaction

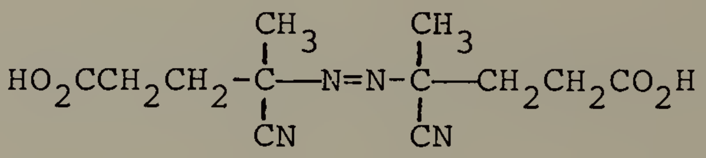
$$S_2O_8^{2-} \longrightarrow 2\ SO_4^{-}\cdot \qquad (26)$$

$$SO_4^{-}\cdot + H_2O \longrightarrow HSO_4^{-} + \cdot OH \qquad (27)$$

$$2\ \cdot OH \longrightarrow H_2O + 1/2\ O_2 \qquad (28)$$

is known to occur in water solutions at almost any pH. In the absence of scavengers for $SO_4^{-}\cdot$ radicals this reaction path is exclusively followed, but even in the presence of a scavenger (e.g., isoprene, butadiene or a polymerizable phenol) it is likely that some oxygen is produced. This oxygen then can react with a growing radical. The resulting peroxy radical reacts with the hydroxyl group of the hindered-phenol monomer in the system, causing inhibition of polymerization (see Section IB).

To preclude the formation of oxygen by reaction of persulfate with water, a water-soluble azo initiator[109] was chosen. 4,4'-Azobis(4-cyanovaleric acid) (ACVA) is a



$$HO_2CCH_2CH_2-\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}-CH_2CH_2CO_2H \qquad (29)$$

commercially available analog of AIBN, and it will dissolve in water, with difficulty, up to a few weight per cent. Using ACVA, copolymer yields increased to 15 to 23%, after 1 week reaction time.

In the copolymerization of 2,6-di-*t*-butyl-4-vinylphenol with 1,3-butadiene, several further problems were encountered. First, the volatility of butadiene (bp = -4°C) made it essential that all manipulations of this material be done below this temperature. Thus, the initial condensation of the butadiene and the deoxygenation of its solution with the phenol were all done in a bucket containing crushed dry ice or a dry ice-isopropanol bath.

Also, considerable pressure (50-60 psi) occurred inside the 360 mL polymerization tube used for this reaction. For this reason medium-wall glass (3.2 mm) or thicker was used to retain a margin of safety against failure of the tube. Annealing of the seal was also carefully done to prevent failure at this point.

Kolthoff has done a great deal of fundamental work on emulsion polymerization, the method of choice for dienes, and the emulsion recipe used in this laboratory is a modification of the one developed by him.[110] In the present work, the mercaptan promoter/molecular-weight modifier was omitted since chain transfer to monomer occurred to modify the molecular weight and the promoting effect of mercaptan on persulfate-initiated polymerizations[110,111,112] does not apply to the case where an azo initiator is used. The original Kolthoff recipe and the modification used here are compared in Table 7.

The emulsion recipe, minus the monomers, was made up, placed in a polymerization tube and deoxygenated. The solution of monomers was deoxygenated separately, then added to the tube containing the aqueous mixture, cooled to -5°C. In order to evacuate and seal the tube, the contents were frozen in liquid nitrogen. At this point, the reaction mixture had to be thoroughly emulsified, otherwise

Table 7. Comparison of Kolthoff Emulsion Recipe and Modified Kolthoff Recipe Used in this Work.

Kolthoff Recipe		Modified Kolthoff Recipe	
Ingredient	Parts by Weight	Ingredient	Parts by Weight
Monomer(s)	100	Monomer(s)	100
Emulsifier(s)	5	Emulsifier(s) (sodium dodecyl sulfate)	5
$K_2S_2O_8$ initiator	0.3	ACVA initiator	2.4
Mercaptan	0.5	--	--
Water	180	Water	180

expansion would occur which was capable of shattering the polymerization tube.

In order to safely open the polymerization tube after the one-week reaction time, the tube was chilled in an ice bath. This reduced the internal pressure to a relatively safe level, but residual pressure was in evidence, and care was exercised.

After coagulating the latex and precipitating the product in methanol, the resulting suspension was kept cold until the product had coalesced into a gelatinous mass. This was dissolved in cyclohexane, reprecipitated into methanol, and again kept cold. Drying of the product took place after decantation of the methanol.

Because of the volume of the product and its nature, drying was difficult. Predrying took place in a bell jar under aspirator vacuum, and some material was lost due to vigorous loss of methanol from the sample at this stage. The polymer was next dried at 0.1 mm in a vacuum dessicator with the aid of an infrared heat lamp. In order to obtain an acceptable elemental analysis, further removal of methanol at 160°C and 0.005 mm was required.

Yield of the polymer was 21% and analysis by gel permeation chromatography (GPC) showed $\bar{M}_n = 16,300$ and $\bar{M}_w = 45,000$. These values are reasonable considering the degradative chain transfer which can occur during polymerization of free, hindered phenols under even oxygen-free conditions.

The infrared spectrum was consistent with a copolymer of butadiene and 2,6-di-*t*-butyl-4-vinylphenol, and the ^{13}C NMR and ^{1}H NMR showed that the butadiene in the copolymer had a random *cis*, *trans* geometry, by comparison with a sample of known geometry (see p. 181).

^{1}H NMR further revealed that the butadiene was over 90% 1,4. Integration of the spectrum gave a copolymer composition of 6% phenol and 94% butadiene, which was borne out by elemental analysis.

No spectral evidence for incorporation of hindered-phenol monomer into the polymer chain through the oxygen atom was seen. This is in line with the small rate constants for reinitiation by hindered phenoxyls.[39]

In the emulsion copolymerization of 2,6-di-*t*-butyl-4-vinylphenol with isoprene, a similar procedure of separate deoxygenation of the monomer mixture and the emulsion matrix was carried out. Isoprene, a liquid with bp = 35°C, was easily handled via pipet. A 23% yield of copolymer was obtained, having $\bar{M}_n = 23{,}500$ and $\bar{M}_w = 121{,}000$ by GPC.

As in the butadiene copolymer, the presence of the hindered phenol was clearly indicated in the infrared (IR) spectrum. Elemental analysis pointed to a copolymer composition of 8% hindered phenol and 92% isoprene. The areas of ^{1}H NMR peaks at 1.6 and 1.7 δ, corresponding to the methyl protons of *cis* and *trans* 1,4-isoprene units, respectively, were in the ratio of approximately 1:1.

2,6-Di-t-butyl-4-vinylphenol was also copolymerized with isoprene in bulk, using AIBN initiator. The copolymer produced was a viscous liquid with $\bar{M}_n$ = 6,300 and $\bar{M}_w$ = 9,000 by GPC. Even at a 1% inclusion of antioxidant monomer (by elemental analysis) the hindered-phenol peak was still visible at 3650 cm^{-1} in the IR spectrum.

C. Preparation and Polymerization of 2,6-Di-t-butyl-4-isopropenylphenol and O-Acetyl-2,6-di-t-butyl-4-isopropenylphenol

1. Introduction. 2,6-Di-t-butyl-4-isopropenylphenol was synthesized in an overall yield of 43%. The monomer was copolymerized in solution, using AIBN initiator, with n-butyl acrylate and styrene. It was copolymerized in radical emulsion with 1,3-butadiene and isoprene.

2. Preparation of 2,6-di-t-butyl-4-isopropenylphenol and O-acetyl-2,6-di-t-butyl-4-isopropenylphenol. The first step in the synthesis (Figure 7) was the diacylation developed by Hewgill[54] and described above.

Reduction of the methyl ketone took place via Grignard reaction with methylmagnesium iodide. Great success was enjoyed in starting this reaction when the magnesium turnings were ground into fine chips in a mortar and pestle, exposing fresh surface area. A crystal of iodine was also routinely used to help start the reaction.

Figure 7. Synthesis of 2,6-di-t-butyl-4-isopropenylphenol and O-acetyl-2,6-di-t-butyl-4-isopropenylphenol.

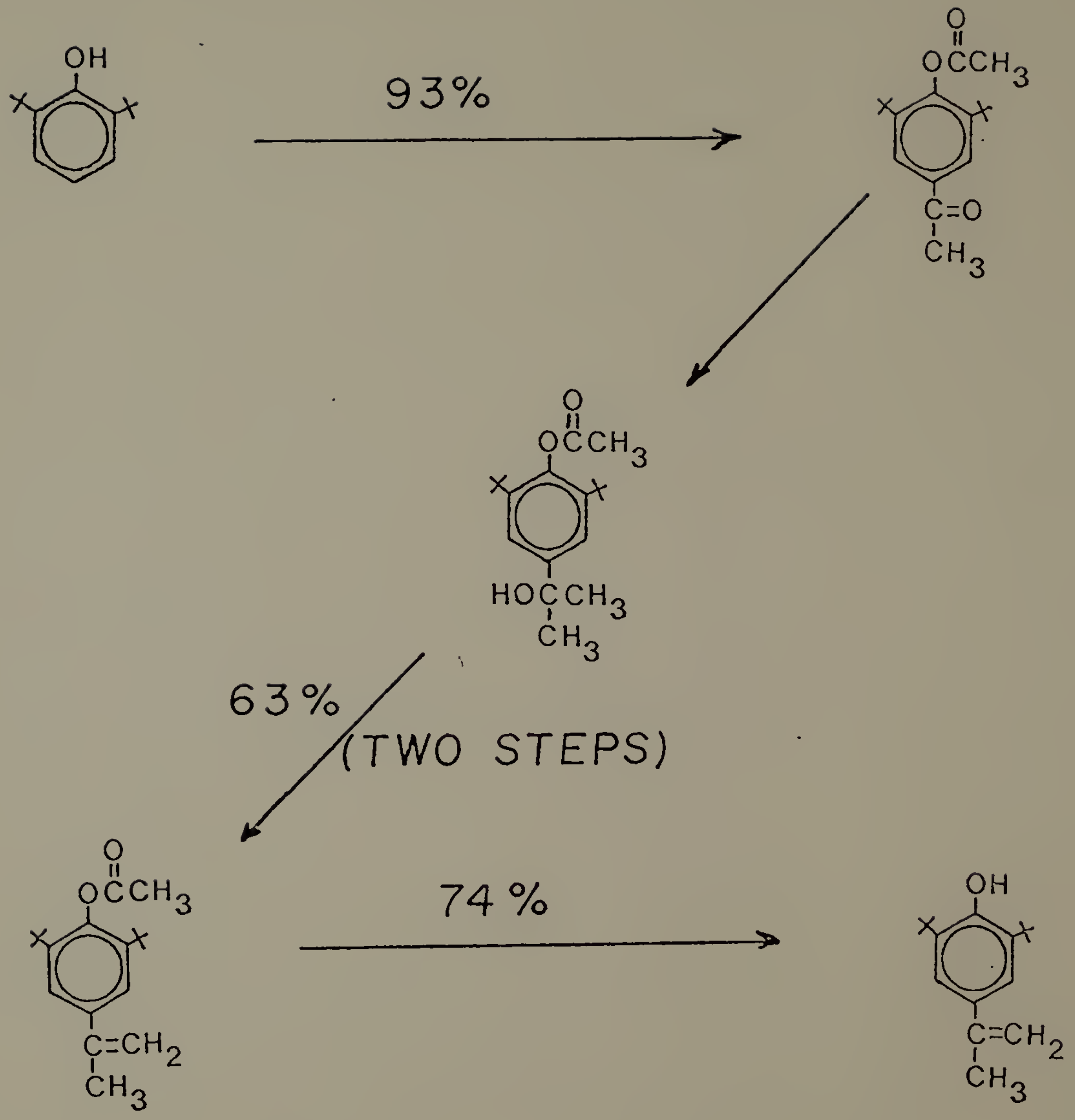


Figure 7.

It was thought that, by using two or more equivalents of Grignard reagent, the ester function might be cleaved at the same time the ketone was being reduced.[113] However, the steric hindrance presented by the two *ortho* *t*-butyl groups imposes a severe barrier to this cleavage. A five-fold excess of Grignard reagent resulted in a loss of only 10% of acetate moieties as determined by ^1H NMR.

The intermediate propanol could not readily be recrystallized, oiling out of methanol-water, ethanol-water, hexane, ether and ethyl acetate. In addition the compound was extremely tacky. Thus it was not purified further, but dehydrated directly after isolation by removal of ether solvent. A ^1H NMR spectrum of the crude material was taken nonetheless. Ill-defined peaks were visible due to *t*-butyl (1.5 δ), 2-propanol methyl (1.7 δ), acetate methyl (2.2 δ), hydroxyl (3.5 δ) and aromatic (7.5 δ) protons.

The propanol was dehydrated over potassium hydrogen sulfate and simultaneously distilled to yield 63% (over two steps) of *O*-acetyl-2,6-di-*t*-butyl-4-isopropenylphenol. The details of the reaction were the same as those for the vinyl compound. The existence of the isopropenyl group was confirmed by ^{13}C NMR, which showed peaks at 22.47 ppm $(CH_2{=}\overset{|}{C}{-}\underline{C}H_3)$, 112.12 ppm $(\underline{C}H_2{=}\overset{|}{C}{-}CH_3)$ and 141.85 ppm $(CH_2{=}\underline{\overset{|}{C}}{-}CH_3)$. ^1H NMR showed isopropenyl peaks at 2.0 δ $(CH_2{=}\overset{|}{C}{-}\underline{C}H_3$, 3H) and 4.8 and 5.1 δ $(C\underline{H_2}{=}\overset{|}{C}{-}CH_3$, 2H).

Finally, hydride cleavage of the ester group, as described in Subsection B2, was used to obtain 2,6-di-*t*-butyl-4-isopropenylphenol in 74% yield versus acetylated monomer. Spectral data for this free-phenol monomer agree with those given by Braun.[51]

The monomer synthesis routes used in this work were chosen because the first intermediate, *O*,4-diacetyl-2,6-di-*t*-butylphenol, provides access to both the vinyl and isopropenyl monomers. It would have been inconvenient, for example, to adapt Braun's decarboxylative synthesis of 2,6-di-*t*-butyl-4-vinylphenol (see p. 25) to synthesis of an isopropenyl monomer.

Also, the bifurcation of the sequence after the first step (diacylation) provides both monomers in blocked, acetylated form. These blocked monomers were of value in the determination of chain-transfer constants (Subsection B3) and for comparing other polymerization characteristics for the blocked and free phenols, such as molecular weight and yield (Subsection C3).

3. Preparation of polymers of 2,6-di-t-butyl-4-isopropenylphenol. Chronologically, the first successful polymerization of a hindered-phenol monomer in our laboratory was the copolymerization of 2,6-di-*t*-butyl-4-isopropenylphenol and *n*-butyl acrylate. Work had previously been done on the copolymerization of phenol-substituted benzotriazoles[114] with n-butyl acrylate, and this comonomer seemed a good place to begin.

The reaction took place in benzene solution using AIBN initiator. The polymerization tube was flushed with prepurified argon only and was degassed during several freeze-thaw cycles. After three days at 70°C the yield of polymer was 40%, but the inherent viscosity was extremely low (0.04 dL/g).

Since workup of n-butyl acrylate copolymers is difficult due to their rubbery properties, further attempts to improve free-phenol polymerizations took place using styrene as comonomer.

A solution copolymerization of 2,6-di-t-butyl-4-isopropenylphenol with styrene gave a yield of 22%, and the polymer had an inherent viscosity of 0.23 dL/g. Once again, prepurified argon was used to flush the polymerization tube and degassing was by the freeze-thaw technique.

The IR spectrum and the ^1H NMR spectrum showed definite inclusion of stabilizer in the copolymer. A feed ratio of 10:1 styrene:phenol gave a polymer composition of 82:18 styrene:phenol.

In an effort to extend this copolymerization to the technique by which the important phenol-diene copolymers would be synthesized, 2,6-di-t-butyl-4-isopropenylphenol was copolymerized in a radical emulsion. In this case, an emulsion recipe different from that shown in Table 7 was employed. A mixture of nonionic (PEG 1000) and anionic (sodium dodecyl sulfate) emulsifiers was used.[115] Deoxygenation of argon used for flushing the tube was accomplished by passing the gas through an Oxy-Trap. This, and the fact that potassium persulfate initiator was used, is probably responsible for the low yield (5%) obtained in the reaction.

A compilation of all copolymerizations of blocked and free hindered phenols, not including dienes, appears in Table 8. These data clearly indicate that, while polymerization is able to proceed in the presence of the free hindered-phenol monomers when oxygen is excluded, the polymers produced are obtained in lower yield and are of lower molecular weight than polymers incorporating blocked hindered phenols. This is in line with conclusions drawn from data in the literature, as discussed in Section B2 of Chapter I.

Copolymerization of 2,6-di-t-butyl-4-isopropenylphenol with butadiene and isoprene was carried out using the same procedure as for the vinyl monomer.

The butadiene copolymer, containing 6 mol % antioxidant according to both ^1H NMR integration and elemental analysis, had $\bar{M}_n = 13,000$ and $\bar{M}_w = 25,700$ by GPC. The yield was 16%.

The isoprene copolymer fit this pattern as well. Yield of poly(2,6-di-t-butyl-4-isopropenylphenol-co-

Table 8. Polymerizations of Blocked and Free Hindered-phenol Monomers with Comonomers Other Than Dienes.

Hindered-phenol Monomer	Amount		Comonomer	Amount		Rxn. Time (d)	Temp. (°C)	Medium*	Yield (%)	η_{inh}, 30°C (dL/g)
	g	mmol		g	mmol					
O-Acetyl-2,6-di-*t*-butyl-4-vinylphenol	0.96	3.5	--	--	--	1.5	70	S	93	0.29
O-Acetyl-2,6-di-*t*-butyl-4-vinylphenol	0.64	2.3	methyl methacrylate	0.70	7.0	1.5	70	S	84	0.35
O-Acetyl-2,6-di-*t*-butyl-4-vinylphenol	0.55	2.0	styrene	2.4	20.0	1.1	50	E	74	0.32
2,6-Di-*t*-butyl-4-isopropenylphenol	0.25	1.0	*n*-butyl acrylate	1.3	10.0	3.0	70	S	40	0.04
2,6-Di-*t*-butyl-4-isopropenylphenol	0.25	1.0	styrene	1.2	10.0	3.0	70	S	22	0.23
2,6-Di-*t*-butyl-4-isopropenylphenol	0.25	1.0	styrene	2.4	20.0	2.0	50	E	5	--

*S = solution; E = emulsion

isoprene) was 18%. $\bar{M}_n$ and $\bar{M}_w$, determined by GPC, were 10,500 and 18,500, respectively.

Table 9 summarizes data from several diene polymerizations with free hindered phenols. Only the products of the reactions listed in the table were used in the catalytic hydrogenations described later, and these molecular-weight data were also used in the calculation of a chain-transfer constant for the 4-hydroxy 2,6-di-t-butylphenyl moiety in these monomers.

Most interesting in this table is the evidence for an absolute limit to the amount of phenolic monomer which can be included in the feed. As indicated by the second entry in the table, if more than about 10% phenol is present, polymerization is totally prevented for all practical purposes. What material is produced is no more than oligomer.

From the data in Table 10 an approximate chain-transfer constant may be calculated, assuming that the hindered phenols in the vinyl and isopropenyl analogs show the same activity in this regard. A plot of $1/\bar{M}_n$ vs. relative concentration of antioxidant monomer appears in Figure 8. The slope of this line, 2.6×10^{-3}, is the chain-transfer constant C. This data compares well with the value of 4.9×10^{-3} measured by Russell for 2,6-di-t-butylphenol.[39]

Table 9. Summary of Molecular-weight Data for Copolymers of Hindered-phenol Monomers and Dienes in Emulsion.

Hindered-phenol Monomer	Amount g	Amount mmol	Comonomer	Amount g	Amount mmol	Yield %	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
A. 2,6-di-*t*-butyl-4-vinylphenol	0.2	0.9	isoprene[a]	4.8	70.0	23	23,500	121,000	5.2
B. 2,6-di-*t*-butyl-4-vinylphenol	13.6	59.0	isoprene	36.4	534	~1	3,500	5,000	1.4
C. 2,6-di-*t*-butyl-4-vinylphenol	10.0	43.0	butadiene	40.0	740	21	16,300	45,000	2.8
D. 2,6-di-*t*-butyl-4-isopropenyl-phenol	6.5	26.0	isoprene	35.8	525	18	10,500	18,500	1.8
E. 2,6-di-*t*-butyl-4-isopropenyl-phenol	10.0	41.0	butadiene	40.0	740	16	13,000	25,700	2.0

Temperature is 65°C in all cases; initiator was ACVA.

Reaction time is 7 days for all reactions except (a), 72 hours.

Table 10. Copolymerizations* of Hindered-phenol Monomers and Isoprene for Determination of C_x.

Tube	[x]/[M]	$\bar{M}_n$	$1/\bar{M}_n$ (x 10^5)
A	0.013	23,500	4.26
D	0.050	10,500	9.52
B	0.110	3,500	28.6

[x] = Concentration of phenol

[M] = Concentration of isoprene

*Letters correspond to those in Table 9.

Figure 8. Plot of $1/\bar{M}_n$ vs. $[x]/[M]$ for X = 2,6-di-*t*-butyl-4-isopropenylphenol. Slope = 2.6×10^{-3}. Correlation coefficient = 0.98.

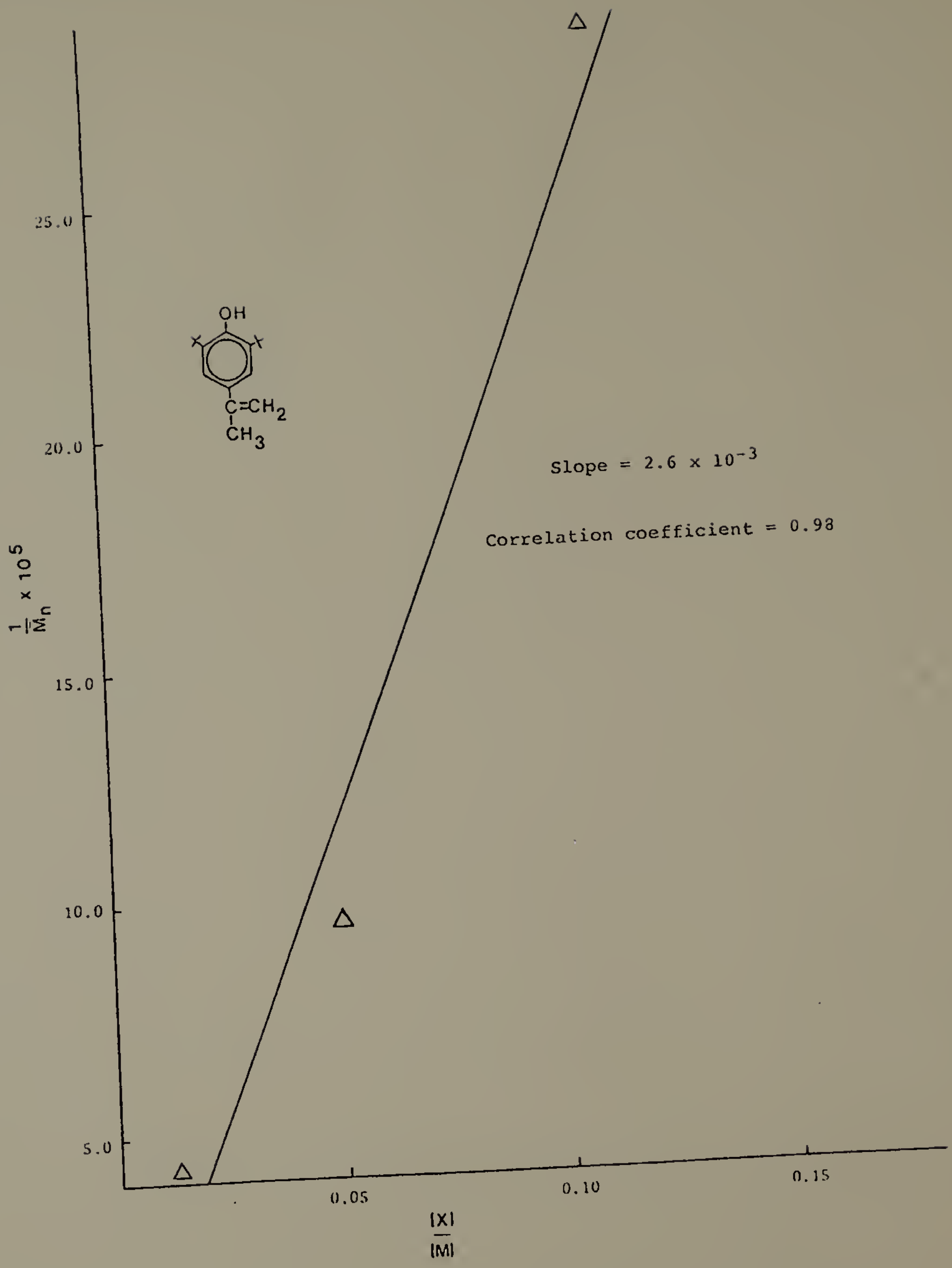

25.0
20.0
15.0
10.0
5.0
$\frac{1}{\bar{M}_n} \times 10^5$
OH
C=CH$_2$
CH$_3$
Slope = 2.6 x 10^{-3}
Correlation coefficient = 0.98
0.05
0.10
0.15
$\frac{[X]}{[M]}$

Figure 8.

D. Attempted Alternate Preparations of 2,6-Di-t-butyl-4-vinylphenol and 2,6-Di-t-butyl-4-isopropenylphenol

1. Introduction. Monomer preparations involving alkylation of 2,6-di-t-butylphenol and a Wittig reaction on 2,6-di-t-butyl-4-formylphenol were investigated, but these procedures were unsuccessful. A successful method of acylating only the 4-position of 2,6-di-t-butylphenol was developed.

2. Preparation of 4-acetyl-2,6-di-t-butylphenol. Monoacylation of 2,6-di-t-butylphenol, in the 4-position (Figure 9), was accomplished by letting stand an ether solution of starting material, acetic anhydride (5:6) and boron trifluoride etherate catalyst[116] at 5°C for seven days. Workup was facile and consisted of pouring the reaction mixture onto a beakerful of ice. The product proved unexpectedly difficult to purify. After two decolorizations and recrystallizations, from 70:30 ethanol-water, the material was still faintly orange. Yield was only 30%.

This product clearly could have provided both 2,6-di-t-butyl-4-vinylphenol and 2,6-di-t-butyl-4-isopropenylphenol by borohydride and Grignard reductions, respectively, followed by dehydration. However, due to the low yield obtained from the monoacylation, overall yields of the monomers by this route would have been unacceptably low.

Figure 9. Synthesis of 4-acetyl-2,6-di-_t_-butylphenol.

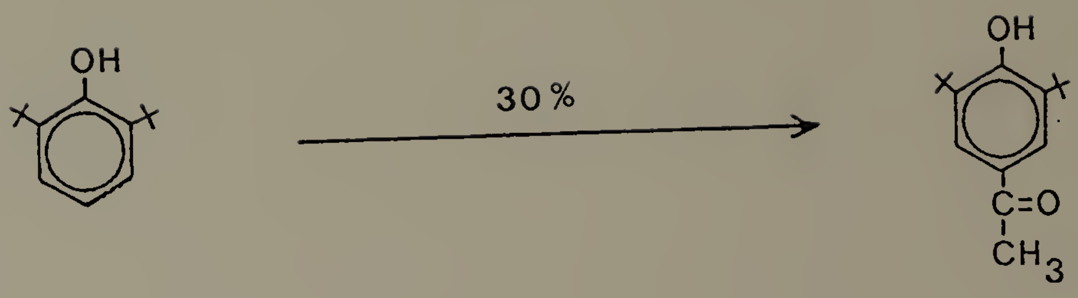


Figure 9.

Thus, this method was abandoned in favor of Hewgill's diacylation reaction.[54]

3. Attempted alkylation of 2,6-di-*t*-butylphenol. As one of two methods potentially providing shortened routes to 2,6-di-*t*-butyl-4-isopropenylphenol, alkylation of 2,6-di-*t*-butylphenol with propylene oxide and aluminum trichloride[117] was investigated. The intended product of this reaction, 2-(4-hydroxy-3,5-di-*t*-butylphenyl)-1-propanol, which would yield monomer after dehydration, was not obtained.

A short time after this investigation was complete, an article by Layer[118] appeared which described the alkylation of 2,6-di-*t*-butylphenol using basic catalysts, namely alkali metal alkoxides, at 220°C in a rocking bomb. Isolated yield in Layer's reaction was 44%, and of this 80% was C-alkylated product (in the 4-position) and 20% was the product of O-alkylation, as determined by GC. The phenoxide ion which forms in the presence of strong base can delocalize the electron pair throughout the aromatic ring, giving rise to anionic character at carbon 4.[119]

Using Layer's technique, 2,6-di-*t*-butyl-4-vinylphenol could be made in two steps (alkylation and dehydration) from 2,6-di-*t*-butylphenol, but a separation of the products of C- and O-alkylation would be necessary, and at best overall yield would be low.

