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## INHIBITION OF VINYL POLYMERIZATION

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## BY LIGNINS

## BY

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## ABSTRACT

The mechanism of inhibition and retardation, caused by lignins, on the polymerization of methyl methacrylate (MMA) in vacuum and in presence of air was investigated. Polymerizations of MMA were carried out with the use of azobisisobutyronitrile (AIBN) as the initiator at 50°C. The effect of lignin origin was studied by means of appropriately substituted phenols, used as lignin model compounds (LMC).

When polymerizations were conducted in vacuum, neither an inhibition period (IP) nor a retardation was noted with low LMC concentration  $(10^{-3}-10^{-2} \text{ M})$  and 5 mg/ml of AIBN. However, under these conditions, large IP occurred in presence of air. At higher LMC concentrations (0.1-2 M), inhibition and retardation became evident also in vacuum. The length of the IP varied according to the 0.6 power of phenol concentration in vacuum, and to the 0.4 power of phenol concentration in presence of air.

If was found that inhibition and retardation resulted from transfer reactions of poly(MMA) radicals with LMC. In order to study the effects of nuclear substituents on these reactions, chain transfer constants for a series of LMC were determined. They were found to increase in the following order:  $4-\underline{n}-propylphenol$  (3.2 x  $10^{-4}$ ),  $4-\underline{n}-propylguaiacol$  (8.3 x  $10^{-4}$ ), and  $4-\underline{n}-propylsingol$  (54.6 x  $10^{-4}$ ). The transfer reactions were shown to be governed chiefly by the resonance stabilization of the phenoxy radicals formed.

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In presence of air, however, the influence of nuclear substituents is determined by their polar character. Indeed, the substituent effects on transfer reaction rates were best analyzed on the basis of the following Hammett equation:  $log[(IP_{substituted phenol})/(IP_{phenol})] = \rho\sigma$ , where ( $\sigma$ ) represents the Hammett polar substituent constant, and ( $\rho$ ) is a reaction constant. A value of -0.83 was obtained for the constant  $\rho$ , indicating that electronegative radicals, such as peroxypoly(MMA) radicals, are actually reacting with LMC.

These results were qualitatively confirmed by experiments with coniferous and pored wood kraft lignins.

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## LIST OF SYMBOLS

Concentration of polymer, g/100 ml
Chain transfer constant
Monomer polarity factor
Fraction of initiator initiating polymerization
Initiator
Lignin
Monomer
Polymer
Polymer molecule with n monomer units
Polymer radical independent of chain length
Polymer radical with n monomer units
Average degree of polymerization
Monomer stabilization factor
Rate of the reaction involved
Organic molecule
Organic radical
Transfer agent or stabilizer molecule
Transfer agent or stabilizer radical
Inhibitor
Viscosity
Average kinetic chain length
Reaction constant in the Hammett equation
Hammett polar substituent constant

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### **1.0** INTRODUCTION

Lignin is the second most important chemical constituent of wood, and represents as much as 30% of the total mass of coniferous plants and 25% of pored wood plants. However, due to its deleterious effect on paper, it is considered by the pulp and paper industry to be a contaminant of cellulose. Thus its separation and disposal as a waste product is necessary. With the ever increasing emphasis on environmental ecology demanding non-polluting disposal of industrial wastes, it is critical to find as many useful applications of lignin as possible.

Despite several decades of intensive applied research into the properties of lignins, uses have been found for only a small portion of the millions of tons that are produced annually. One commercial use of lignin is as raw material in the preparation of low molecular weight chemicals such as vanillin and dimethyl sulfoxide (41). In obtaining these compounds advantage can be taken of the highly organized structure of the lignin molecule. However, the prohibitive costs of separating such chemicals limits the production to only a few simple products.

Lignin is also used as a polymeric material in which utilization is based on its physical properties (49). Thus, lignin is utilized as oil well drilling mud, cement and concrete additive, dispersant, emulsifier, and stabilizer, binder and adhesive, rubber additive, and sequestering agent.

Modification of lignin physical and chemical properties might increase its commercial utilization. One way to achieve this goal would be by grafting vinyl polymers onto the lignin backbone structure. It would thus be possible to obtain lignin copolymers having properties which fall between those of lignin and the grafting partner. These new properties could perhaps be tailored for a predetermined purpose. For example, semi-conductive properties of such products have been reported (64,96).

However, it has also been noted that such graft polymerization