4. Attempted Wittig reaction on 2,6-di-t-butyl-4-formylphenol. The other short route to 2,6-di-t-butyl-4-vinylphenol which was examined experimentally involved a Wittig reaction on 2,6-di-t-butyl-4-formylphenol. This reaction too was unsuccessful, and the partial negative charge on C-4 of a phenoxide ion, discussed in the previous subsection, is likely the cause.

2,6-Di-t-butyl-4-formylphenol was reacted with methylenetriphenylphosporane, the ylid formed by reaction between triphenylmethylphosphonium bromide and the methyl sulfinyl carbanion.[120] After a two-day reaction period at room temperature, workup yielded only starting aldehyde.

In the strongly basic medium of the Wittig reaction, a fair amount of phenoxide is no doubt formed from the formylphenol. The unshared electron pair of the phenoxide is then delocalized through the aromatic ring to carbon 4, where it can interact with the dipole of the aldehyde carbonyl (Figure 10). This extensive electron-pair delocalization has been shown to occur in 4-benzoyl-2,6-di-t-butylphenol[119] (Figure 10). This resonance drastically decreases the electrophilicity of the carbonyl carbon, and attack of the ylide at this site becomes unlikely.

A Wittig reaction which would give vinyl monomer

Figure 10. Electron-pair delocalization in 4-acyl-2,6-di-_t_-butylphenoxides.

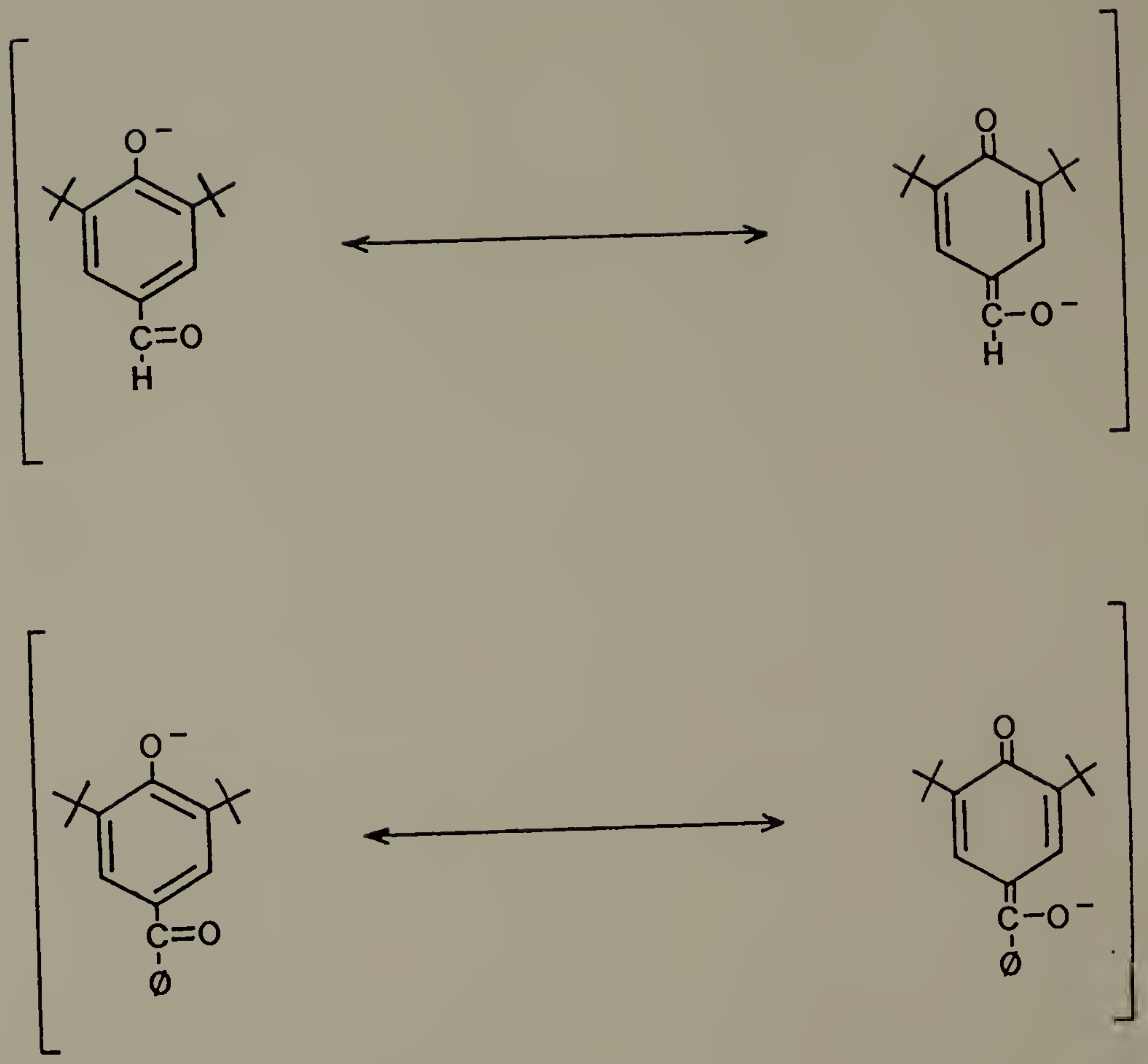


Figure 10.

by an inverse route can be envisioned based on the work of Neckers et al.,[121] although this was not tested experimentally.

In Neckers' work, a dimethyl benzophenone was converted by reaction with NBS and benzoyl peroxide to di(bromomethyl)benzophenone. This material, after reaction with triphenylphosphine followed by sodium methoxide, gave the diphosphorous ylide. Attack of the ylide on formaldehyde yielded divinyl benzophenone (70%). Application of the same procedure to BHT (2,6-di-t-butyl-4-methylphenol) should give the desired vinylphenol in good yield.

It was reasoned that reversibly blocking the hydroxyl group of 2,6-di-t-butyl-4-formylphenol would preclude anion formation in basic solution and concomitant deactivation of the carbonyl toward ylide attack. The next subsection chronicles efforts in that direction.

5. Attempted silylation of 2,6-di-t-butyl-4-formylphenol. Silylation was chosen as the means of blocking the hindered hydroxyl group of 2,6-di-t-butyl-4-formylphenol. Trimethylsilyl ethers are easily formed and readily cleaved by fluoride ion. Provided the trimethylsilyl ether could be synthesized in this case, it would be likely that the t-butyldimethylsilyl ether would also be attainable. t-Butyldimethylsilyl ethers are relatively stable to base,[122] and better able to survive the conditions of the

Wittig reaction.

Unfortunately, the trimethylsilyl ether was not synthesized, under conditions which were sufficient to nearly quantitatively silylate 2,4,6-tri-*t*-butylphenol[122] (reaction with 1 equivalent of chlorotrimethylsilane in refluxing acetonitrile). More forcing conditions[123] (reaction in bistrimethylsilyl solvent) also yielded only starting phenol.

A comparison of inductive effects in the two phenolic species provides an explanation of these observations. In the case of tri-*t*-butylphenol, there are three electron-donating alkyl substituents *ortho* and *para* to the hydroxyl group, leading to sufficient electron density on oxygen for it to act as a nucleophile toward chlorotrimethylsilane.

For the formylphenol, on the other hand, it seems that the electron-donating tendencies of the alkyl groups are overwhelmed by the electron-withdrawing power of the *para* aldehyde group, which renders the hydroxyl oxygen nearly unreactive as a nucleophile.

E. Catalytic Hydrogenation of Copolymers of 2,6-Di-t-butyl-4-vinylphenol and 2,6-Di-t-butyl-4-isopropenylphenol with 1,3-Butadiene and Isoprene

The hydrogenation of copolymers of 2,6-di-*t*-butyl-4-vinylphenol and 2,6-di-*t*-butyl-4-isopropenylphenol with butadiene and isoprene was accomplished using an Al/Co homogeneous catalyst system developed by Falk.[124,125,126]

These catalysts rapidly, selectively and mildly hydrogenate polymer backbone unsaturation while aromatic unsaturation which may be present is unaffected.[124]

The particular catalyst used in this work was made by slow addition of cobalt 2-ethylhexanoate to a cyclohexane solution of triethyl aluminum. The catalyst thus produced had an aluminum/cobalt ratio of 3.25, which is ideal from the standpoint of efficiency of the catalyst. According to data published by Falk[124] this metal ratio gives 100% hydrogenation of polybutadiene unsaturation in 10 minutes. Only 0.3 mol % catalyst was necessary, and reaction took place at 50°C under only 50 psi hydrogen.

The activity of the catalyst as produced in this laboratory was confirmed by performing the same polybutadiene hydrogenation, and indeed similar results were obtained.

Falk noted that polyisoprene was hydrogenated more slowly under these conditions,[124,126] and he demonstrated that by using a 3.45 Al/Co ratio complete loss of butadiene unsaturation could be obtained for a butadiene-isoprene copolymer while the amount of isoprene unsaturation was unchanged.[126] Prud'homme[127] has observed that a two-hour reaction period was required to effect complete removal of isoprene unsaturation using an Al/Co ratio of 4.0, a hydrogen pressure of 50 psi and 5 mol % catalyst. This was also confirmed, using the catalyst with Al/Co 3.25 described above, in this laboratory.

Poly(2,6-di-t-butyl-4-vinylphenol-co-butadiene) and poly(2,6-di-t-butyl-4-isopropenylphenol-co-butadiene) (phenol-butadiene copolymers, collectively) were more difficult to hydrogenate than a butadiene homopolymer. 7 mol % of triethyl aluminum/cobalt 2-ethylhexanoate catalyst were required to effect complete reaction. (The other conditions were a hydrogen pressure of 50 psi and a temperature of 50°C.) The phenol-isoprene copolymers were also more difficult to hydrogenate than the equivalent diene homopolymer, requiring a full 10% of Al/Co catalyst and two hours to react quantitatively, all other conditions being kept constant.

The presence of the phenolic moiety in the polymers seems to be the cause of the relative unreactivity of the phenol-diene copolymers. The hydroxyl oxygen is capable of complexing with the catalyst, reducing its activity. Thus, in all cases an amount of catalyst several mol % greater than the amount of antioxidant in the copolymer was required for hydrogenation to occur. For butadiene copolymers, one mol % catalyst greater than the amount of phenol was needed, and for isoprene copolymers two to four mol % of catalyst were needed in excess of the amount of phenol. This information is contained in Table 11.

Table 11. Conditions Used to Effect Quantitative Conversions in Catalytic Hydrogenations.

Substrate	Time (h)	Temp. (°C)	H_2 Pressure (psi)	mol % Al/Co Catalyst[a]
random cis, trans-Polybutadiene	1	50	50	0.3
cis-Polyisoprene	2	50	50	5.0
Poly(2,6-di-*t*-butyl-4-vinylphenol-co-1,3-butadiene), 6 mol % phenol	1	50	50	7.0
Poly(2,6-di-*t*-butyl-4-isopropenylphenol-co-1,3-butadiene), 6 mol % phenol	1	50	50	7.0
Poly(2,6-di-*t*-butyl-4-vinylphenol-co-isoprene), 8 mol % phenol	2	50	50	10.0
Poly(2,6-di-*t*-butyl-4-isopropenylphenol-co-isoprene), 6 mol % phenol	2	50	50	10.0

[a] Al/Co ratio = 3.25.

It is interesting to note at this point that a similar problem was overcome by Mitsui Petrochemical Industries[83] in their coordination polymerization of 2,6-di-*t*-butyl-4-vinylphenoxide. The functional monomer was precomplexed with diethylaluminum chloride before being combined with titanium trichloride to form the active catalyst.

One limitation of this hydrogenation reaction is the solubility of the product in the reaction medium. Falk[126] claims that the reaction can be run in solutions as concentrated as 17 weight %, but in this author's experience as little as 2 wt % resulted in precipitation of the product during the reaction. The precipitate was black with occluded catalyst, and could not be made colorless under any circumstances. An 0.5 wt % solution gave fairly clean products and a far cleaner autoclave.

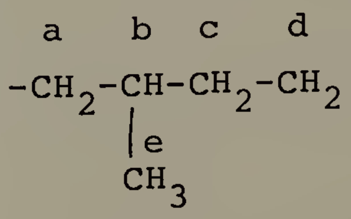
Workup of the hydrogenated copolymers consisted of vigorous shaking of the black polymer solution with 10% HCl to destroy the catalyst and remove it from the organic phase. A pink color developed during the washing, and this was due to the formation of the aquo cobalt complex,[128] $[CO(H_2O)_6]^{2+}$.

Use of this procedure resulted in the formation of a pink emulsion in the case of hydrogenated butadiene copolymers. The emulsion was extremely stable, and could not be broken. Polymer product was isolated by dropwise addition of the emulsion to methanol, causing the polymer to precipitate.

The emulsion which formed during workup of hydrogenated isoprene copolymers separated readily, and the organic phase alone was added to methanol to precipitate the product.

Each polymer was taken up in cyclohexane and reprecipitated into methanol.

Analysis of the hydrogenated copolymers by IR, ^{1}H NMR, and ^{13}C NMR indicated no residual unsaturation. The major peak in the ^{13}C NMR spectrum of hydrogenated butadiene copolymers, at 30.2 ppm, is due to $-\underline{C}H_2-$,[129] of course, but the spectrum of hydrogenated isoprene copolymers is much more complicated. The four major peaks at 38.1, 33.4, 25.1 and 20.1 ppm correspond to carbons a, c, b, d, and e, respectively, below.[127,130]



$$\overset{a}{-CH_2}-\overset{b}{\underset{\underset{CH_3}{|e}}{CH}}-\overset{c}{CH_2}-\overset{d}{CH_2} \qquad (30)$$

A more serious drawback to the use of Falk's Al/Co catalyst system to hydrogenate polymeric antioxidants is the purity of the product. Approximately 2% ash was found in the polymers reacted with 7 to 10 mol % catalyst. The found carbon and hydrogen values, when corrected for the ash present, agree well with the theoretical values. For example, a 2,6-di-*t*-butyl-4-vinylphenol-butadiene copolymer (6 mol % phenol) has a calculated analysis of C, 85.45 and H, 14.13. When the found values of C, 83.78 and H, 13.76 are multiplied by 1.021 to correct for the 2.1% ash found, acceptable values of C, 85.54 and H, 14.05 result.

The presence of so much ash is unwelcome because of its effect on the autoxidation of polymers stabilized with the hydrogenated material, and its effective diminution of the activity of the polymeric antioxidant. It is not known whether other workers who have used Al/Co catalysts have been faced with similar residual ash values because all discussion of elemental analysis of saturated products is strangely absent.[124,125,126,127,131]

It would be well to make a polymeric antioxidant as pure as possible to avoid extraneous influences on the functional activity of the additive, but problems in this regard seem to be inherent in reactions on polymers. Another hydrogenation method which was investigated for application to phenol-diene copolymers, the generation of diimine *in situ* by thermolysis of *p*-toluenesulfonhydrazide,[132,133,134,135] caused up to 0.31% sulfur and 0.32% nitrogen to be included in the polymer.

F. Blending of Copolymers and Testing of Blends

1. Introduction. Phenol-diene copolymers were blended with commercial polydienes and hydrogenated phenol-diene copolymers were blended with commercial polyolefins.

The blends were tested via DSC in an attempt to determine compatibility and by oxygen uptake to assess stabilization against thermooxidative degradation afforded by the polymeric antioxidants.

2. Solution blending of phenol-diene copolymers and hydrogenated phenol-diene copolymers. Solution blending of phenol-diene copolymers and hydrogenated phenol-diene copolymers was straightforward and was accomplished without complications. The solution method was chosen because it allowed for simultaneous blending of the polymers and removal of any low-molecular-weight stabilizers which might be present in the host polymer.

The blends made for oxygen-uptake testing are listed in Tables 1 and 3, and the stock solutions used for this appear in Tables 2 and 4. Each blend had an antioxidant content of 0.1 weight %.

A second series of blends, with higher copolymer content, was made for the study of compatibility by DSC. These make up Table 5.

The oxygen-uptake blends were stored at -5°C to minimize degradation before the actual testing took place. Each sample was dried at 60°C and 0.005 mm prior to testing as well.

3. Thermal analysis of blends. Glass-transition temperatures (T_g) for the pure phenol-diene copolymers were readily determined by low-temperature DSC. These are given in Table 12, and the DSC traces are shown in Figure 11. All were measured after several heating-cooling cycles to ensure that artifacts were not being recorded.

Hydrogenated phenol-butadiene polymers appear to be insufficiently amorphous to exhibit a DSC-visible glass transition. A very broad melting endotherm occurred on heating samples of these polymers to 360K, also indicating a high degree of crystallinity. An example of such a trace appears in Figure 12a. This behavior is not surprising. The polymer, essentially a phenol-ethylene copolymer, should have thermal properties approaching those of polyethylene.

Hydrogenated phenol-isoprene copolymers (phenol-ethylene-propylene terpolymers), being less crystalline, show a glass transition at 222K (Figure 12b), which compares well with a literature value of 218K for a 60:40 ethylene:propylene rubber.[136]

Samples of HDPE, LDPE and LLDPE were also tested by DSC and, due to high crystallinity which is difficult to

Table 12. Glass-transition Temperatures* for Phenol-diene Copolymers.

Copolymer	T_g (K)	Phenol Content (mol %)
A. Poly(2,6-di-_t_-butyl-4-vinylphenol-co-isoprene)	217	8
B. Poly(2,6-di-_t_-butyl-4-isopropenylphenol-co-isoprene)	221	6
C. Poly(2,6-di-_t_-butyl-4-vinylphenol-co-butadiene)	202	6
D. Poly(2,6-di-_t_-butyl-4-isopropenylphenol-co-butadiene)	201	6

*Determined at a heating rate of 20K/min.

Figure 11. DSC traces for phenol-diene copolymers. Letters correspond to those in Table 12.

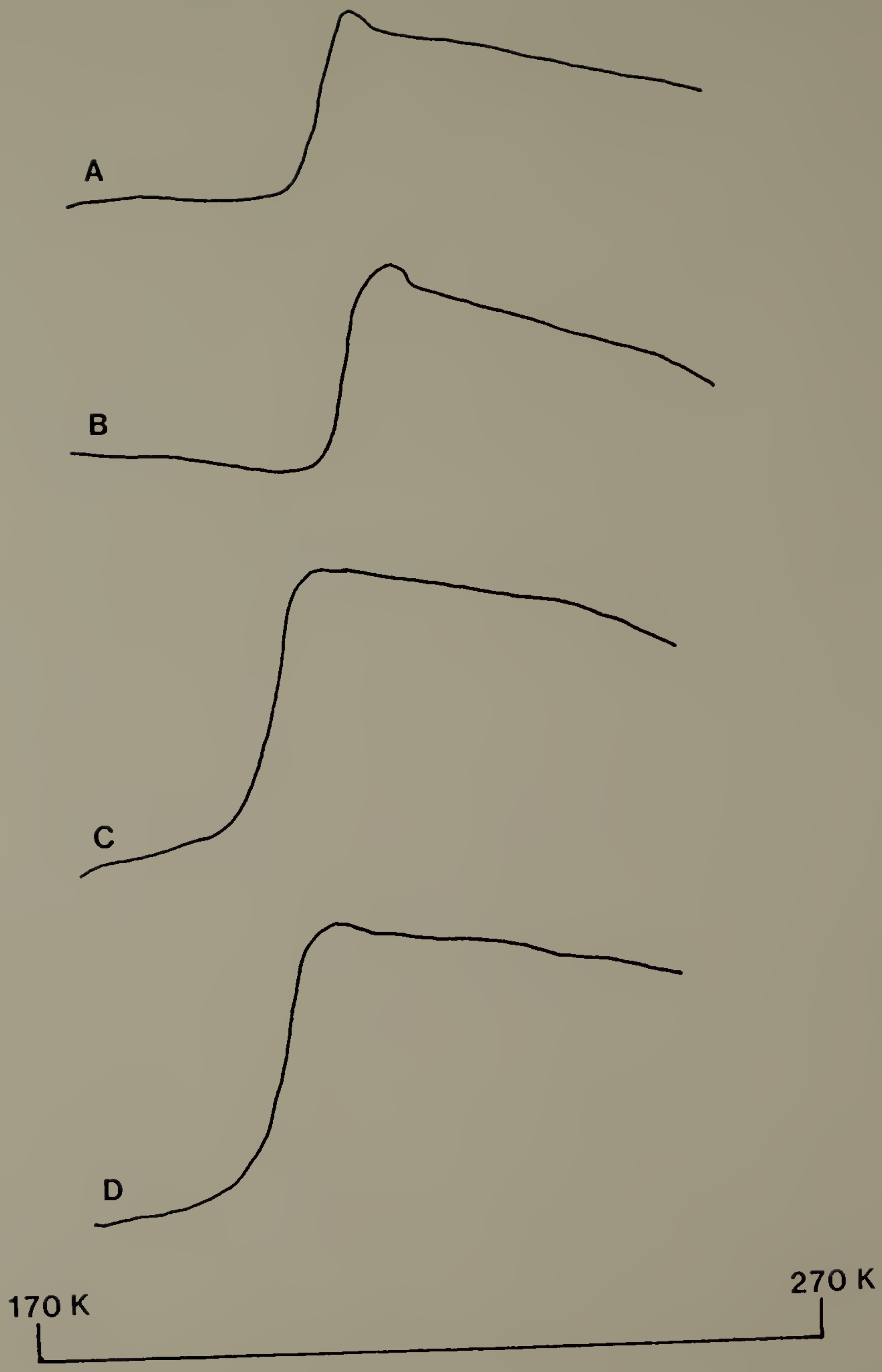


Figure 11.

Figure 12. DSC traces for (A) hydrogenated poly(2,6-di-t-butyl-4-vinylphenol-co-butadiene), and (B) hydrogenated poly(2,6-di-t-butyl-4-isopropenylphenol-co-isoprene).

Figure 12.

quench out of these polymers, no T_g's were observable. It is known that linear and branched polyethylenes exhibit three weak transitions[137] which are observable by more sensitive techniques. Furthermore, the position of these transitions tends to move as a function of crystallinity.[137] Thus, it would be very difficult to say anything meaningful concerning compatibility in PE blends by observing the change in T_g with blend composition.

Figure 13 emphasizes the point. The DSC trace is for a blend consisting of 67 weight % hydrogenated poly(2,6-di-t-butyl-4-vinylphenol-co-butadiene) and 33 weight % HDPE. Neither polymer exhibits a T_g in the pure state, yet the blend clearly has a transition at 218K. It would not be prudent to make any statements concerning the compatibility of this blend. Unfortunately, all of the blends tested in this study gave rise to similarly unpredictable behavior. Perhaps a technique such as torsion-braid analysis or rheo-vibron could shed some light on this matter. For now, the question of compatibility between polyolefin host and polymeric stabilizer remains an open one.

4. Oxygen-uptake studies of blends. Preliminary results from oxygen-uptake experiments appear in Appendix D. Data are shown for unstabilized polydienes and polyolefin samples (controls) and selected polydienes and polyolefins

Figure 13. DSC trace for the blend consisting of 67% hydrogenated poly(2,6-di-*t*-butyl-4-vinylphenol-co-butadiene) and 33% HDPE.

Figure 13.

stabilized with 0.1 weight % antioxidant moieties.

Oxygen absorbed is expressed in terms of ml of oxygen absorbed per gram of polymer. Sample size was 50 ±1 mg.

No induction period was observed in the case of the control samples. Periods of reduced oxygen uptake are seen for the stabilized samples. It seems that the diene copolymers show a functional activity similar to the hydrogenated copolymers.

G. Conclusions and Further Work

This dissertation describes the synthesis and testing of polymeric antioxidants containing hindered-phenol, chain-terminating stabilizer moieties.

Four specific goals have been reached in this work. First, two polymerizable, hindered-phenol antioxidants were efficiently synthesized (2,6-di-*t*-butyl-4-vinylphenol and 2,6-di-*t*-butyl-4-isopropenylphenol) as well as their acetylated analogs. Second, the free-phenol monomers were successfully copolymerized, by free-radical initiation, with butadiene and isoprene. The polymerizations only occurred in the absence of oxygen. Third, the phenol-diene copolymers were hydrogenated using triethyl aluminum/cobalt 2-ethylhexanoate catalyst under mild conditions to yield polymeric antioxidants with saturated backbones. Finally, these polymeric antioxidants, both unsaturated and saturated, were blended with commercial polydienes and polyolefins, respectively. The blends were tested for their thermal behavior by DSC and for thermo-oxidative stability by oxygen-uptake measurements.

For the future, more thorough testing of the polymers so far produced would be worthwhile. Delineation of the limits of permanence of these stabilizers under more rigorous conditions such as forced-air oven tests or after processing would shed more light on the relative value of polymeric versus low-molecular-weight antioxidants. Another interesting study would be the evaluation of the stabilizing activity of a mixture of both kinds of additive, one to protect a polymer from autoxidation during the high-temperature, short-duration processing period and the other to act during long-term use.

Methods of copolymerizing the functional monomers directly with olefins might also be explored. This strategy would likely serve to improve yields of polymeric stabilizer and might ameliorate the problem of ash in the additive. Already, preliminary results from this laboratory[138] have demonstrated that this is feasible using a Ziegler-Natta system similar to that used by Mitsui Petrochemical (see Section E). It is so far unclear whether the product of this reaction is a true copolymer or a mixture of homopolymers, but increased stability against thermal degradation in air was observed for this material.

Whatever the direction this research takes in the future, it is clear that polymeric antioxidants are of value as stabilizers and that they should receive increasing attention.

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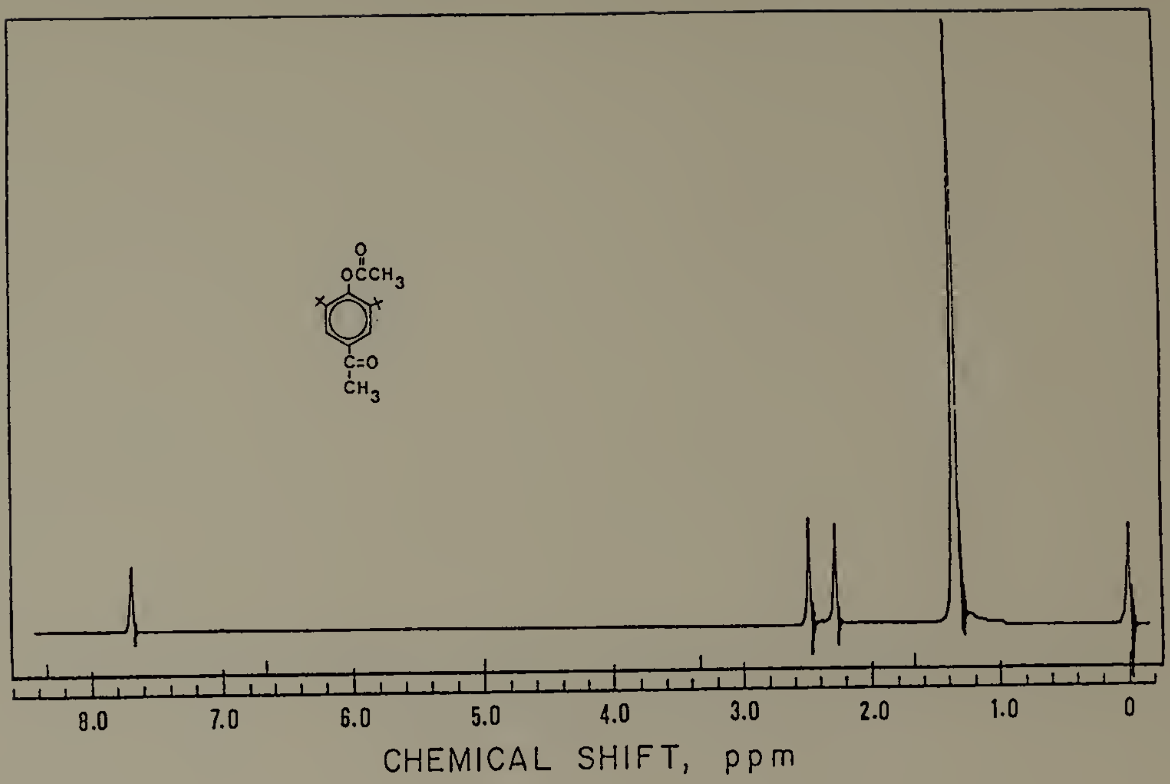
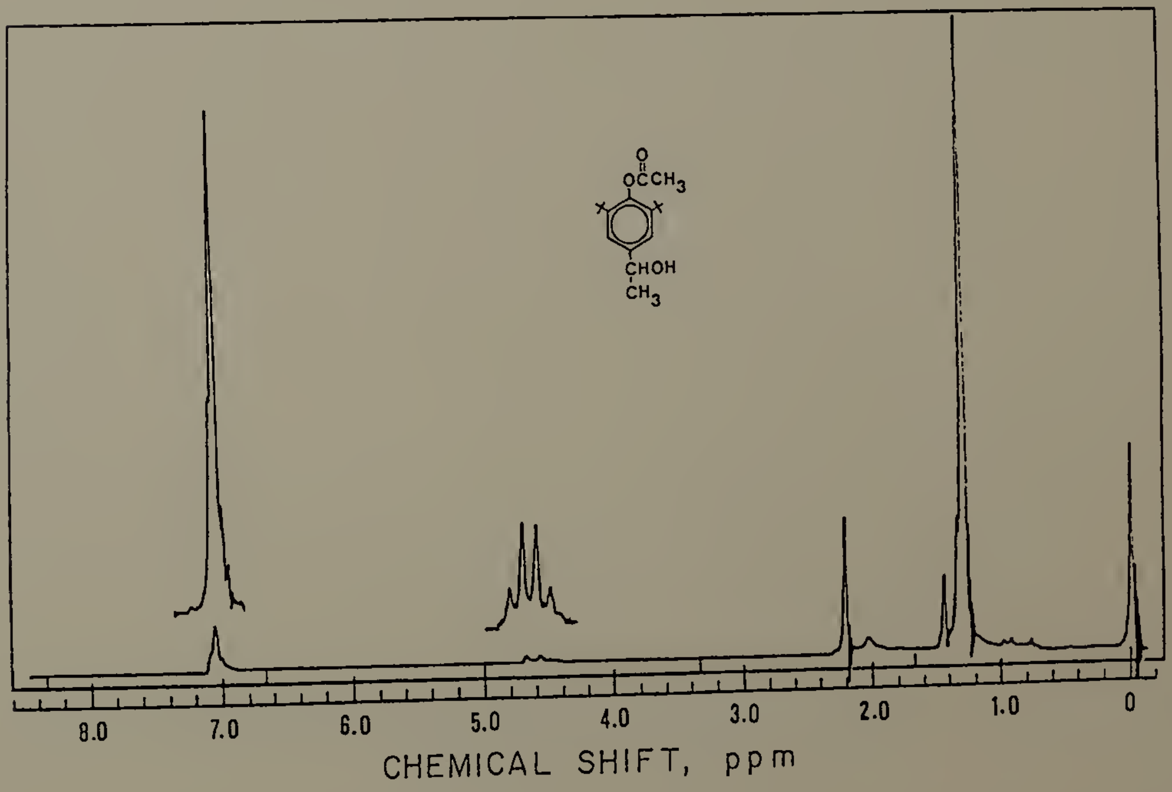
APPENDIX A

PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA


O
OCCH3
C=O
CH3
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
CHEMICAL SHIFT, ppm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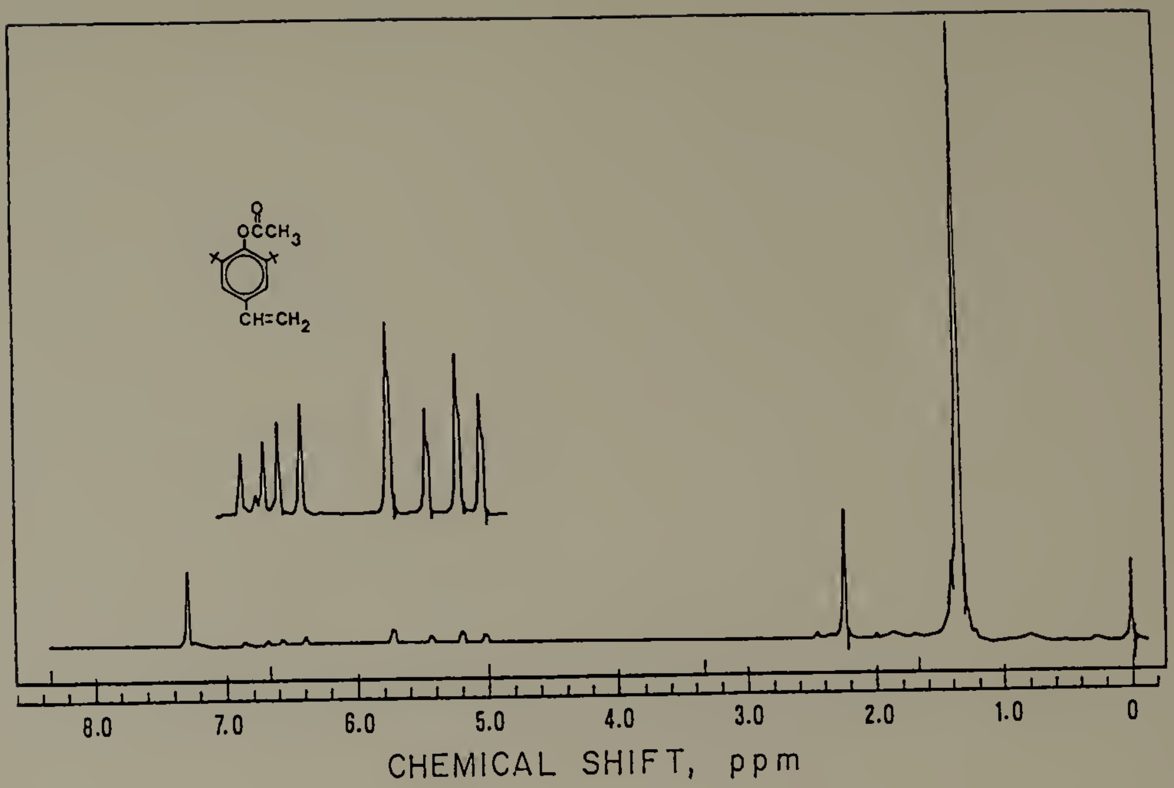
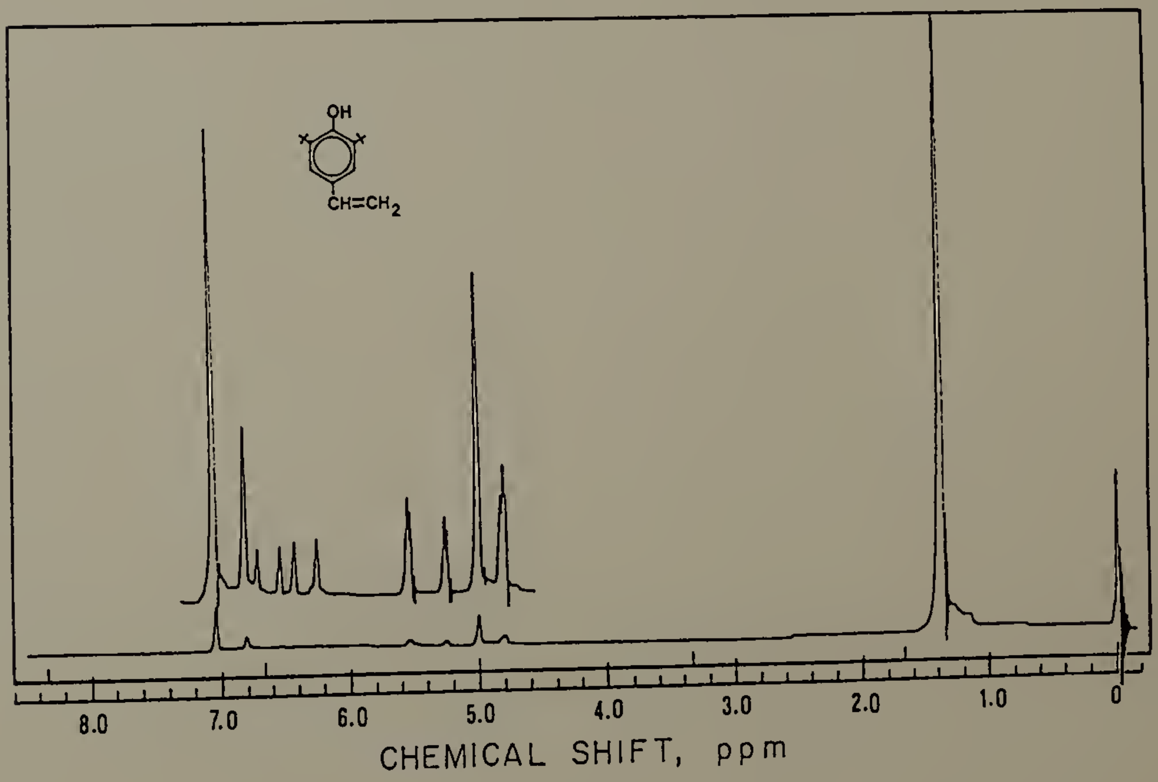
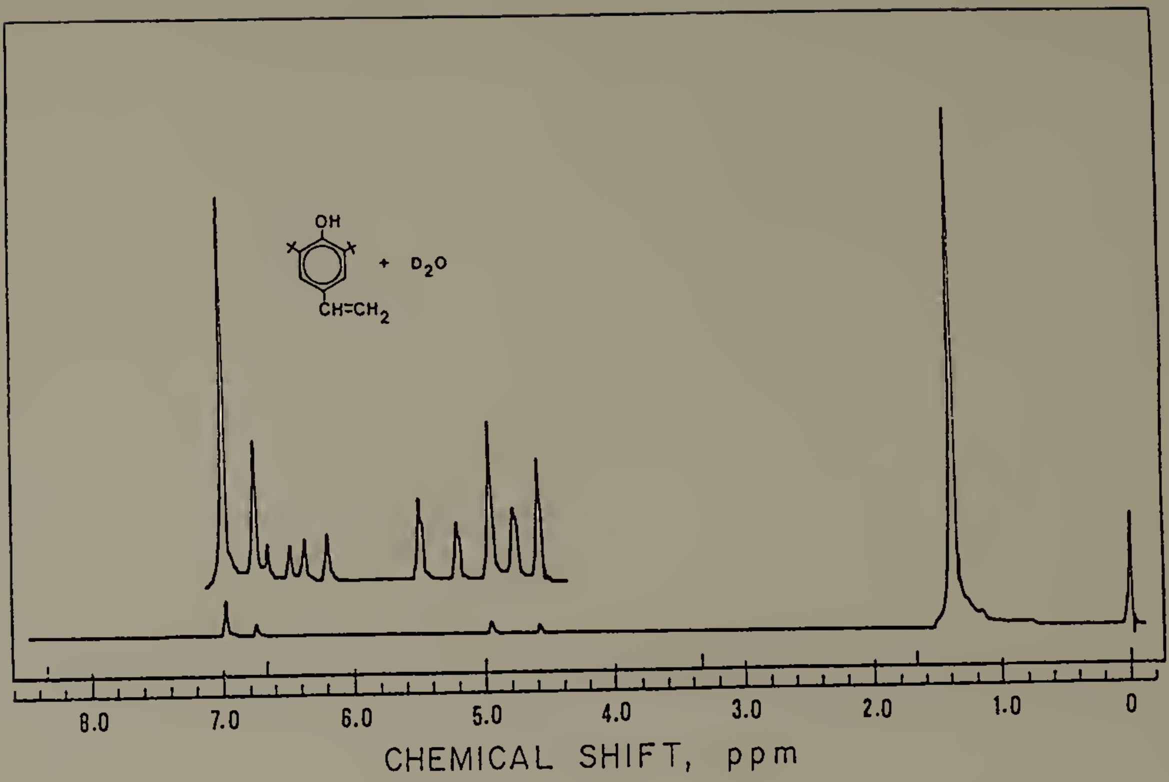
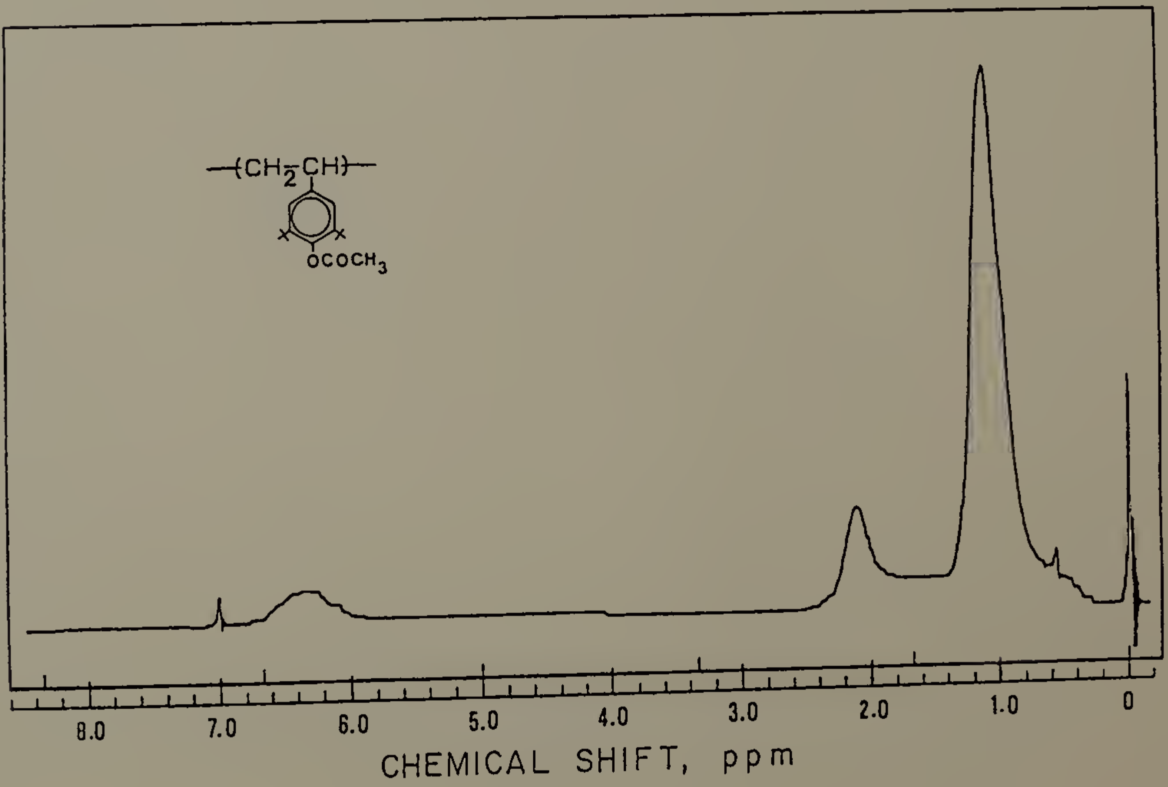
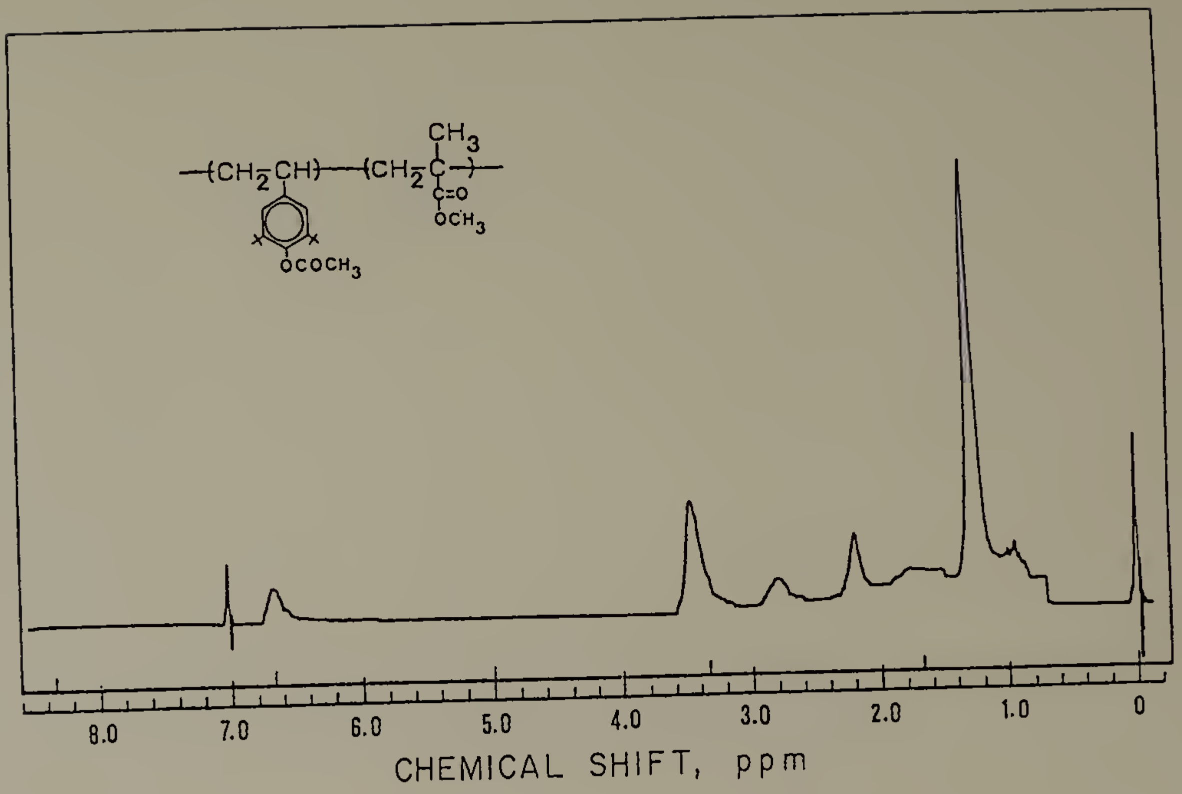
OCCH3
CHOH
CH3
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
CHEMICAL SHIFT, ppm

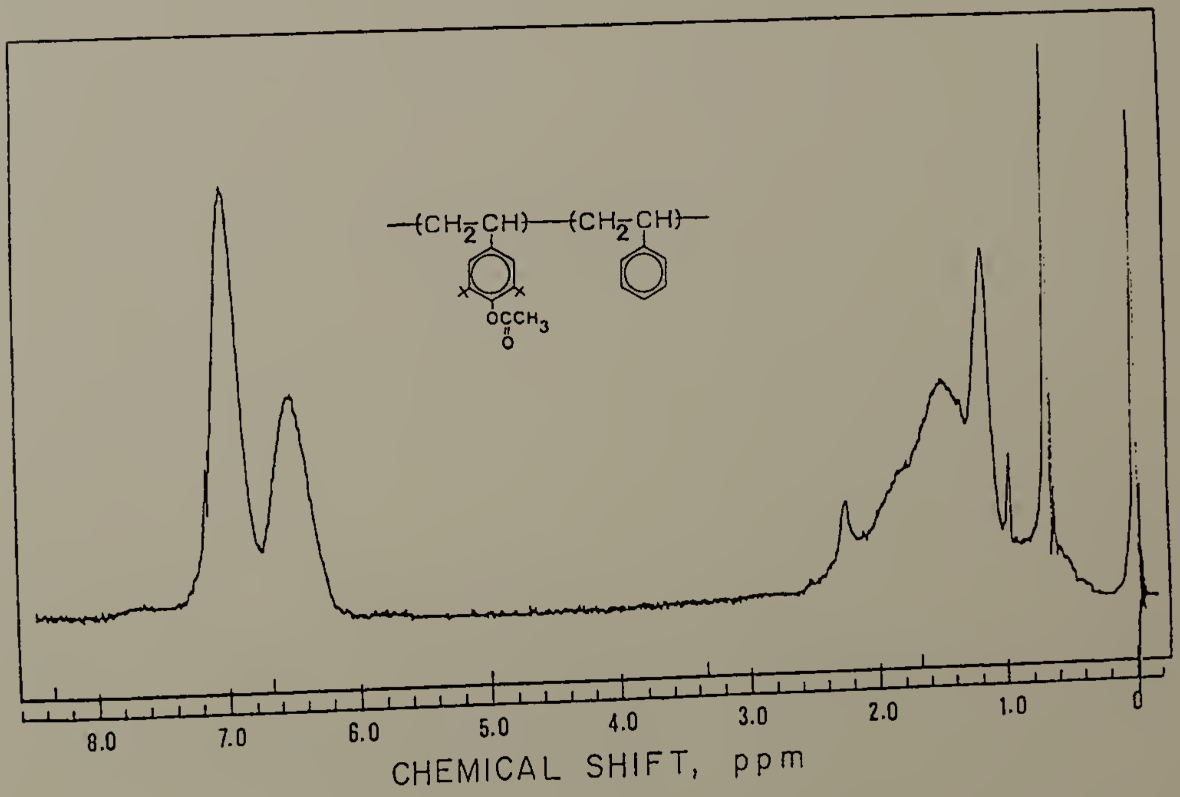

O
OCCH3
CH=CH2
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
CHEMICAL SHIFT, ppm

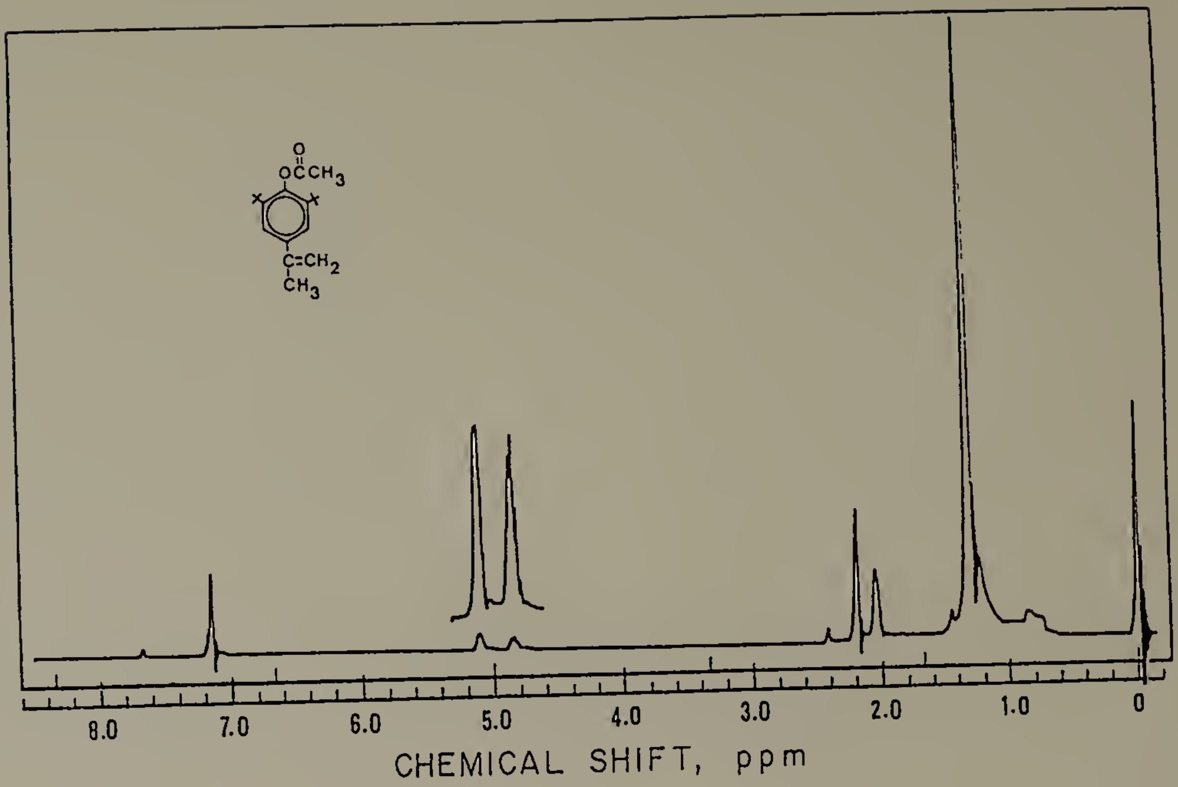

OH
CH=CH2
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
CHEMICAL SHIFT, ppm

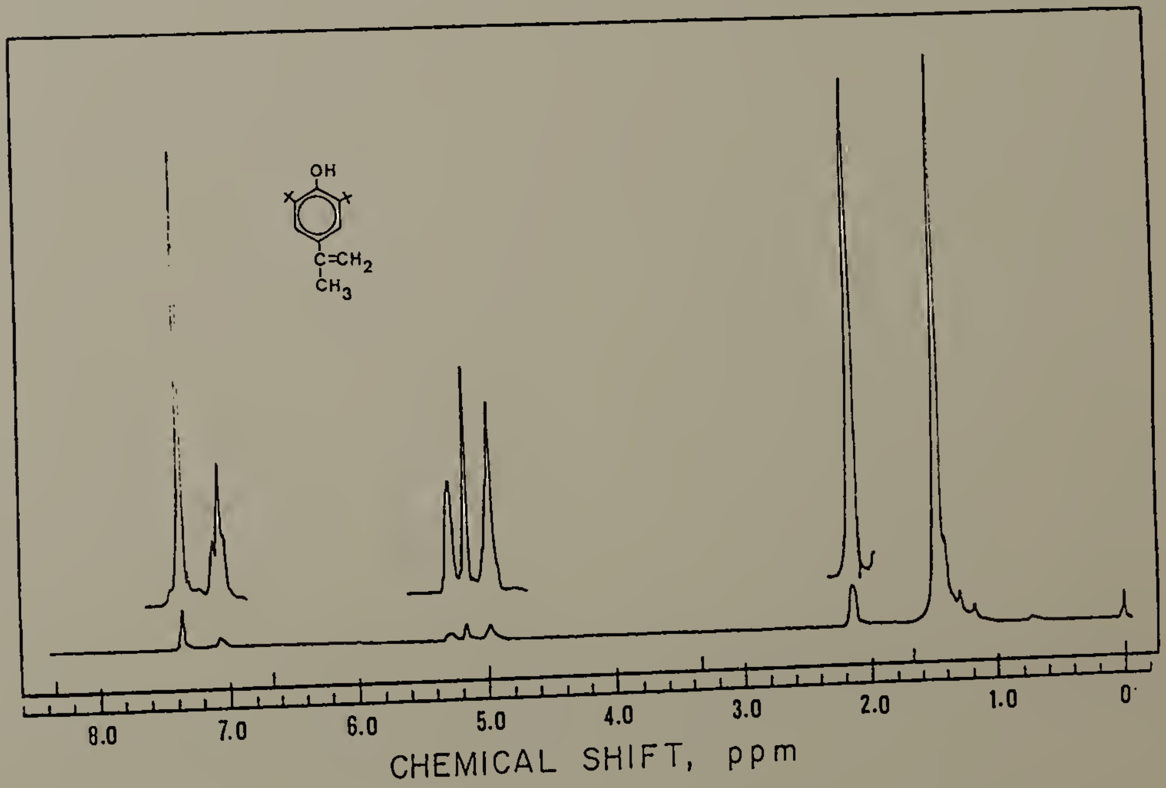

OH
CH=CH2
+ D2O
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
CHEMICAL SHIFT, ppm

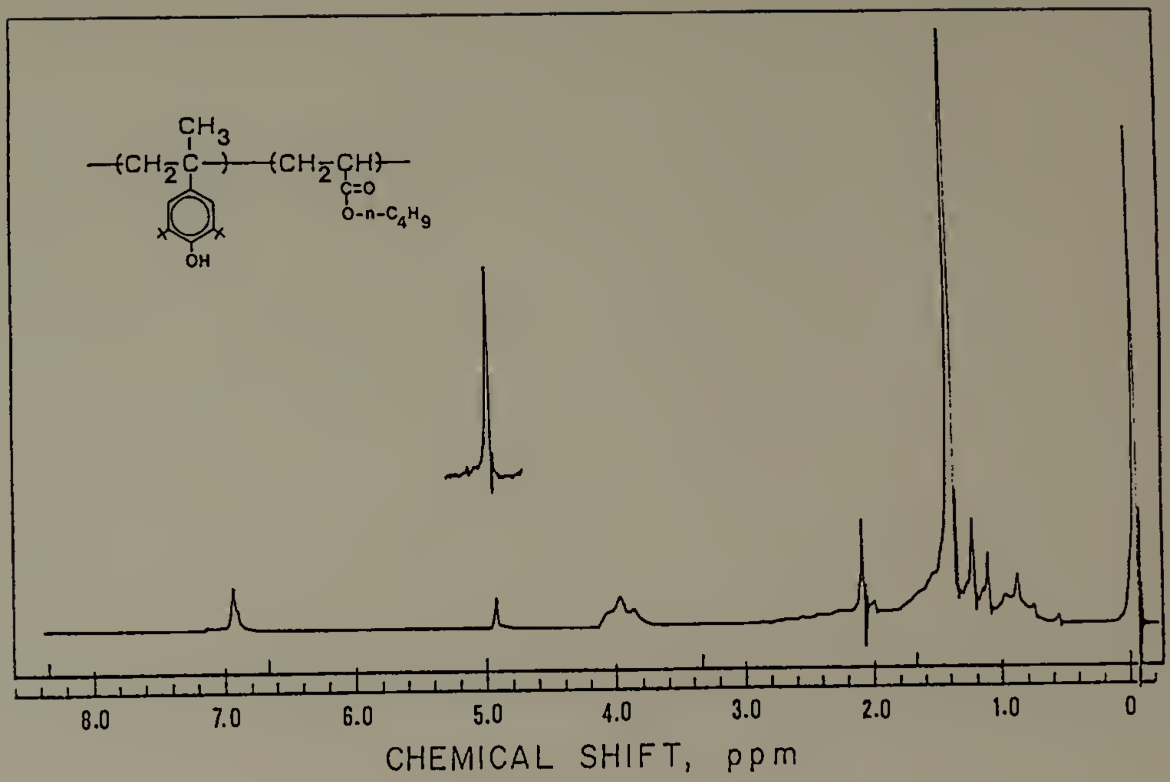

—(CH2–CH)—
OCOCH3
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
CHEMICAL SHIFT, ppm

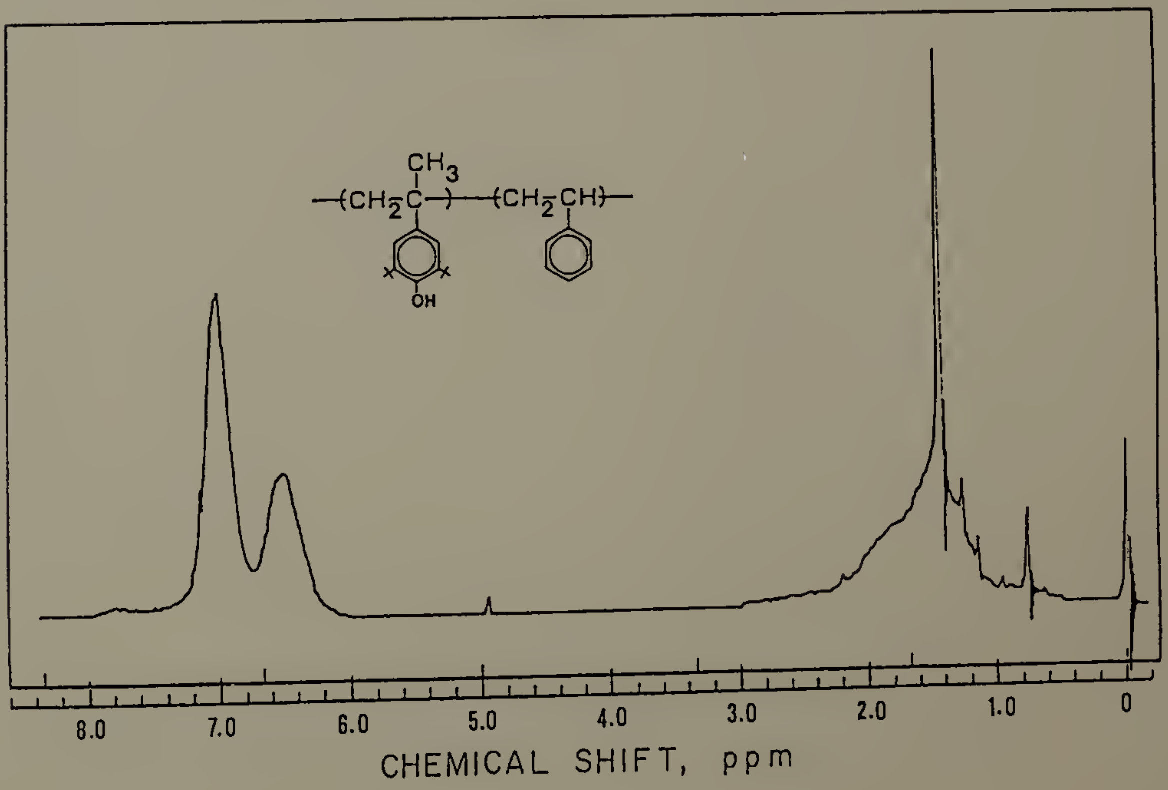

CH3
—(CH2–CH)—(CH2–C—)—
C=O
OCH3
X
X
OCOCH3
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
CHEMICAL SHIFT, ppm

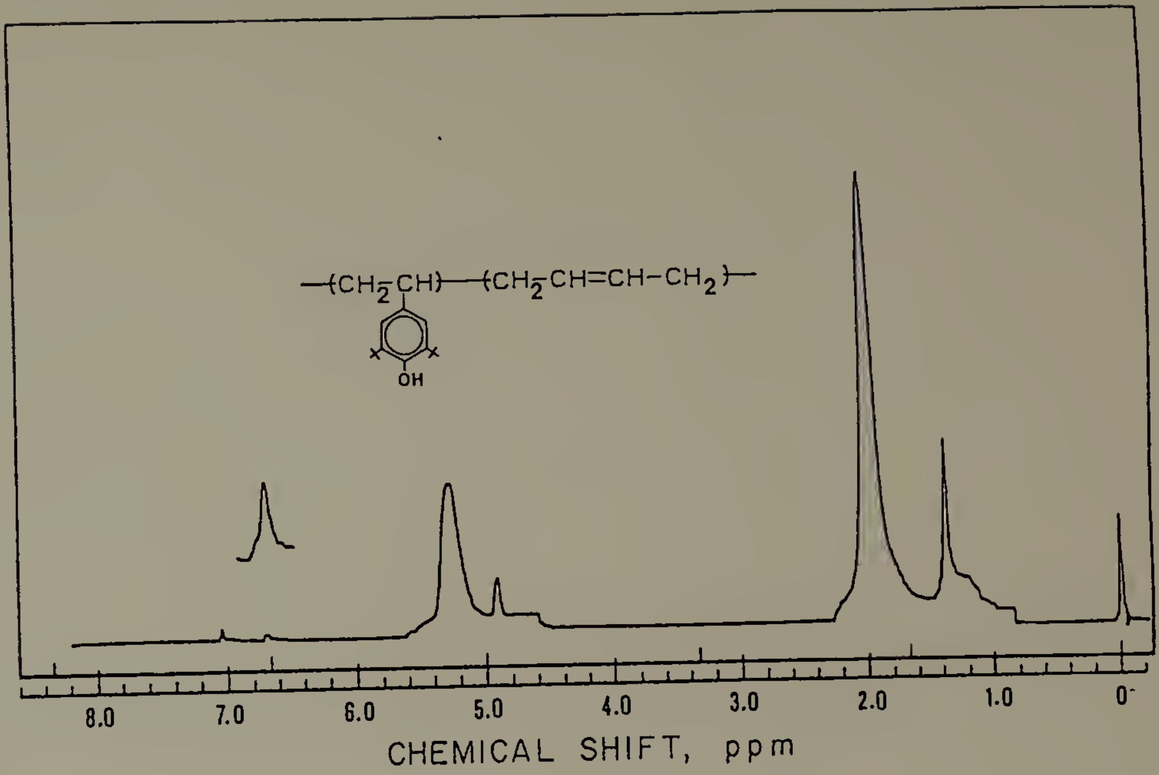

—(CH2–CH)—(CH2–CH)—
X
X
OCCH3
O
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
CHEMICAL SHIFT, ppm

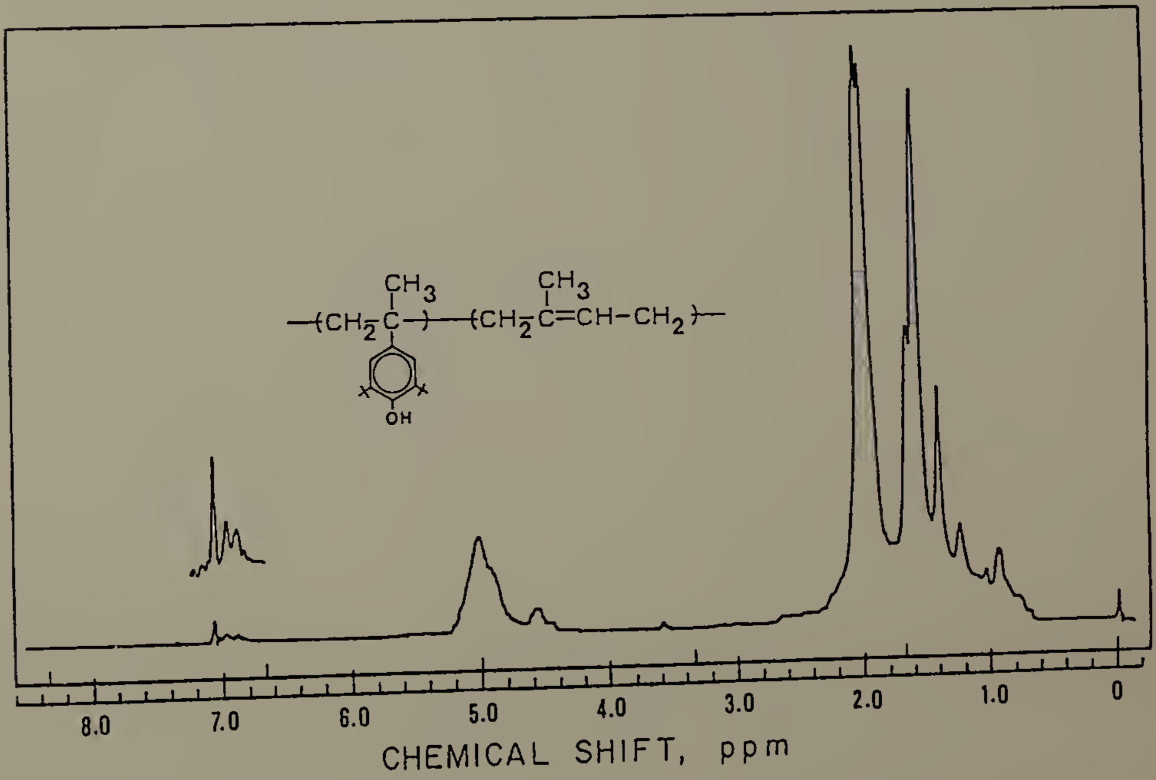

O
OCCH3
C=CH2
CH3
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
CHEMICAL SHIFT, ppm

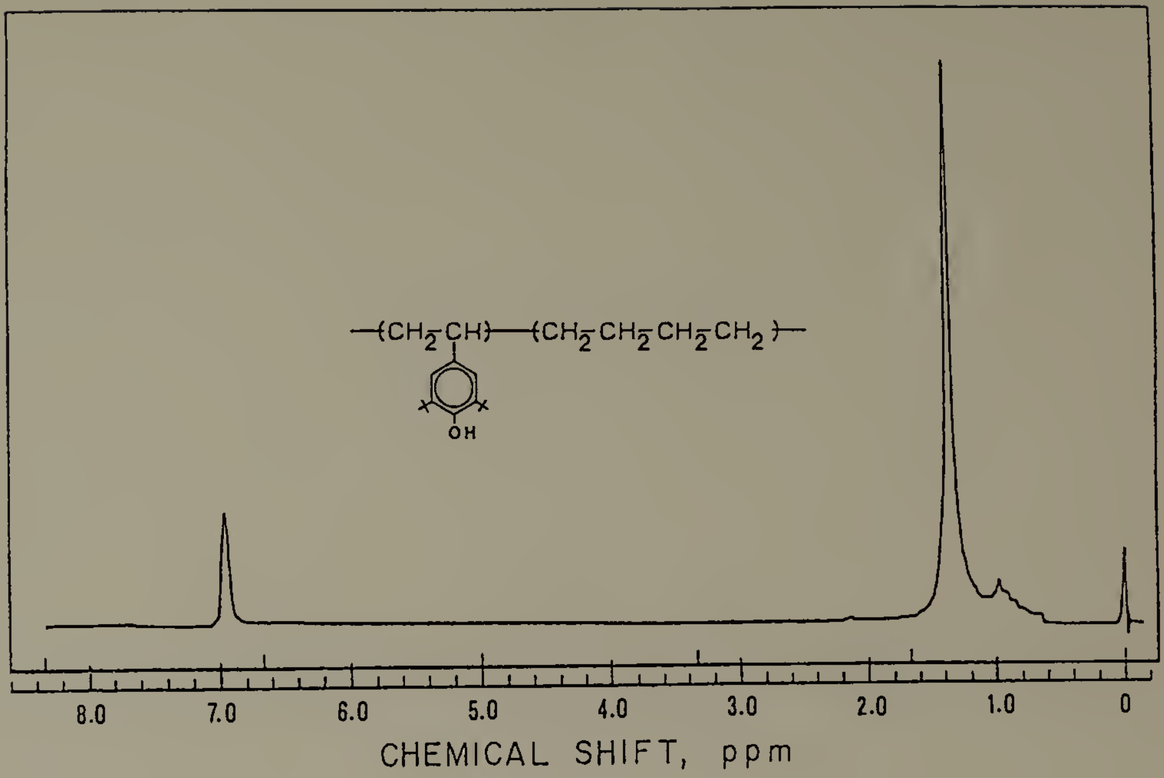

OH
C=CH2
CH3
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
CHEMICAL SHIFT, ppm

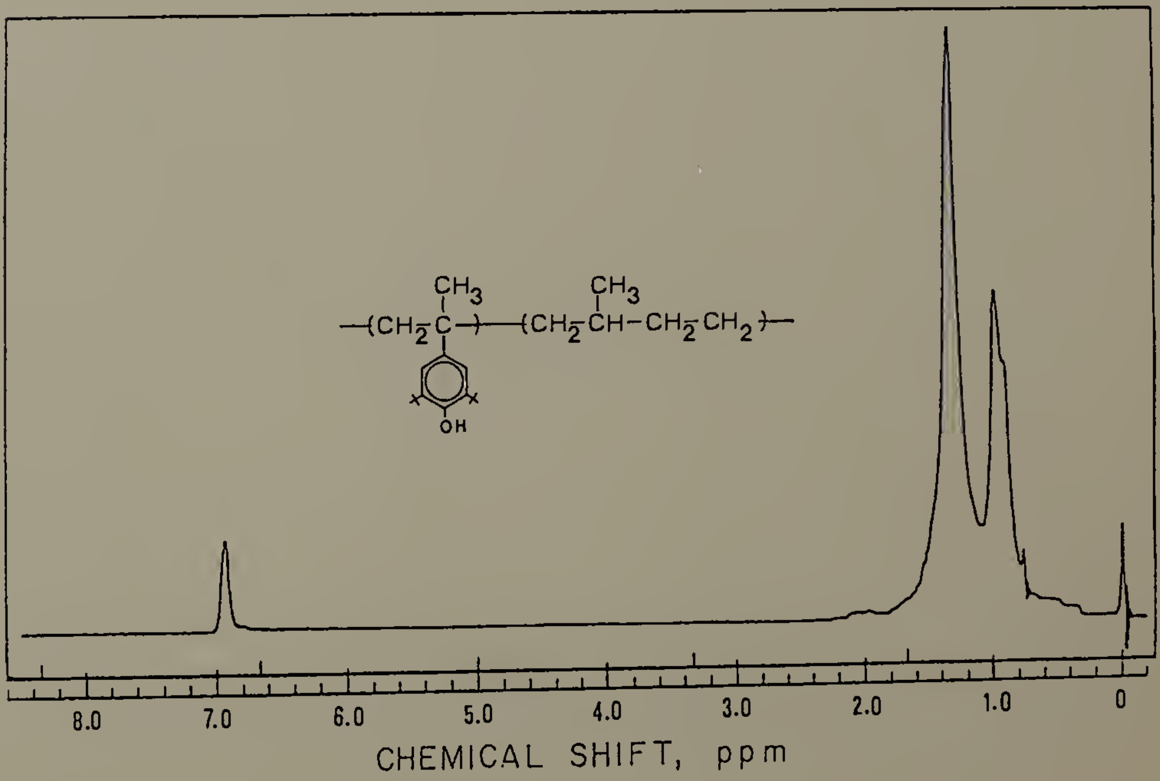

CH3
—(CH2—C—)—(CH2—CH)—
C=O
O-n-C4H9
OH
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
CHEMICAL SHIFT, ppm

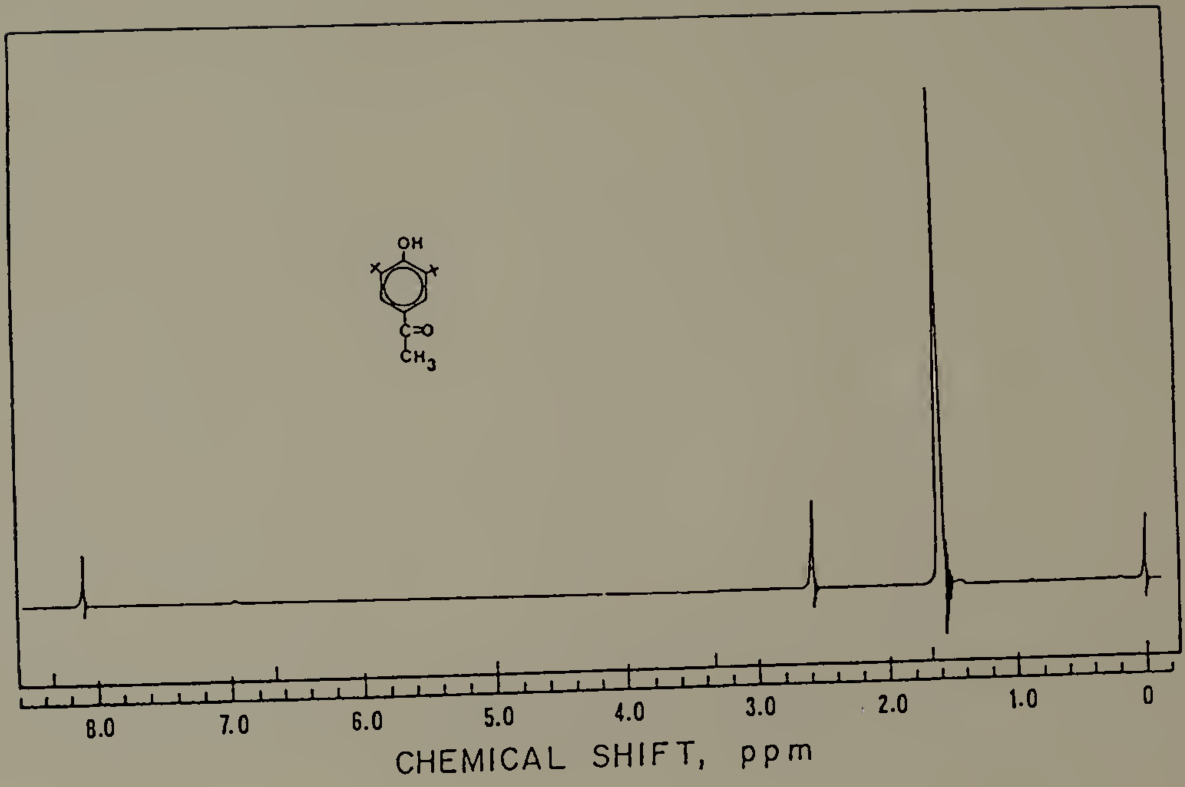

CH3
—(CH2—C—)—(CH2—CH)—
OH
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
CHEMICAL SHIFT, ppm


—(CH2-CH)—(CH2-CH=CH-CH2)—
OH
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
CHEMICAL SHIFT, ppm


CH3
CH3
—(CH2-C—)—(CH2-C=CH-CH2)—
OH
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
CHEMICAL SHIFT, ppm

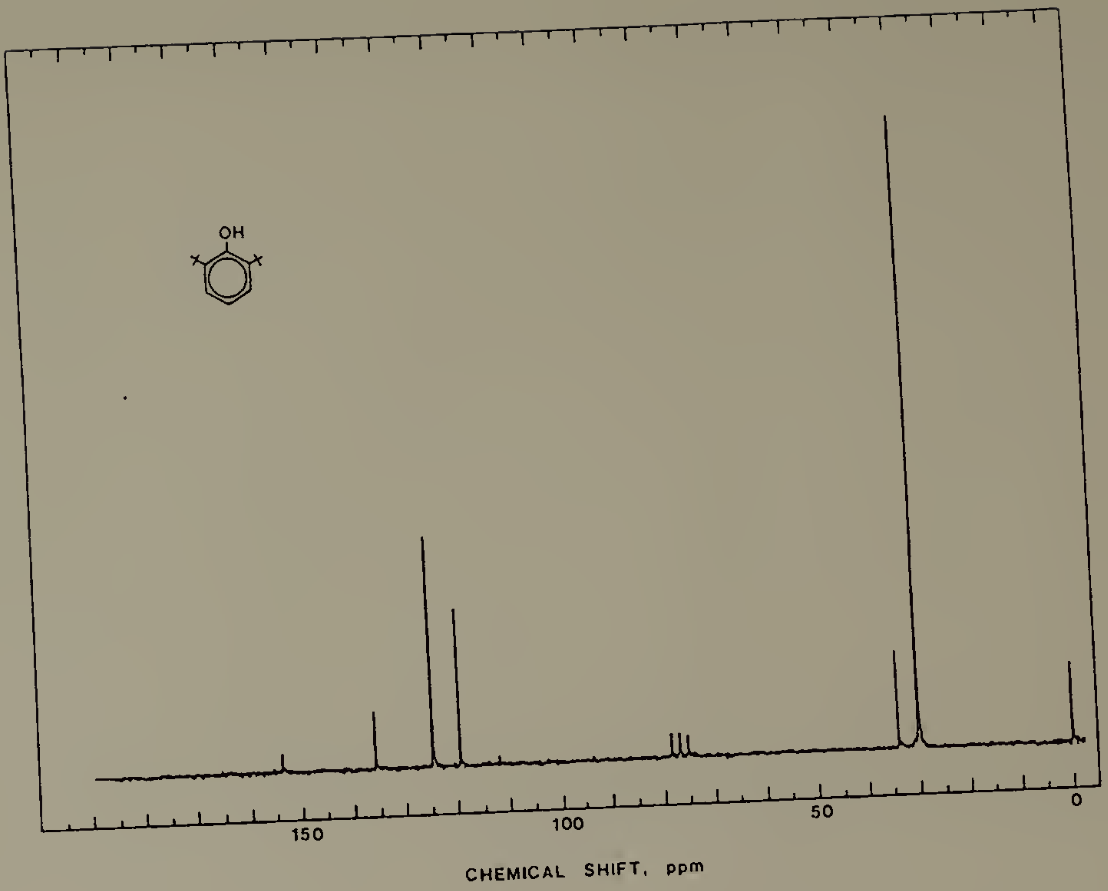

—(CH2-CH)—(CH2-CH2-CH2-CH2)—
OH
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
CHEMICAL SHIFT, ppm

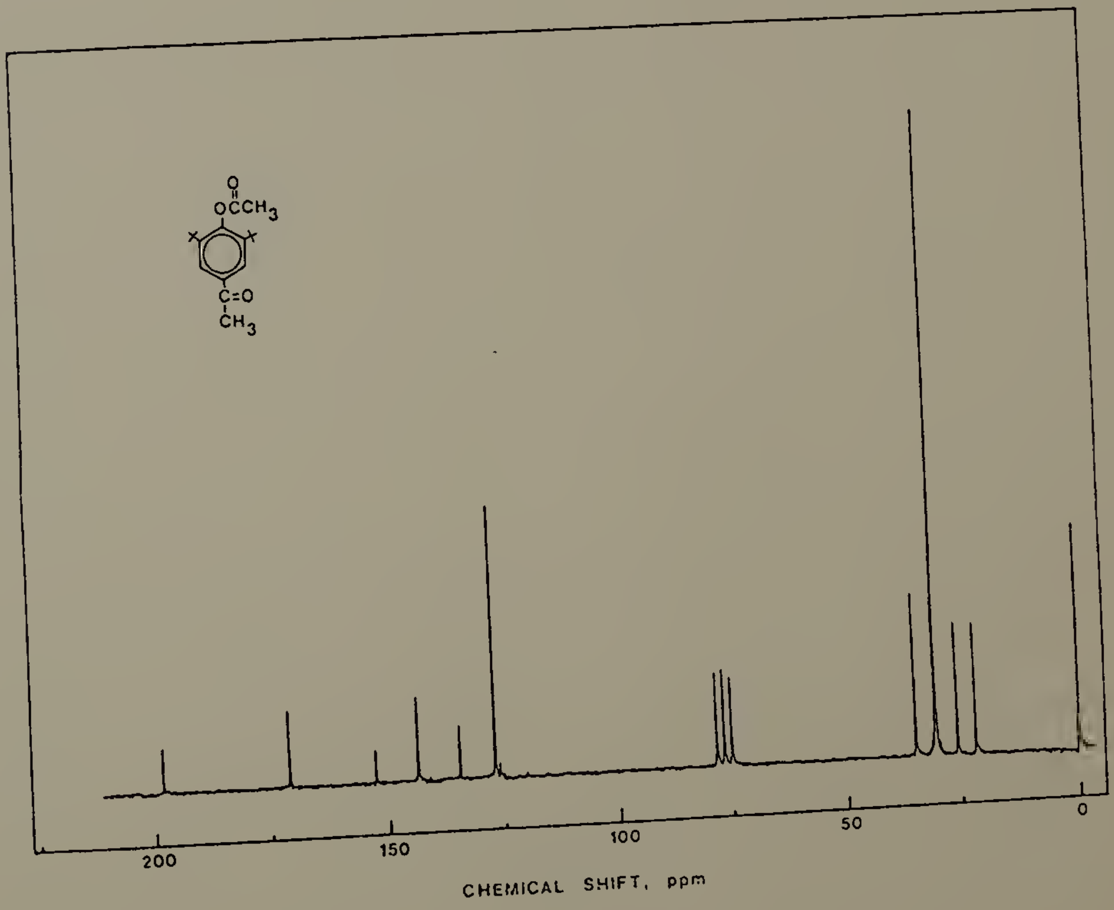

CH3
CH3
—(CH2-C)—(CH2-CH-CH2-CH2)—
OH
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
CHEMICAL SHIFT, ppm

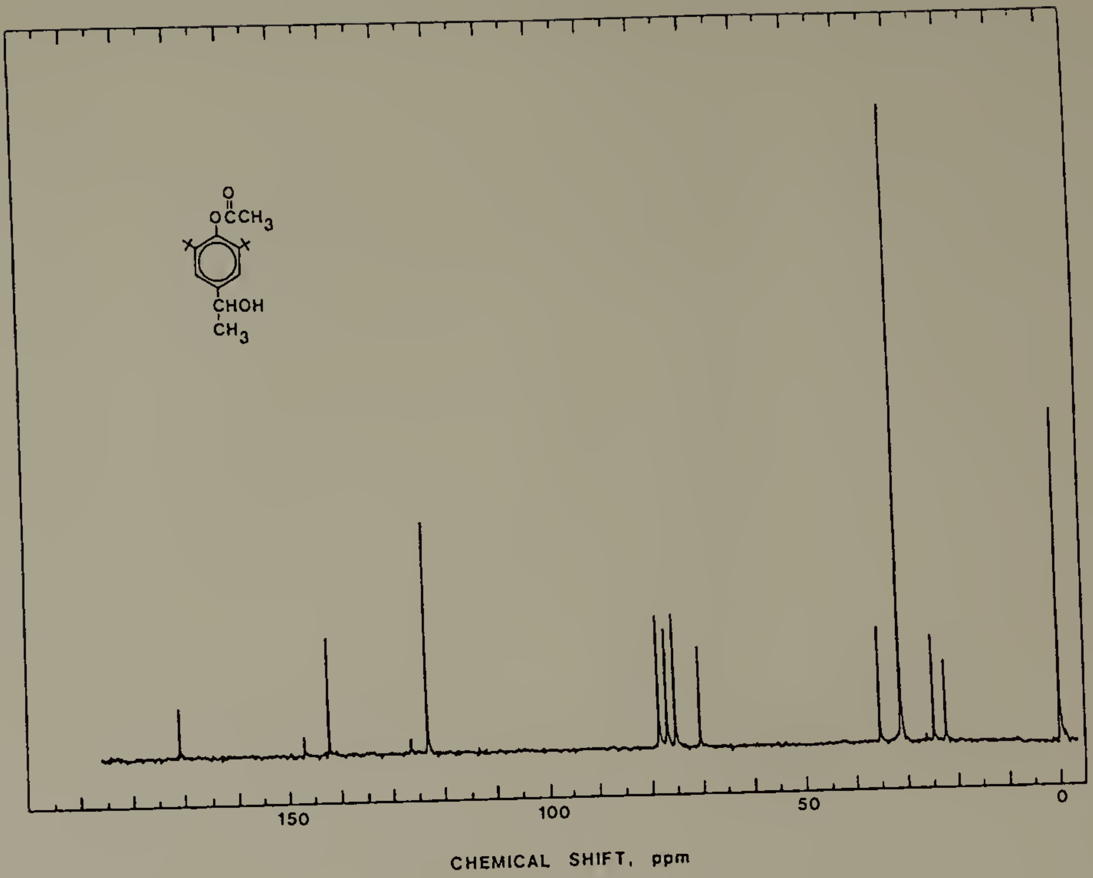

OH
C=O
CH3
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
CHEMICAL SHIFT, ppm

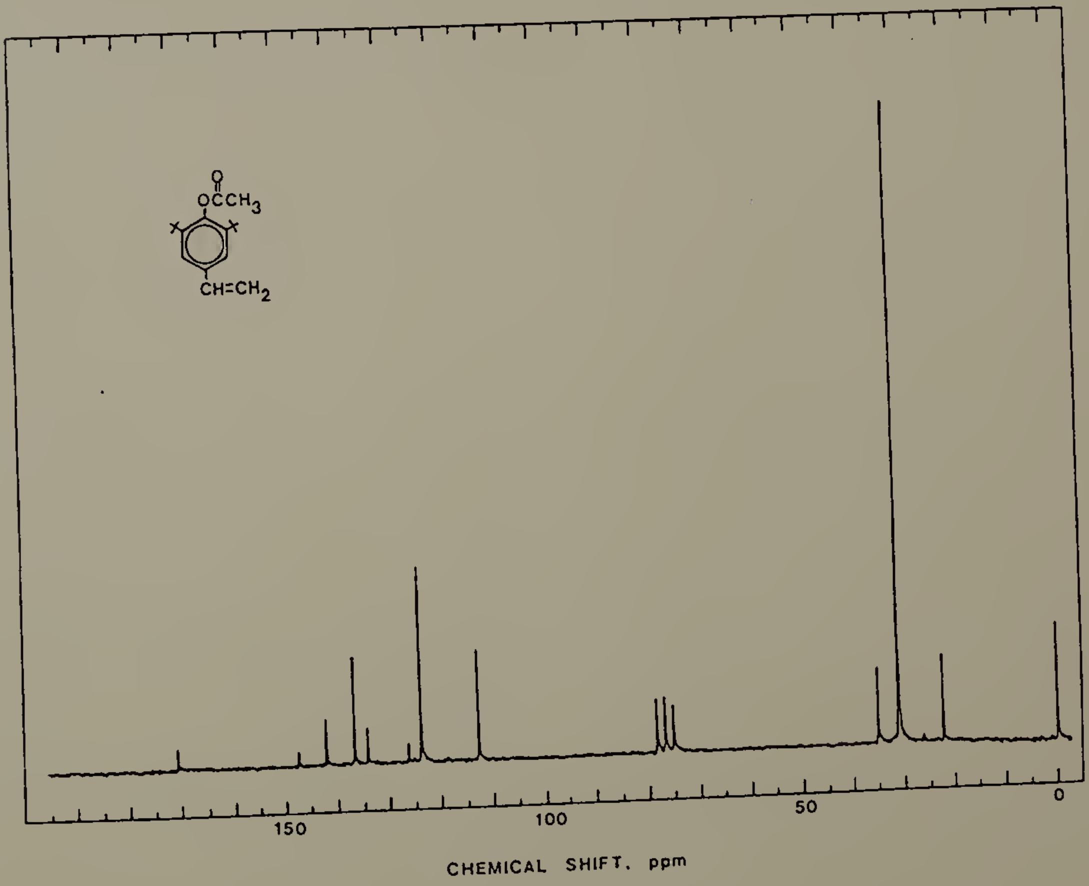
APPENDIX B

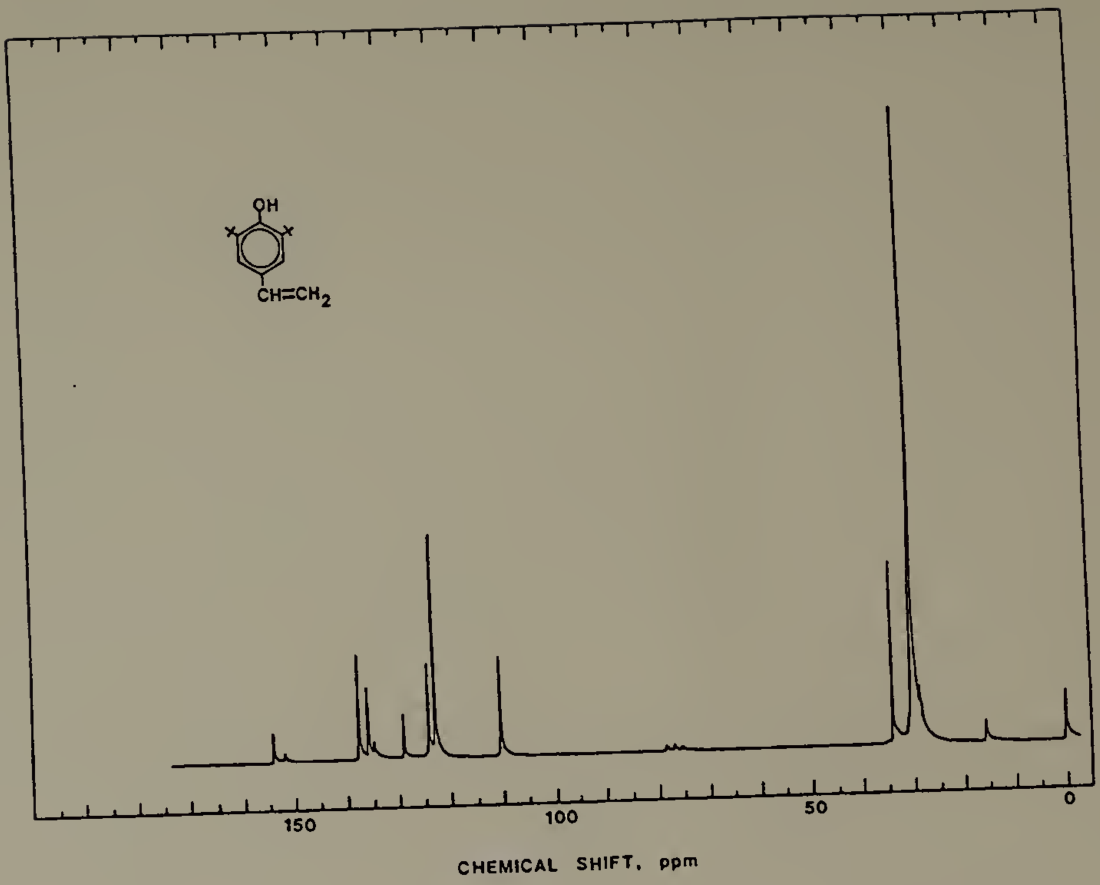
CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTRA

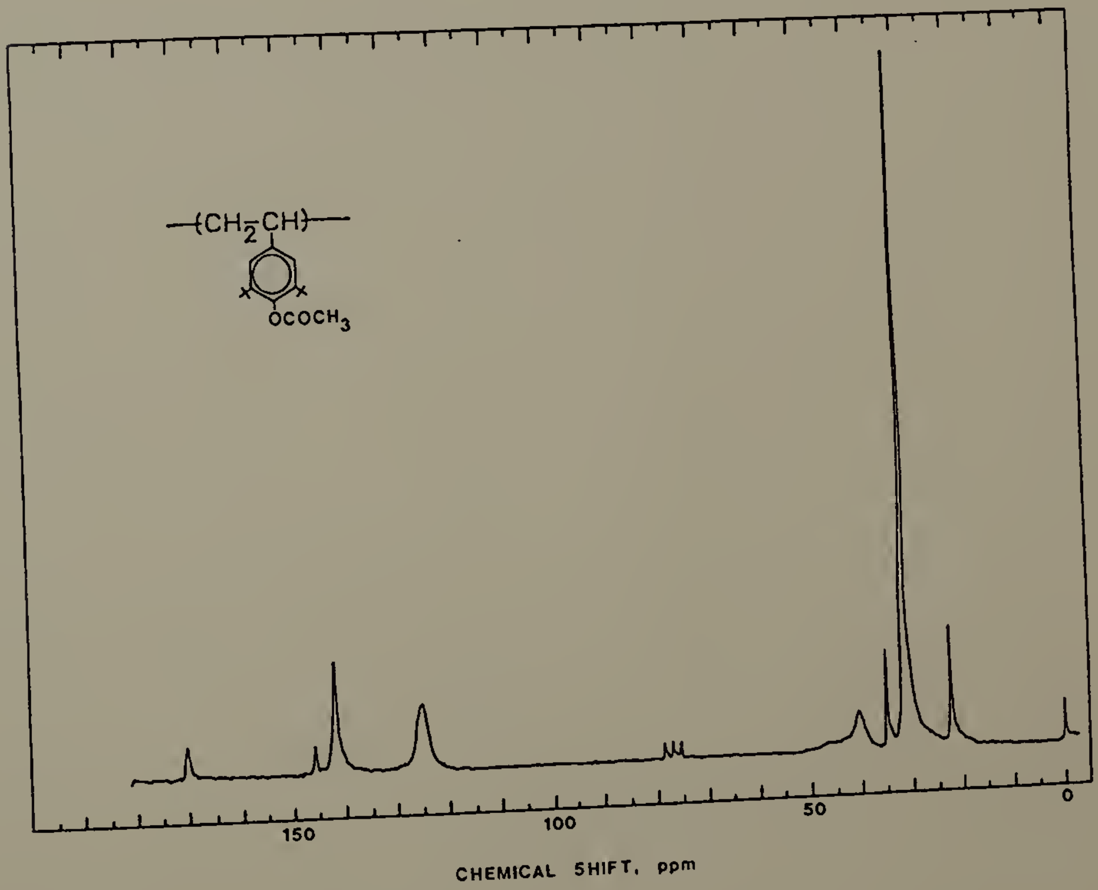

OH
150
100
50
0
CHEMICAL SHIFT, ppm

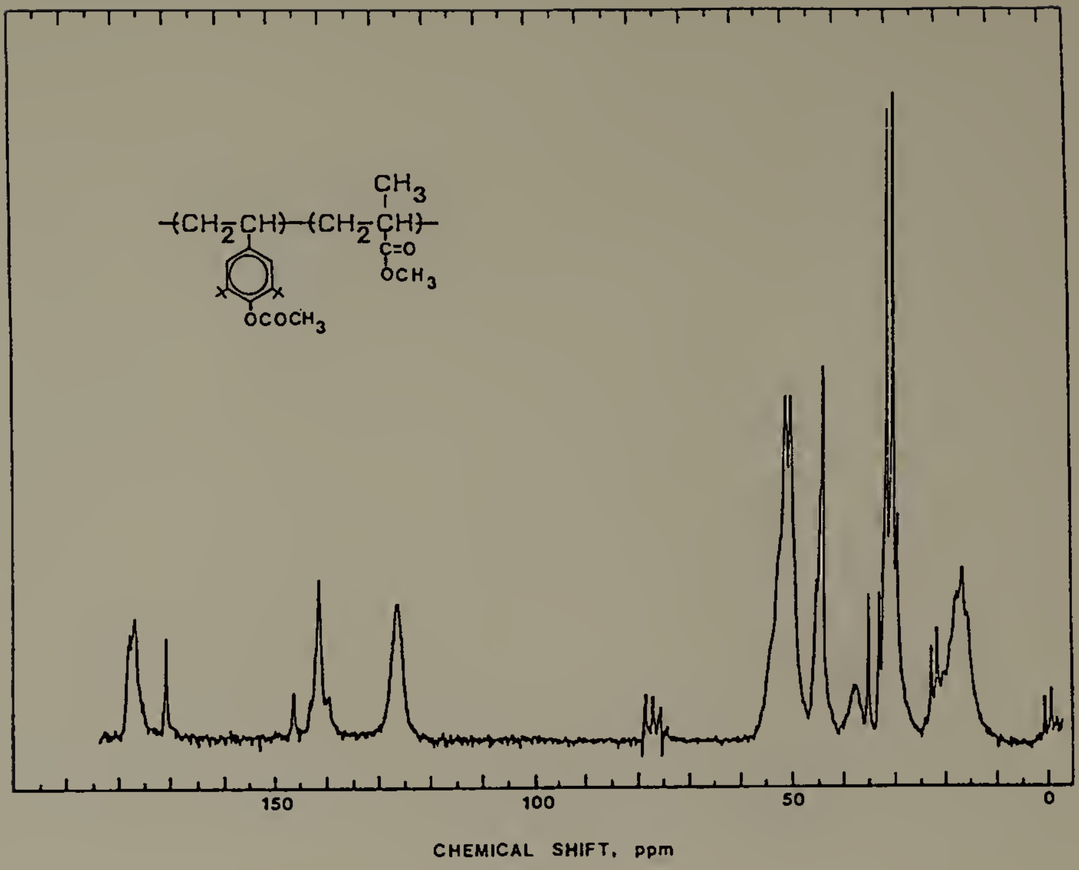

O
OCCH3
C=O
CH3
200
150
100
50
0
CHEMICAL SHIFT, ppm

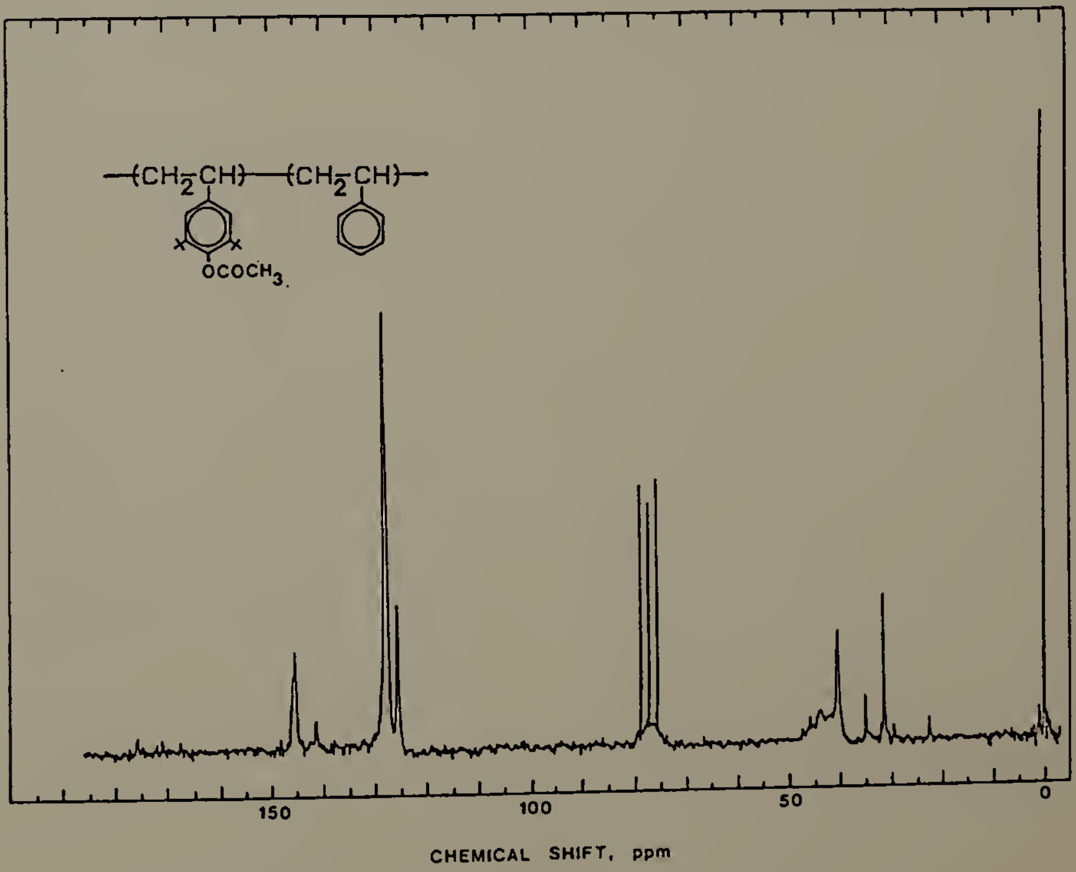

OCCH3
CHOH
CH3
150
100
50
0
CHEMICAL SHIFT, ppm

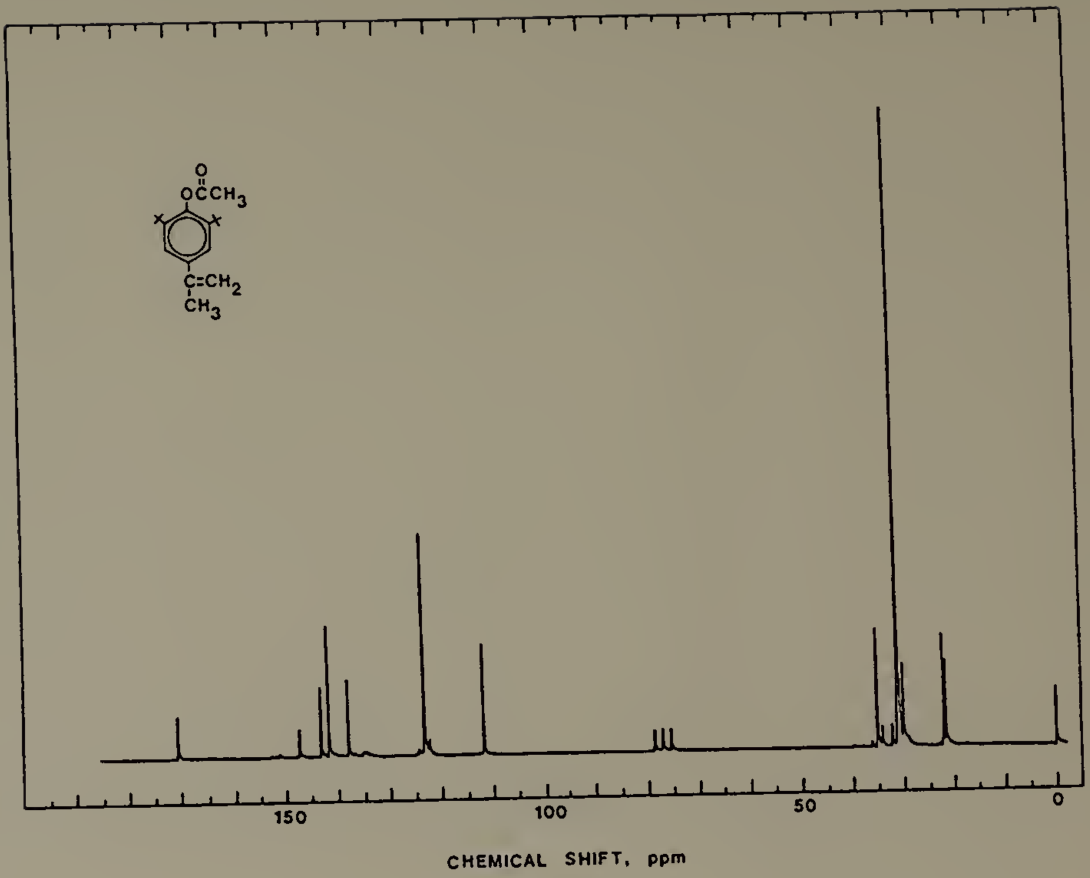

OCCH3
CH=CH2
150
100
50
0
CHEMICAL SHIFT, ppm

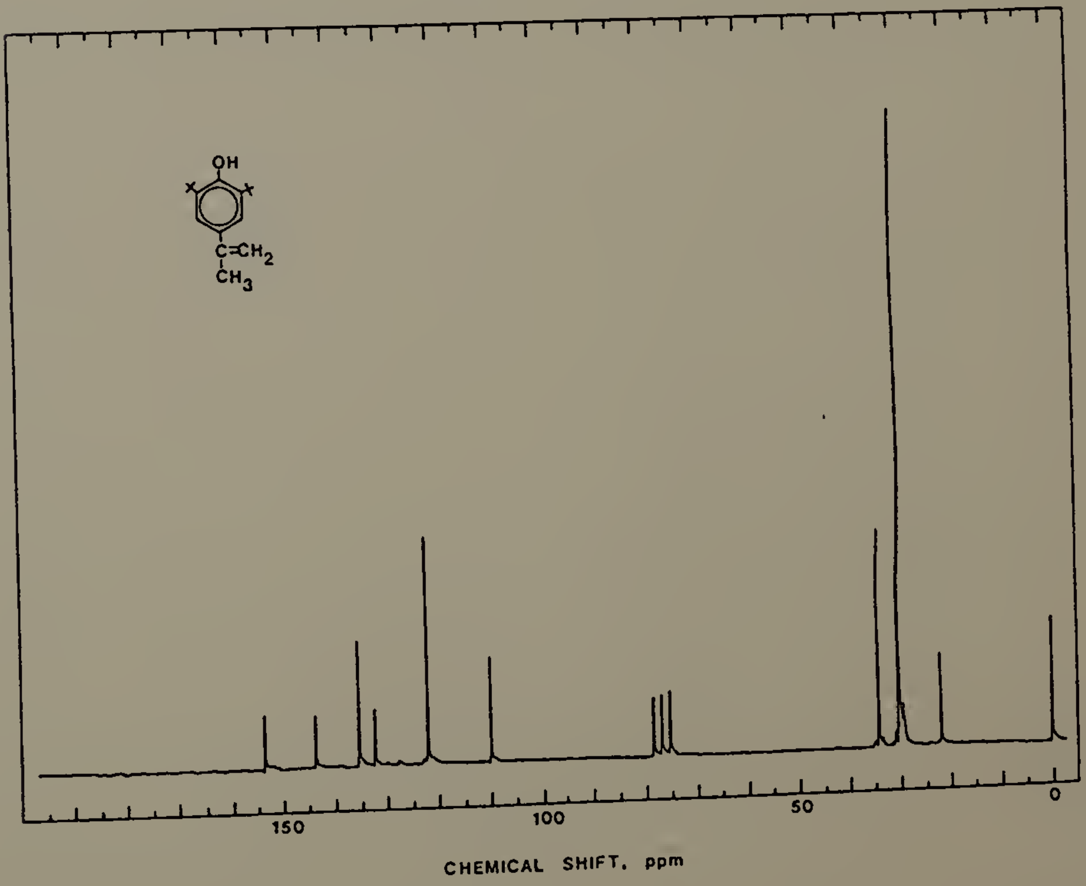

OH
CH=CH2
150
100
50
0
CHEMICAL SHIFT, ppm

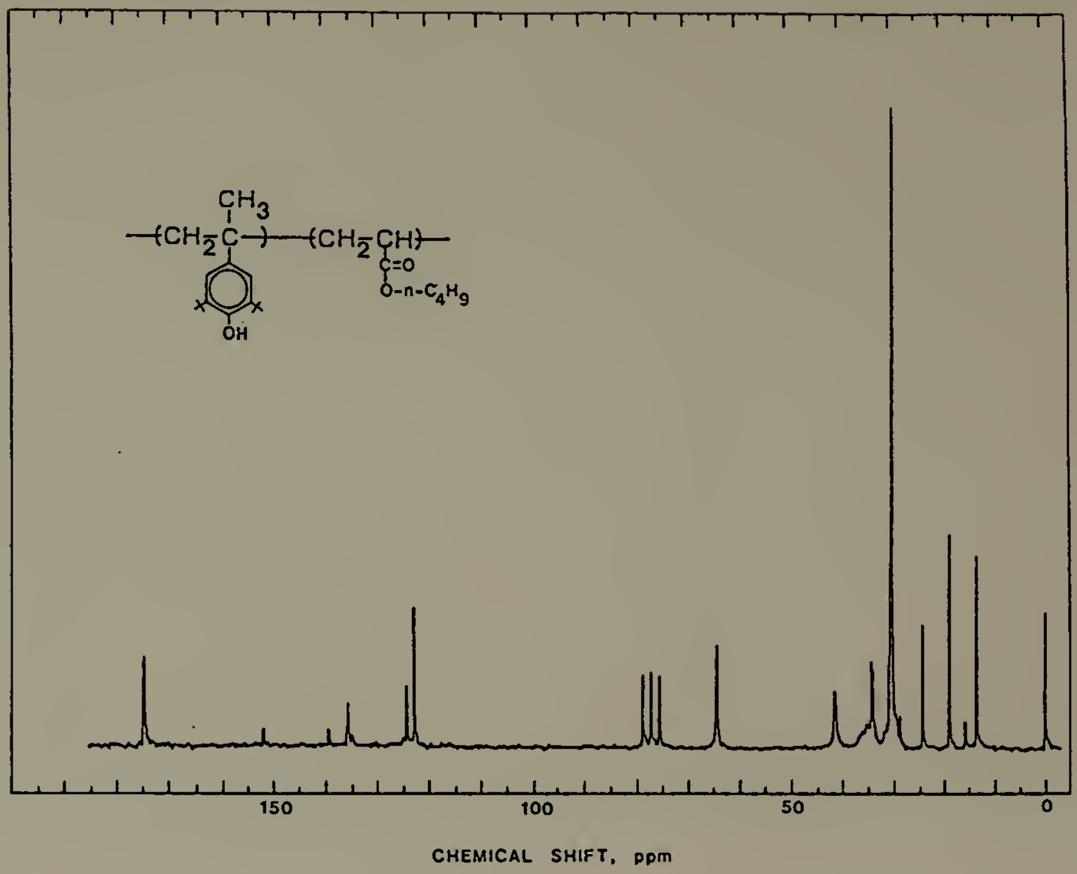

—(CH2–CH)—
OCOCH3
150
100
50
0
CHEMICAL SHIFT, ppm


CH3
-(CH2-CH)-(CH2-CH)-
C=O
OCH3
OCOCH3
150
100
50
0
CHEMICAL SHIFT, ppm

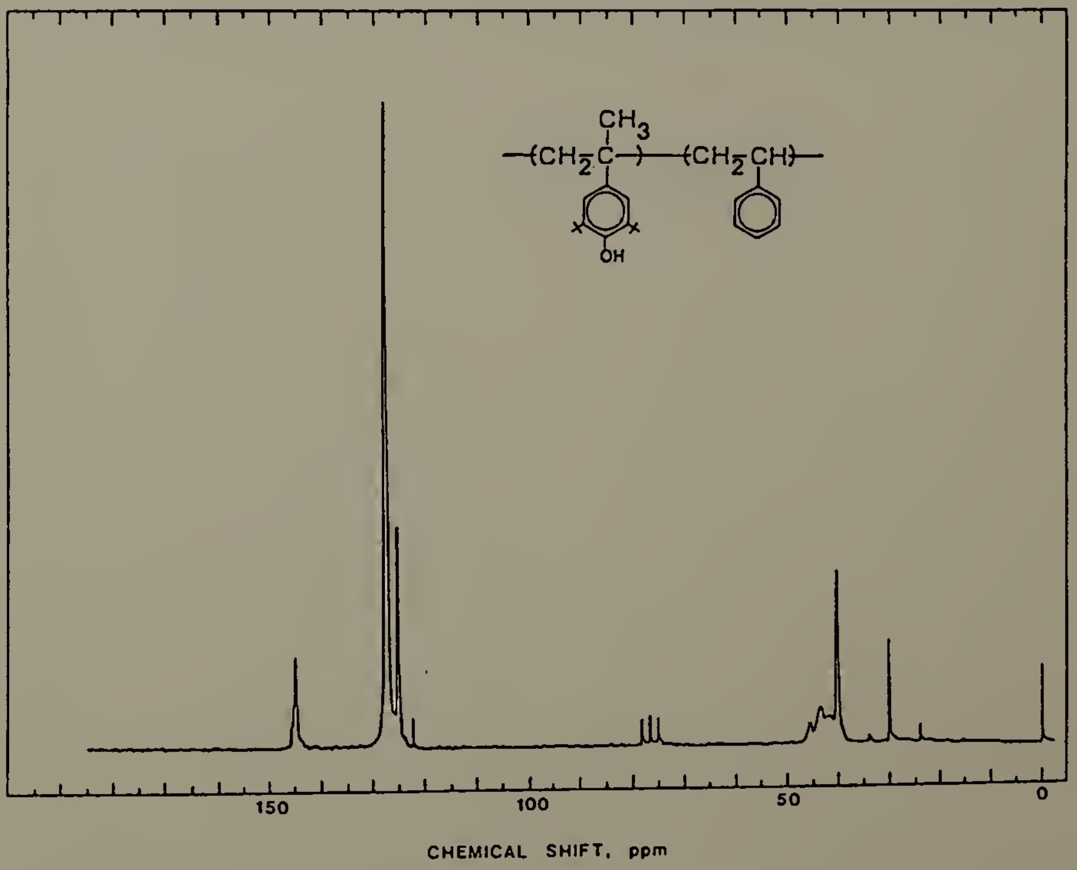

-(CH2-CH)-(CH2-CH)-
OCOCH3.
150
100
50
0
CHEMICAL SHIFT, ppm


O
OCCH3
C=CH2
CH3
150
100
50
0
CHEMICAL SHIFT, ppm

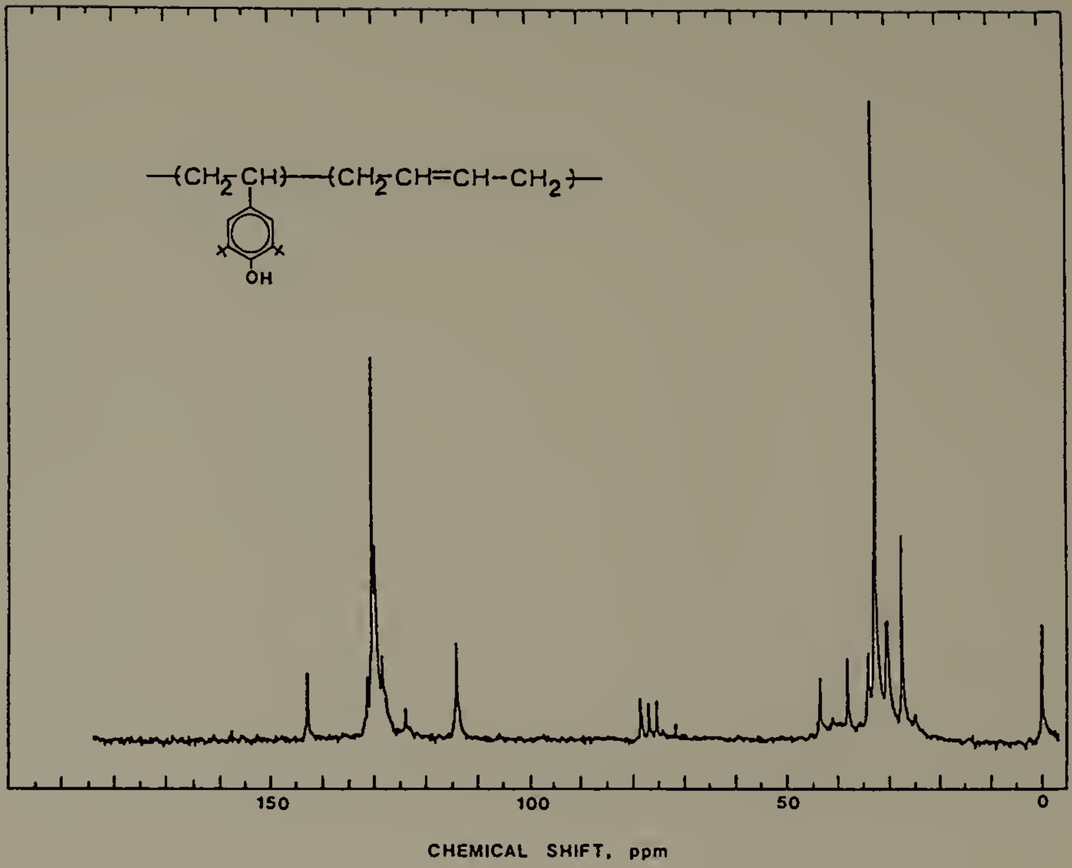

OH
C=CH2
CH3
150
100
50
0
CHEMICAL SHIFT, ppm

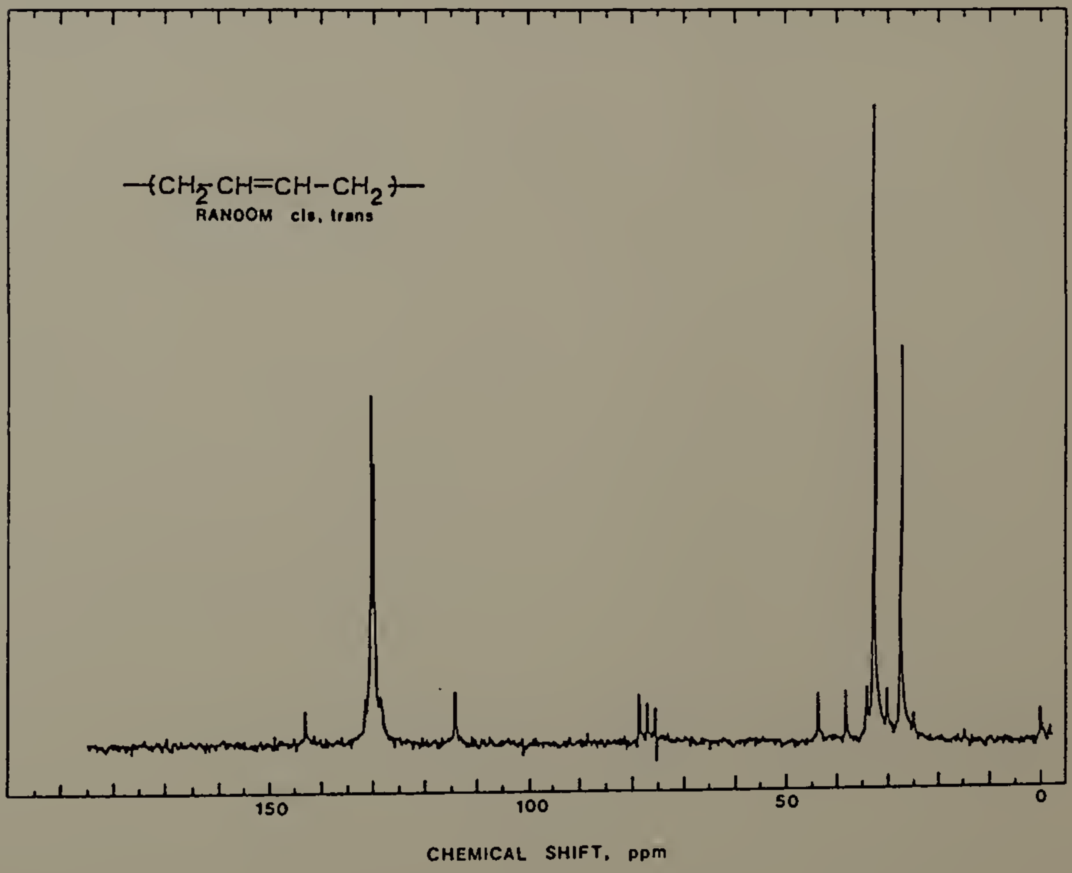


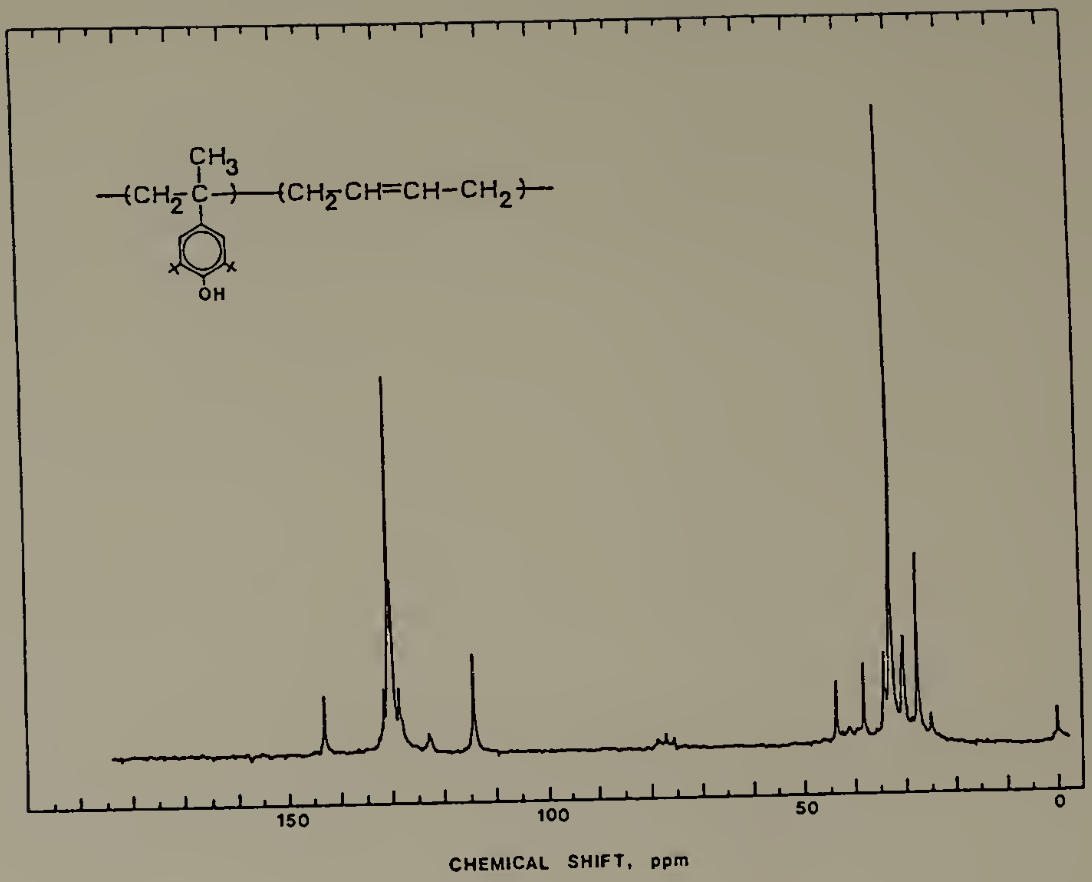
CH3
(CH2-C)
(CH2-CH)
C=O
O-n-C4H9
OH
x
150
100
50
0
CHEMICAL SHIFT, ppm

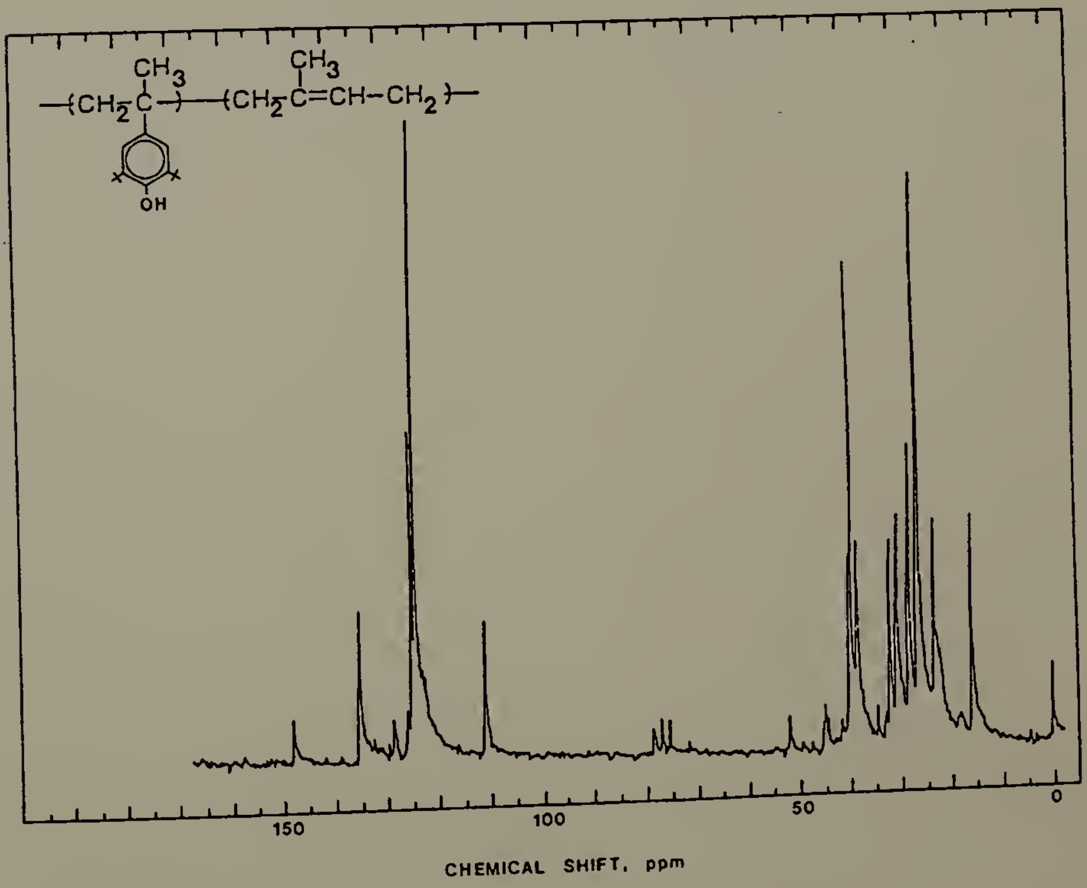


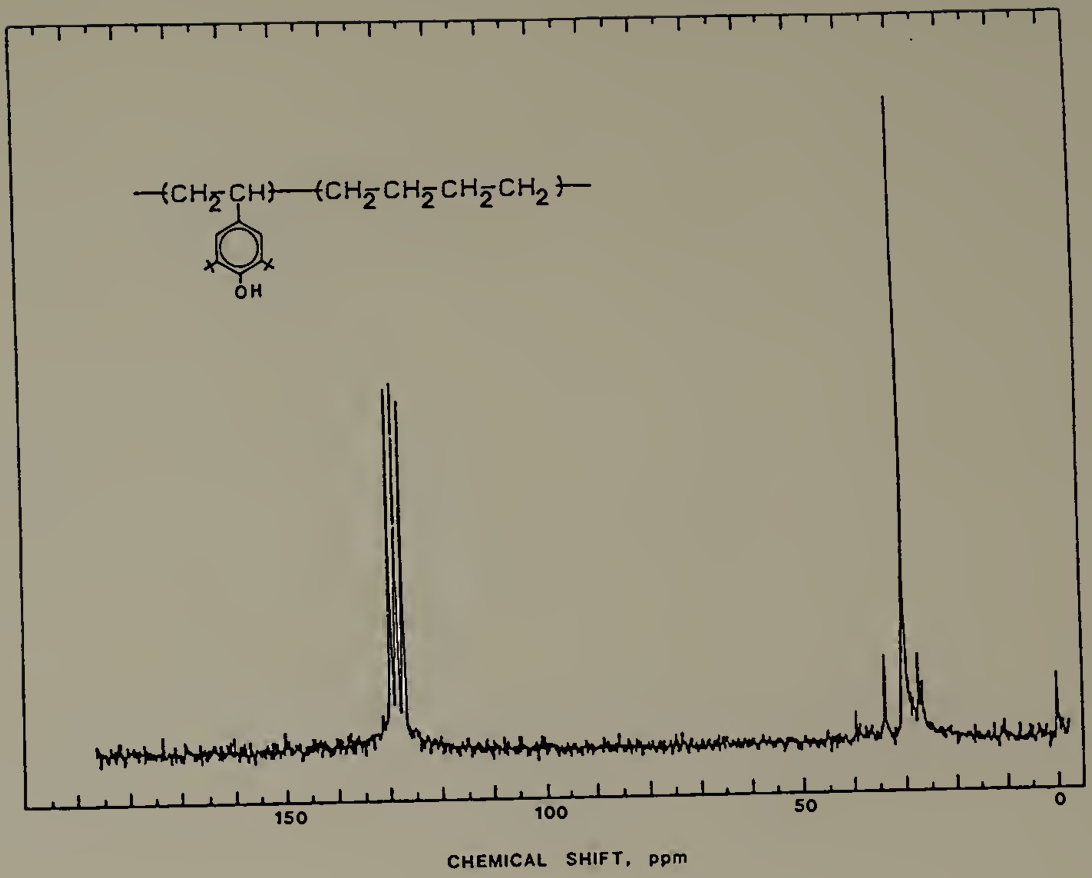
CH3
(CH2-C)
(CH2-CH)
OH
x
150
100
50
0
CHEMICAL SHIFT, ppm

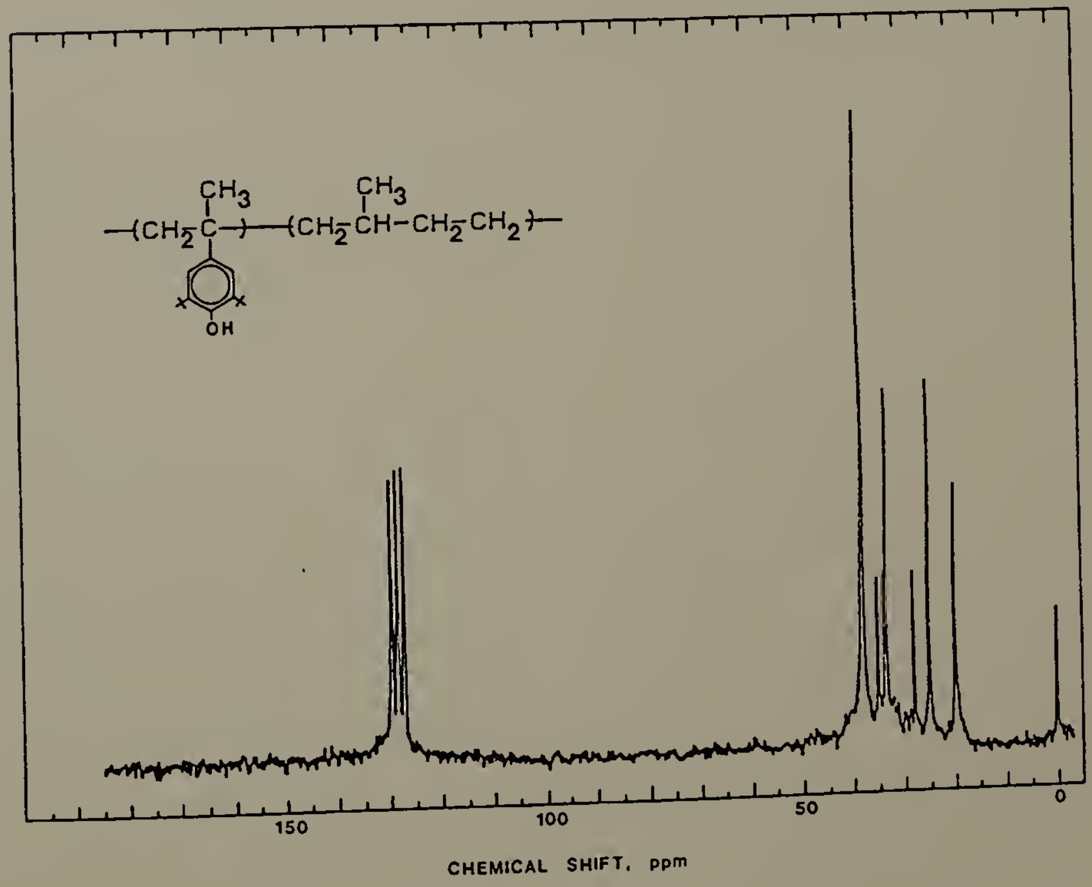

—(CH2-CH)—(CH2-CH=CH-CH2)—
OH
150
100
50
0
CHEMICAL SHIFT, ppm

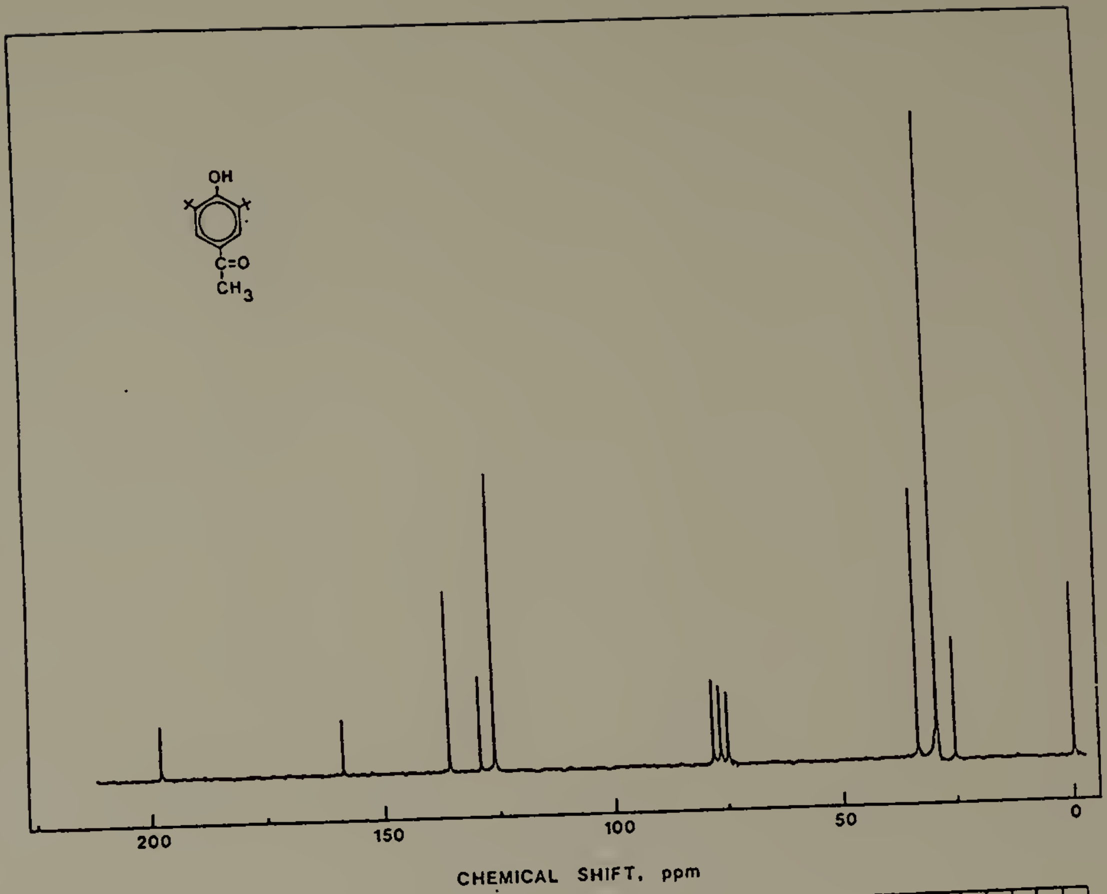

—(CH2-CH=CH-CH2)—
RANDOM cis, trans
150
100
50
0
CHEMICAL SHIFT, ppm

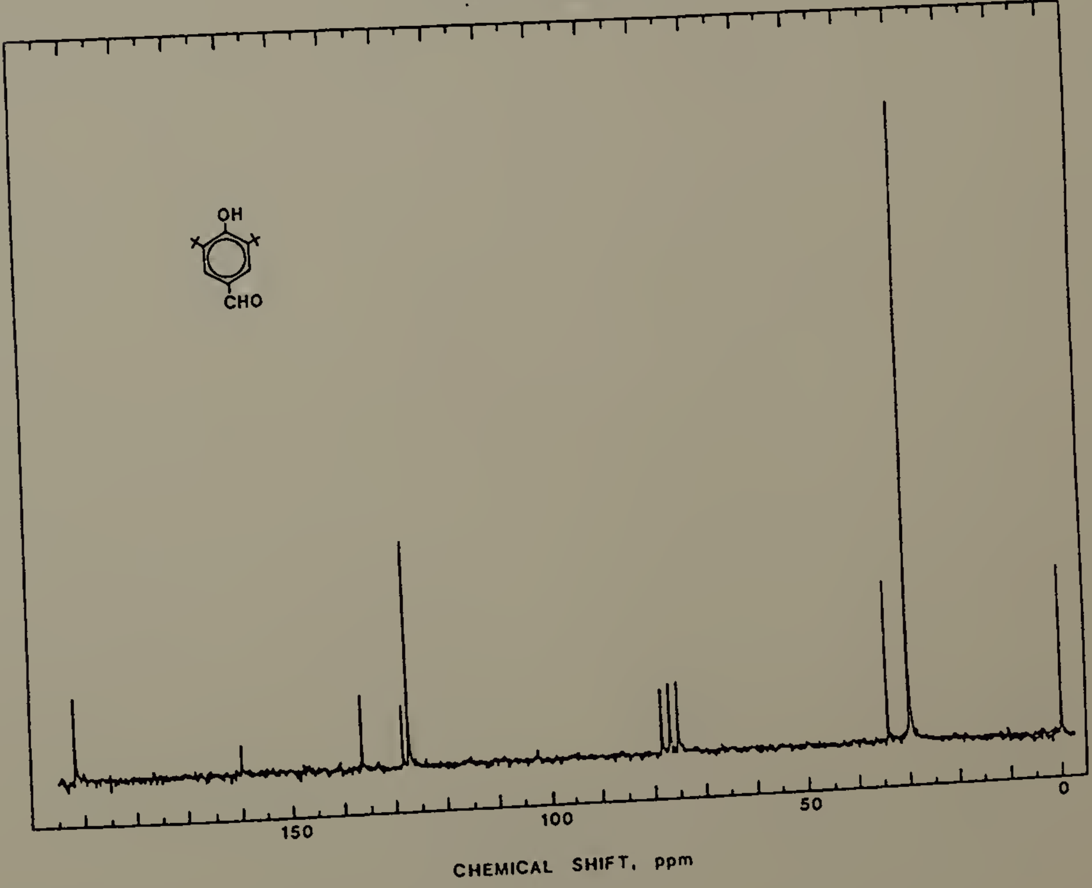

CH3
—(CH2-C—)—(CH2-CH=CH-CH2)—
OH
150
100
50
0
CHEMICAL SHIFT, ppm


CH3
CH3
—(CH2-C—)—(CH2-C=CH-CH2)—
OH
150
100
50
0
CHEMICAL SHIFT, ppm


—(CH₂-CH)—(CH₂-CH₂-CH₂-CH₂)—
OH
150
100
50
0
CHEMICAL SHIFT, ppm

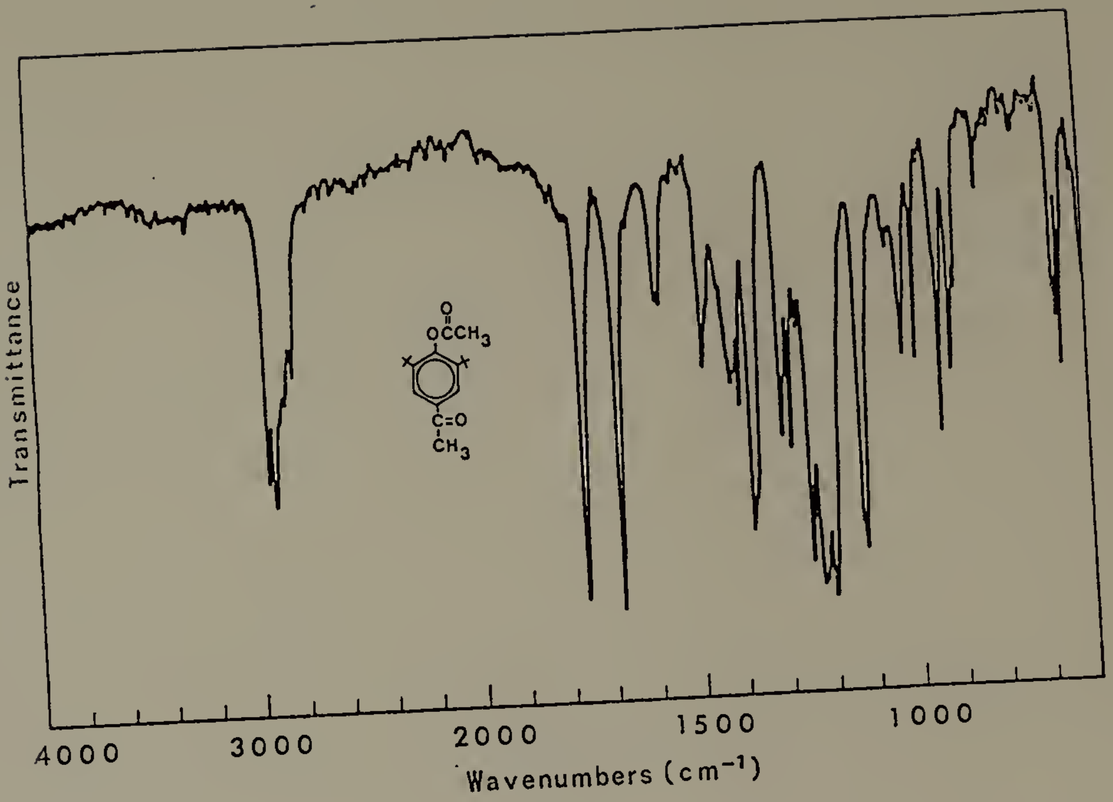

CH₃
CH₃
—(CH₂-C—)—(CH₂-CH-CH₂-CH₂)—
OH
150
100
50
0
CHEMICAL SHIFT, ppm

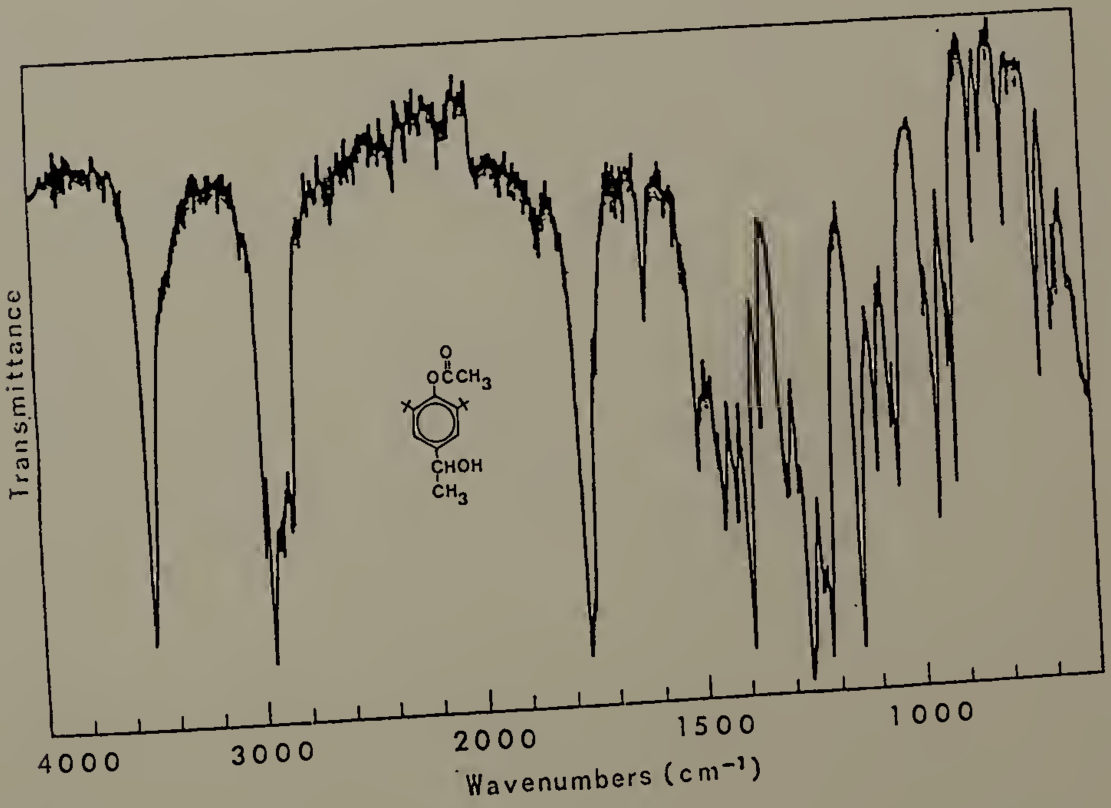

OH
C=O
CH3
200
150
100
50
0
CHEMICAL SHIFT, ppm

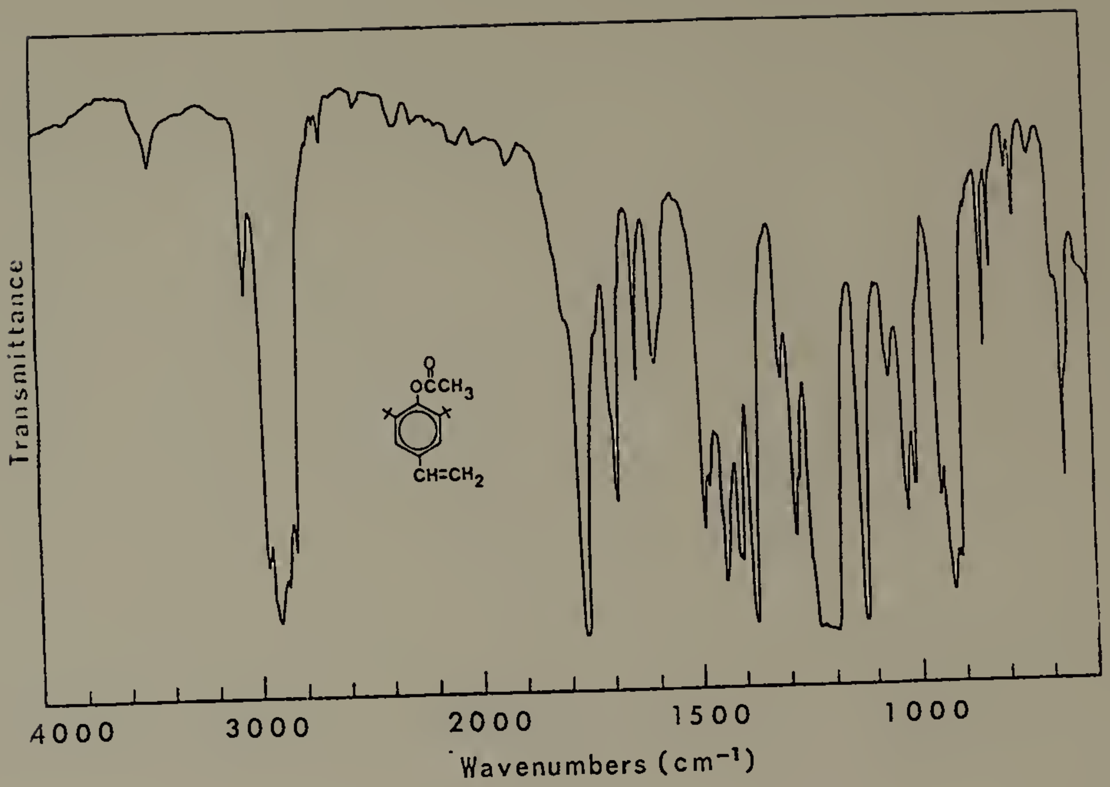

OH
CHO
150
100
50
0
CHEMICAL SHIFT, ppm

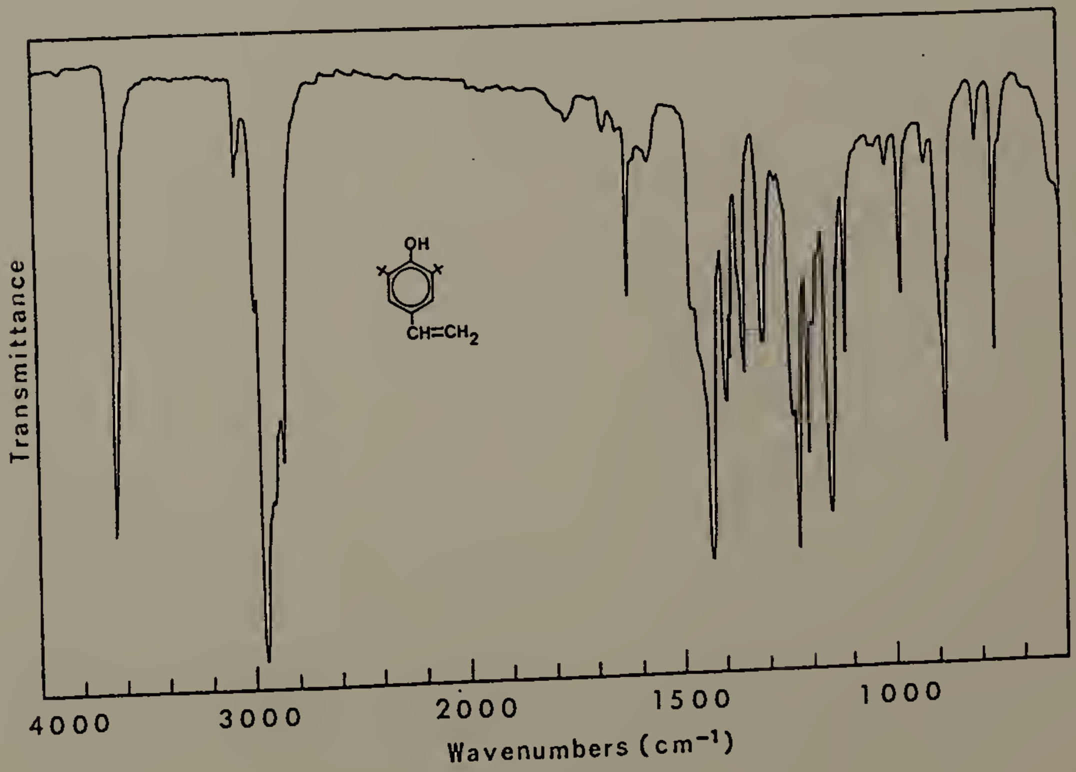
APPENDIX C

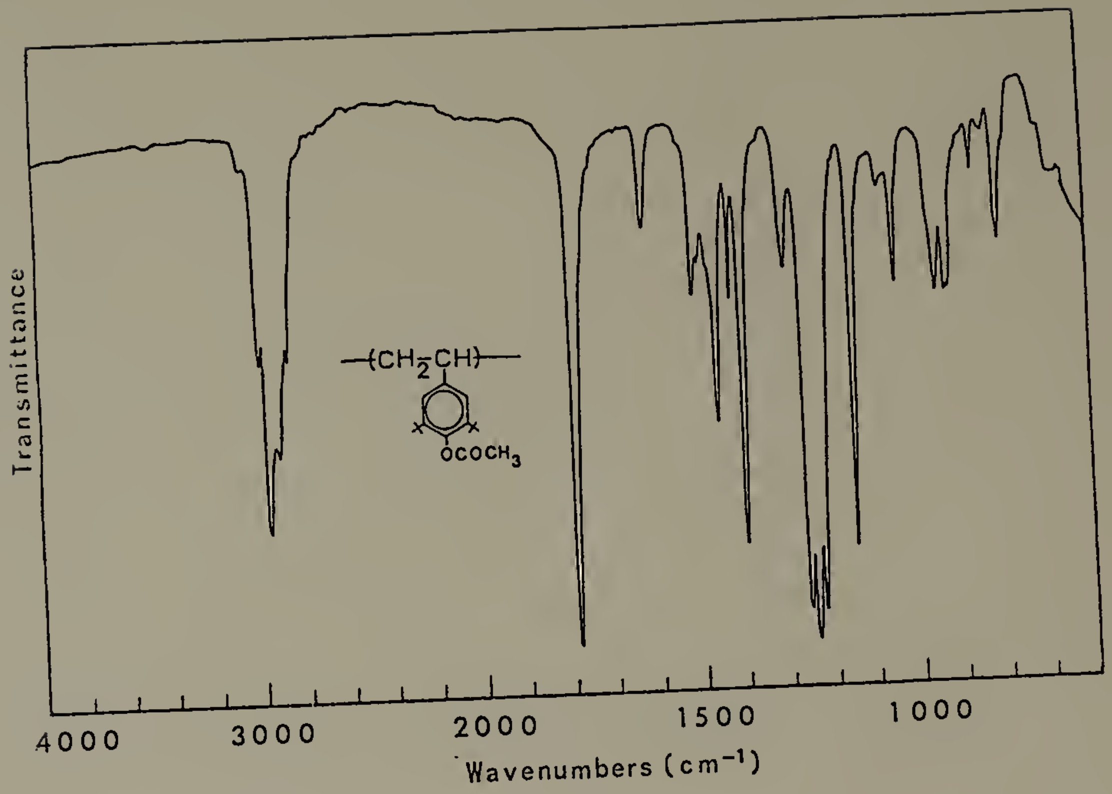
INFRARED SPECTRA

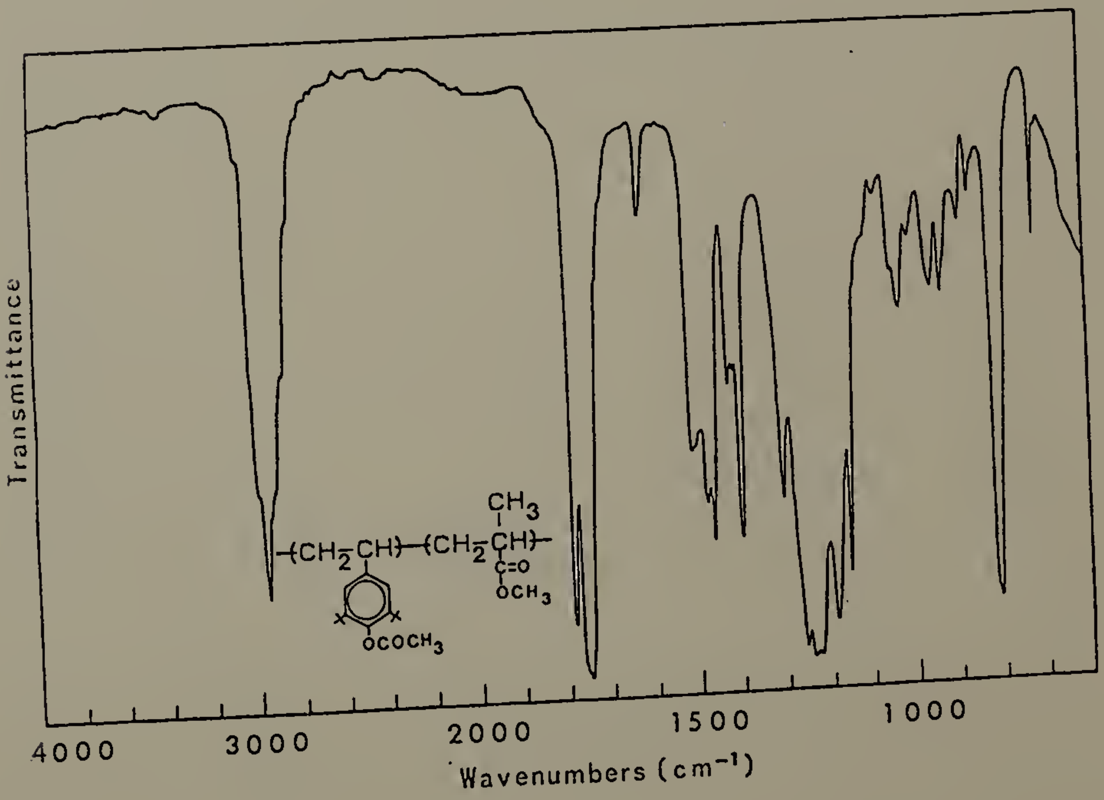

Transmittance
O
OCCH3
C=O
CH3
4000
3000
2000
1500
1000
Wavenumbers (cm-1)

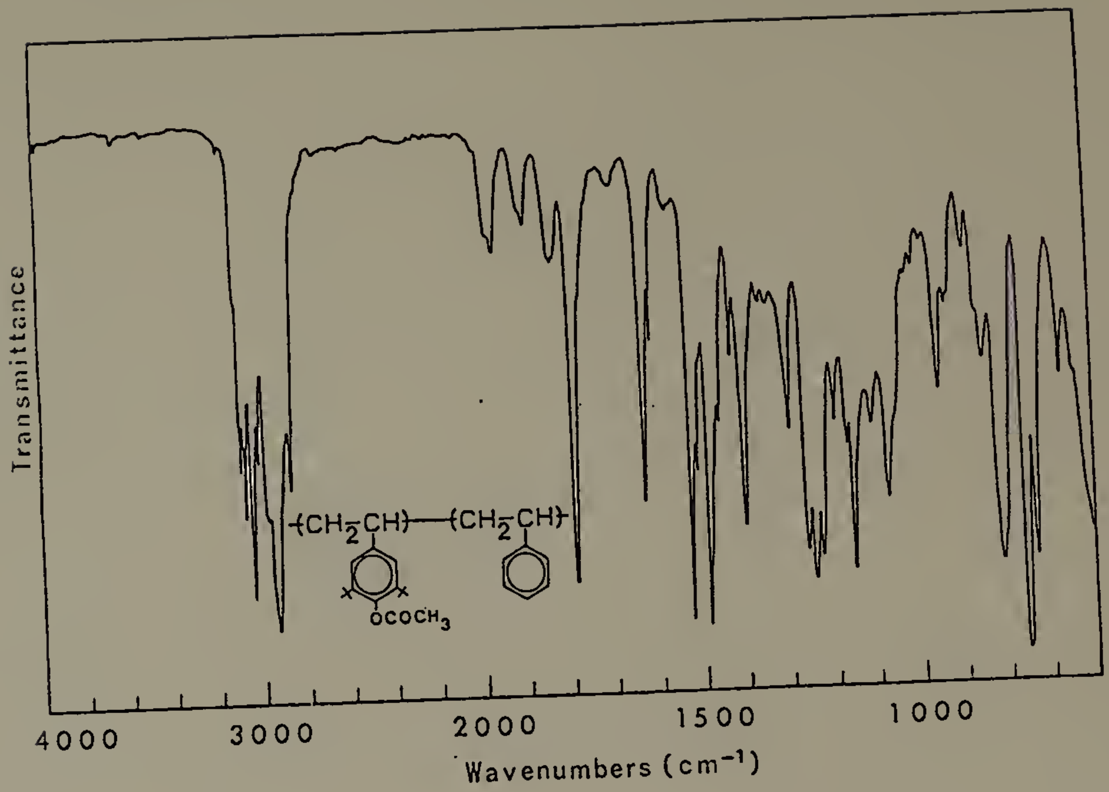

Transmittance
O
OCCH3
CHOH
CH3
4000
3000
2000
1500
1000
Wavenumbers (cm-1)

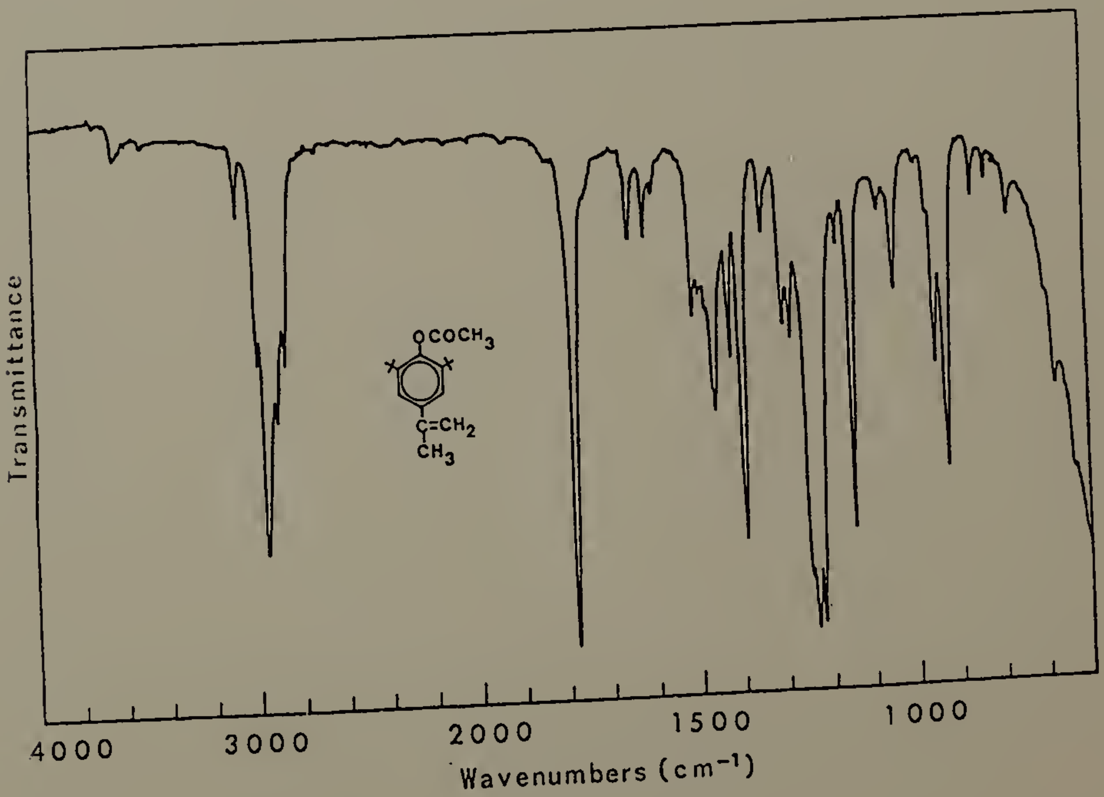

Transmittance
O
OCCH3
CH=CH2
4000
3000
2000
1500
1000
Wavenumbers (cm-1)

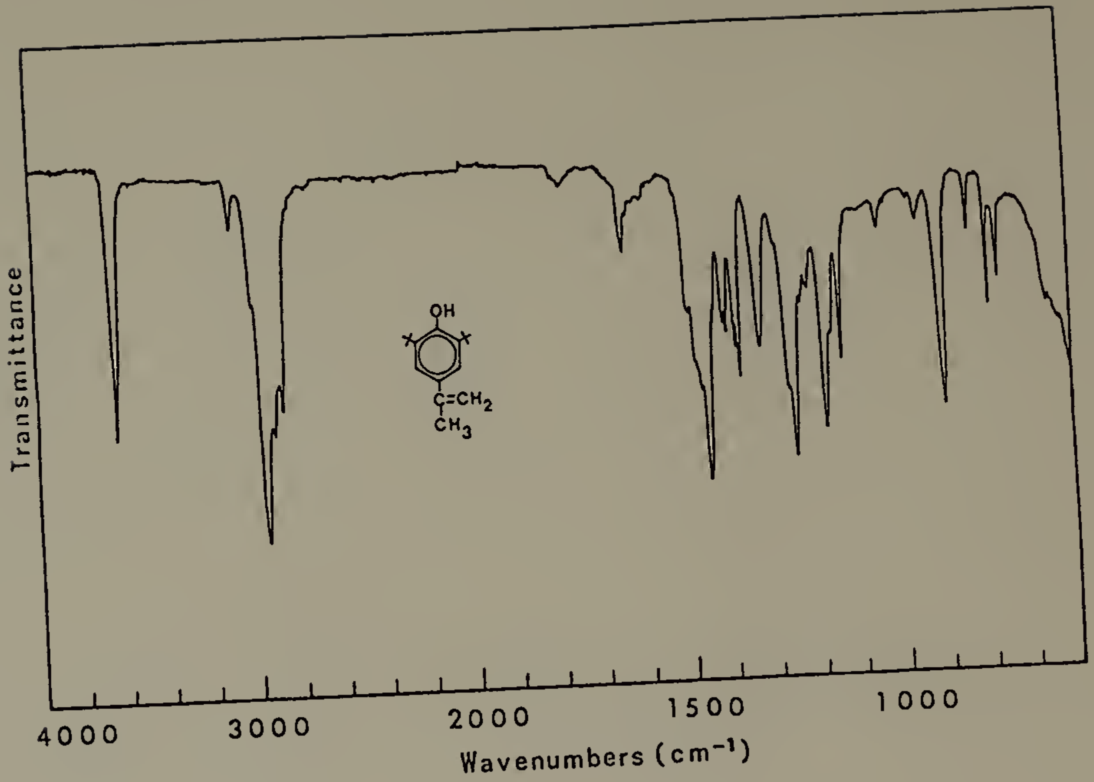

Transmittance
OH
CH=CH2
4000
3000
2000
1500
1000
Wavenumbers (cm-1)

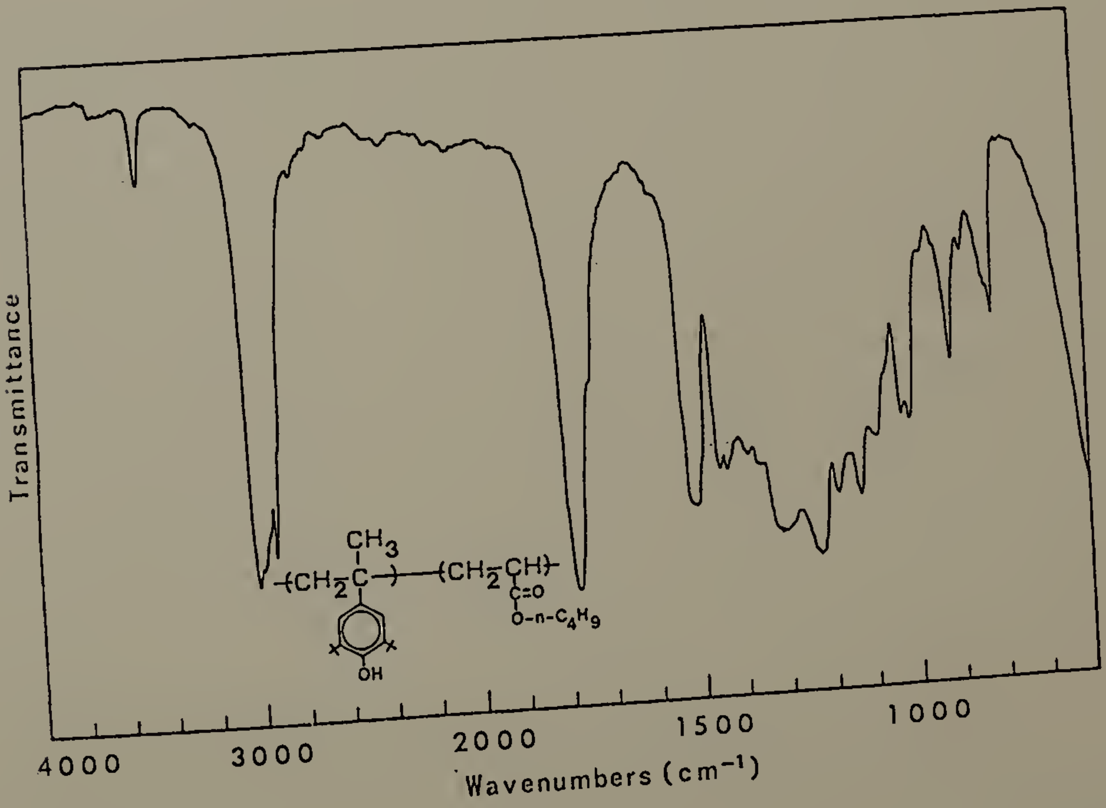

Transmittance
4000
3000
2000
1500
1000
Wavenumbers (cm^{-1})
$-(CH_2-CH)-$
x
x
$OCOCH_3$

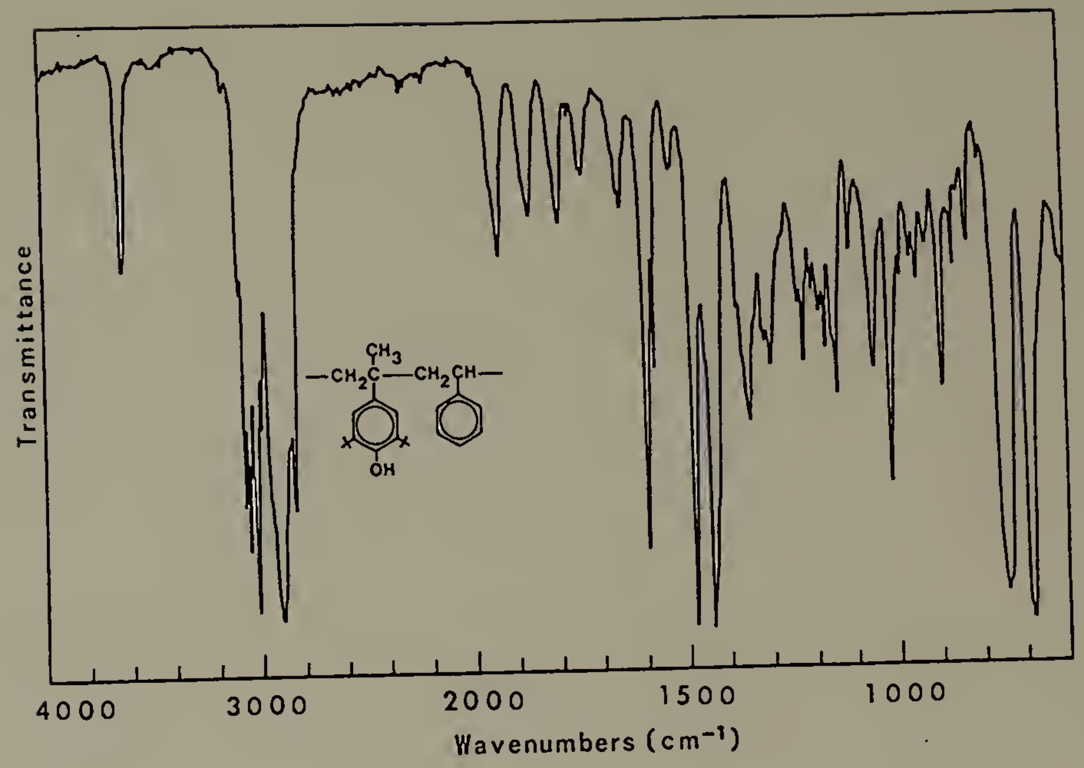

Transmittance
4000
3000
2000
1500
1000
Wavenumbers (cm^{-1})
$-(CH_2-CH)-(CH_2-CH)-$
CH_3
$C=O$
OCH_3
x
x
$OCOCH_3$

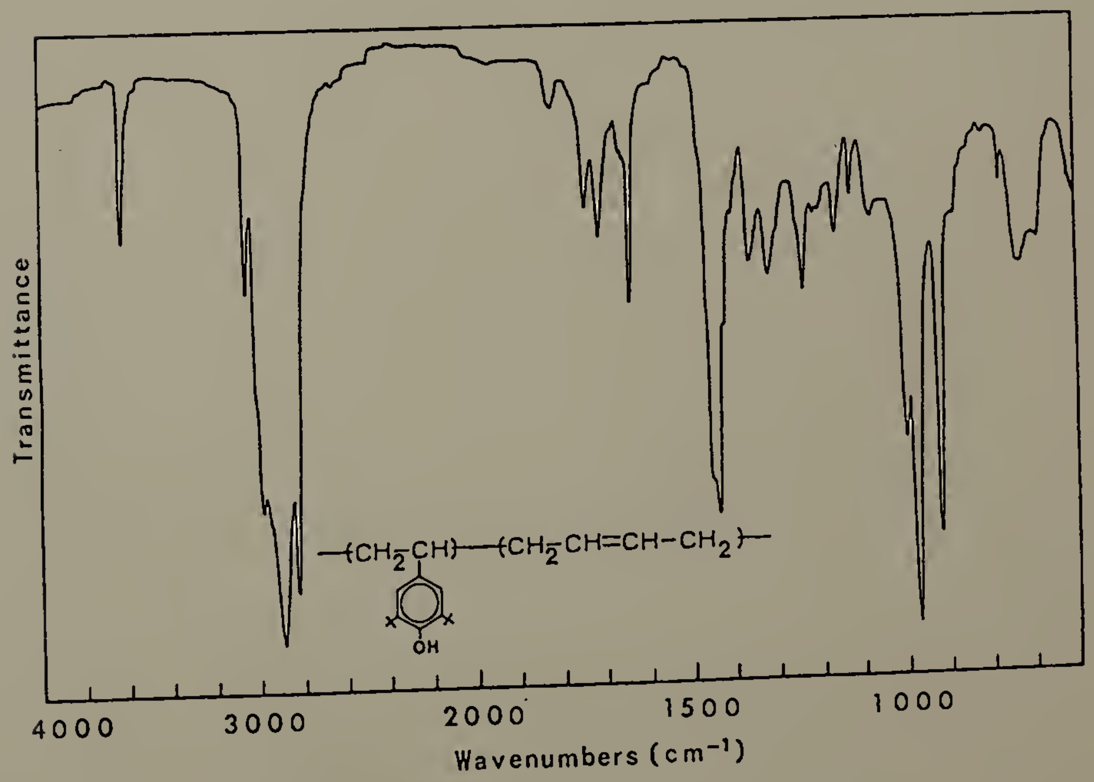

Transmittance
4000
3000
2000
1500
1000
Wavenumbers (cm⁻¹)
OCOCH3

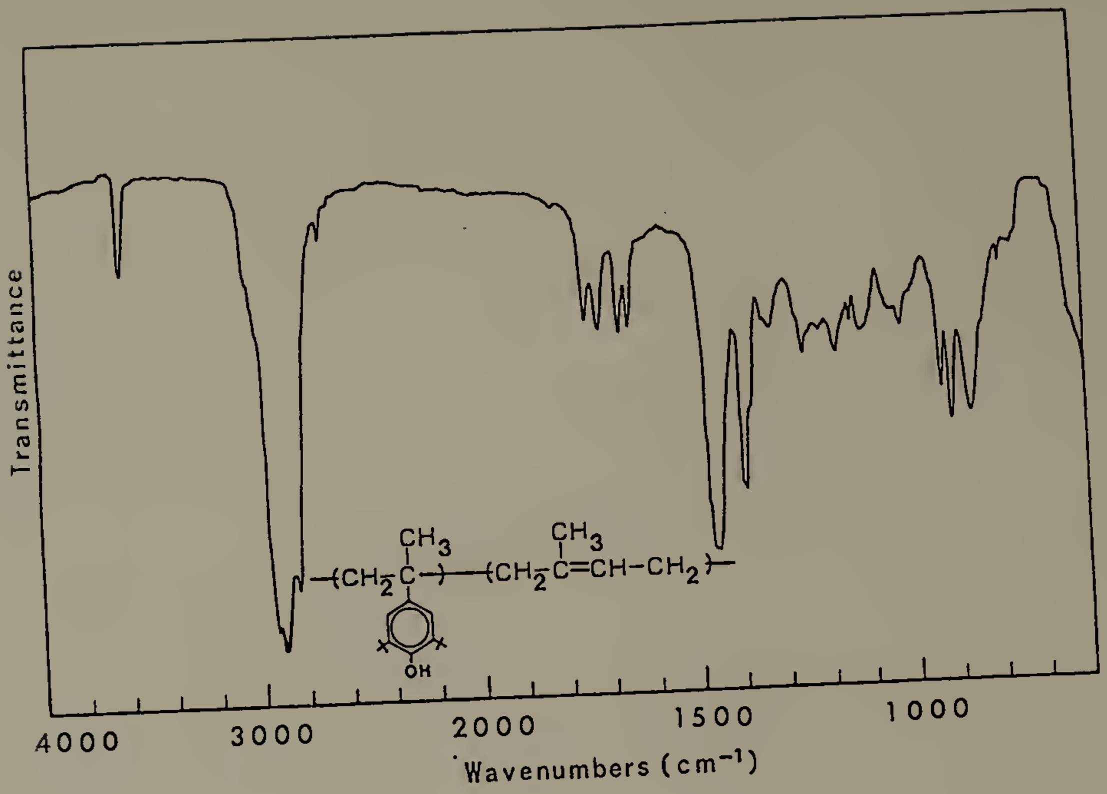

Transmittance
4000
3000
2000
1500
1000
Wavenumbers (cm⁻¹)
OCOCH3
C=CH2
CH3

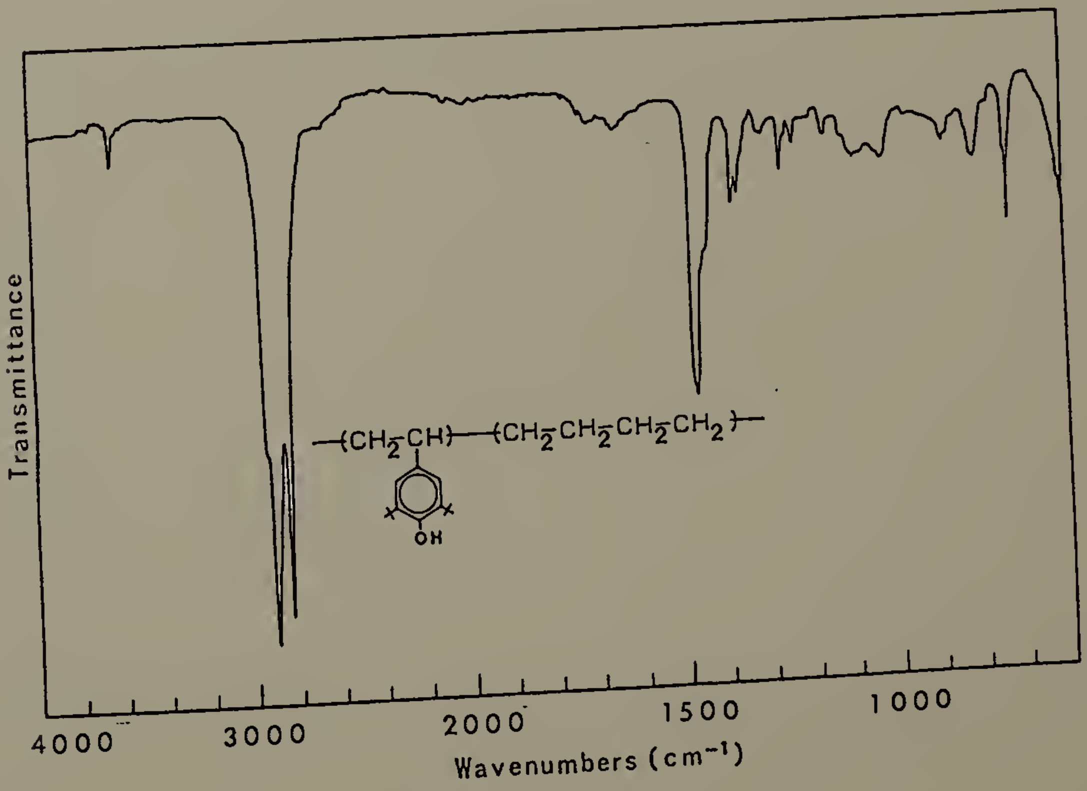

Transmittance
OH
C=CH2
CH3
4000
3000
2000
1500
1000
Wavenumbers (cm-1)

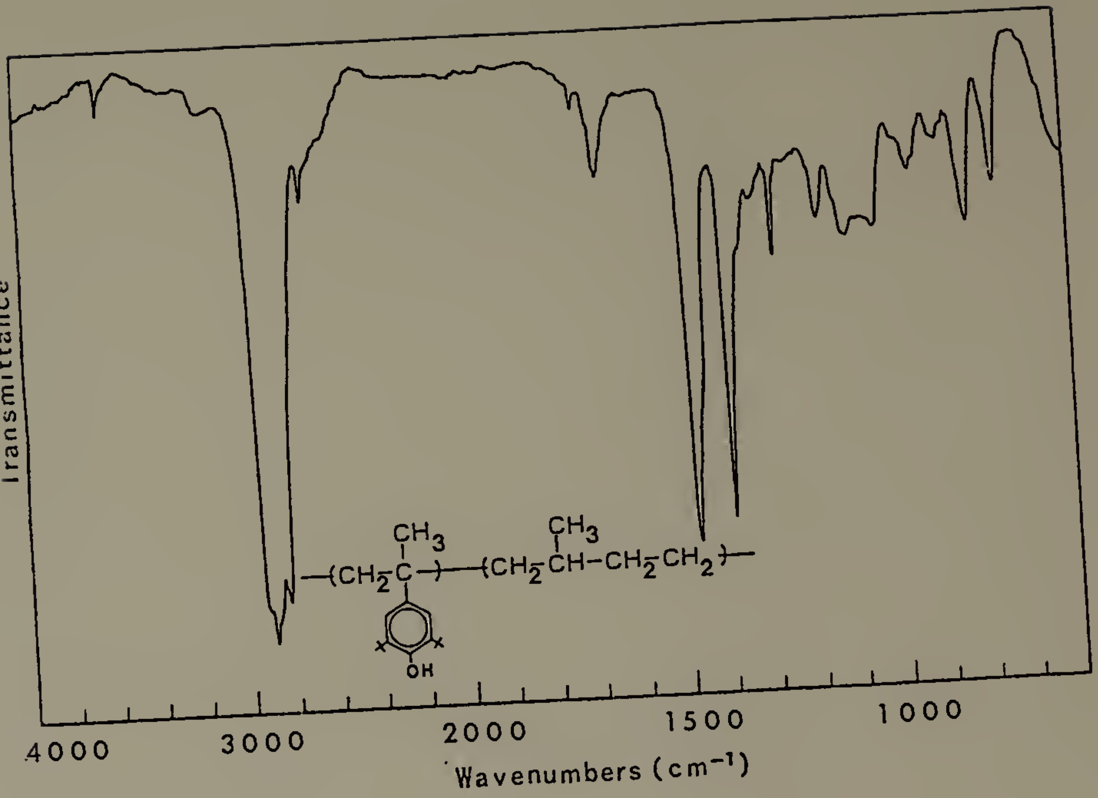

Transmittance
CH3
(CH2-C)
OH
(CH2-CH)
C=O
O-n-C4H9
4000
3000
2000
1500
1000
Wavenumbers (cm-1)

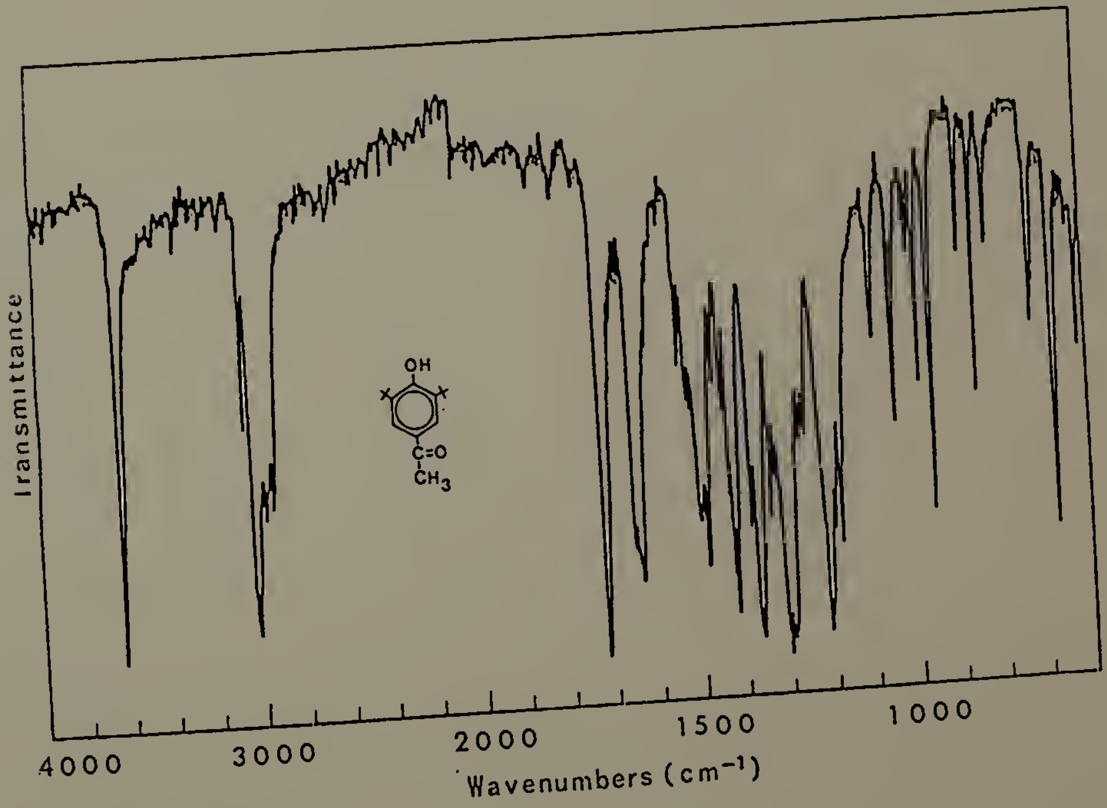

Transmittance
4000
3000
2000
1500
1000
Wavenumbers (cm^{-1})
CH$_3$
—CH$_2$C—CH$_2$CH—
X
X
OH


Transmittance
4000
3000
2000
1500
1000
Wavenumbers (cm^{-1})
—(CH$_2$–CH)—(CH$_2$–CH=CH–CH$_2$)—
X
X
OH


Transmittance
CH3
CH3
—(CH2-C—)—(CH2-C=CH-CH2)—
OH
4000
3000
2000
1500
1000
Wavenumbers (cm-1)


Transmittance
—(CH2-CH)—(CH2-CH2-CH2-CH2)—
OH
4000
3000
2000
1500
1000
Wavenumbers (cm-1)


Transmittance
4000
3000
2000
1500
1000
Wavenumbers (cm⁻¹)
CH3
CH3
(CH2-C)
(CH2-CH-CH2-CH2)
OH


Transmittance
4000
3000
2000
1500
1000
Wavenumbers (cm⁻¹)
OH
C=O
CH3

APPENDIX D

RESULTS OF PRELIMINARY OXYGEN-UPTAKE EXPERIMENTS

Results from preliminary oxygen-uptake testing of samples stabilized with the polymeric antioxidants prepared by the author appear on the following pages.

The specific blends tested at 150°C are: HDPE stabilized with hydrogenated poly(2,6-di-t-butyl-4-vinylphenol-co-butadiene), Figure 14; LLDPE stabilized with hydrogenated poly(2,6-di-t-butyl-4-vinylphenol-co-butadiene), Figure 15; cis-polyisoprene stabilized with poly(2,6-di-t-butyl-4-isopropenylphenol-co-isoprene), Figure 16; and random cis, trans-polybutadiene stabilized with poly(2,6-di-t-butyl-4-vinylphenol-co-butadiene), Figure 17. All blends contained 0.1 weight % phenolic monomer unit. Unstabilized controls and samples with 0.1 weight % monomeric stabilizer are also plotted. For details of the preparation of the blends, see p. 84.

The polymeric antioxidants appear to be very weak stabilizers, and the unusual lineshapes of the data for the stabilized samples may be a result of this. The scatter in some of the graphs is due to inadequate control of temperature, with as much as ±5°C variation. This affected the internal pressure of the apparatus. It must be emphasized that these are preliminary data, and that refinements should be made to the apparatus if the thermo-oxidative stability of these blends is investigated more fully in the future.

Figure 14. Oxygen-uptake curves for unstabilized and stabilized HDPE.

Figure 14. Oxygen-uptake curves for unstabilized and stabilized HDPE.

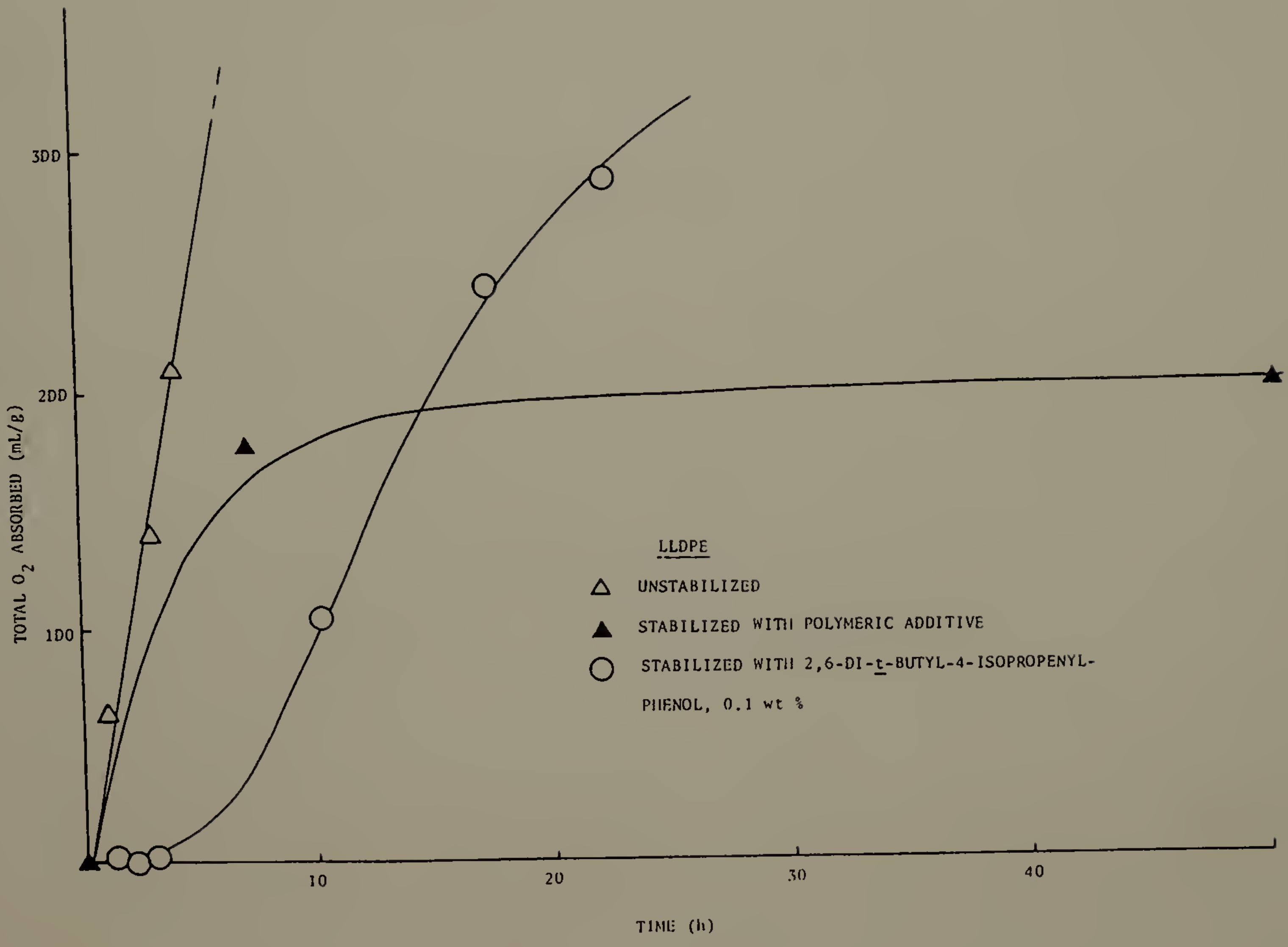

TOTAL O_2 ABSORBED (mL/g)
300
200
100
10
20
30
40
TIME (h)
LLDPE
△ UNSTABILIZED
▲ STABILIZED WITH POLYMERIC ADDITIVE
○ STABILIZED WITH 2,6-DI-t-BUTYL-4-ISOPROPENYLPHENOL, 0.1 wt %

Figure 15. Oxygen-uptake curves for unstabilized and stabilized LLDPE.

Figure 16. Oxygen-uptake curves for unstabilized and stabilized *cis*-polyisoprene.

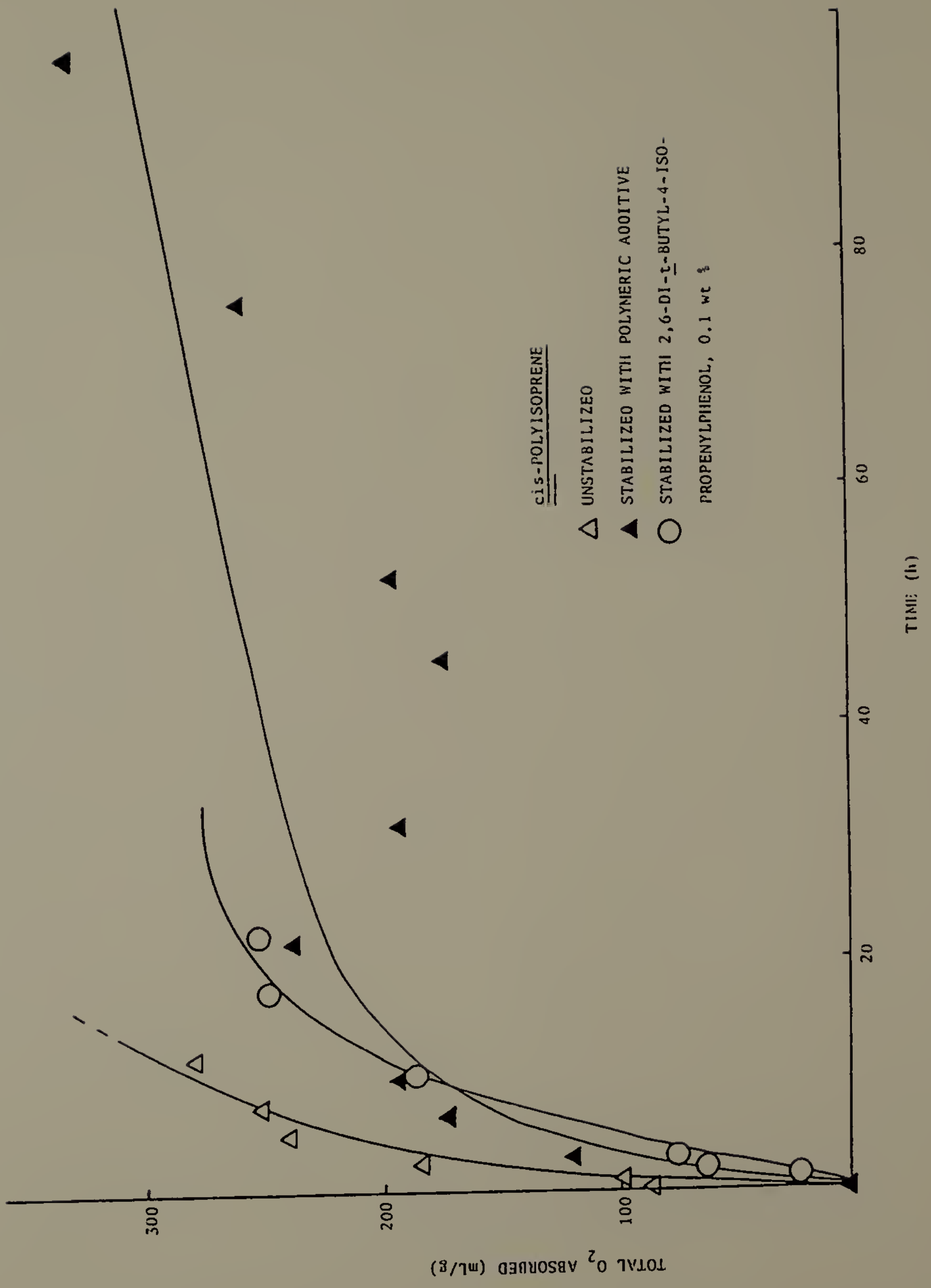
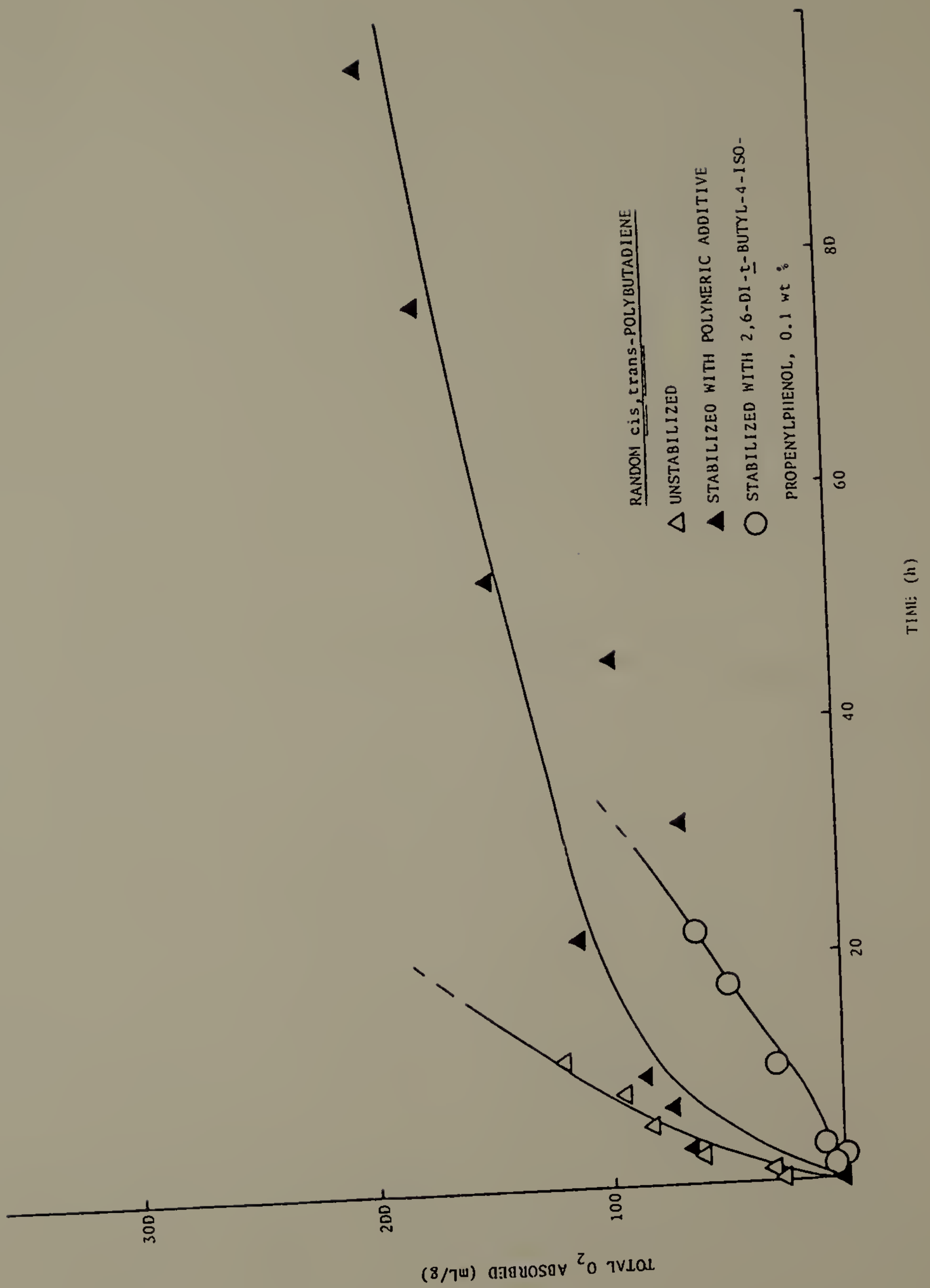

cis-POLYISOPRENE
△ UNSTABILIZED
▲ STABILIZED WITH POLYMERIC ADDITIVE
○ STABILIZED WITH 2,6-DI-t-BUTYL-4-ISOPROPENYLPHENOL, 0.1 wt %
TOTAL O_2 ABSORBED (mL/g)
100
200
300
TIME (h)
20
40
60
80

Figure 17. Oxygen-uptake curves for unstabilized and stabilized random *cis*, *trans*-polybutadiene.


RANDOM cis,trans-POLYBUTADIENE
△ UNSTABILIZED
▲ STABILIZED WITH POLYMERIC ADDITIVE
○ STABILIZED WITH 2,6-DI-t-BUTYL-4-ISO-PROPENYLPHENOL, 0.1 wt %
TOTAL O2 ABSORBED (mL/g)
300
200
100
TIME (h)
20
40
60
80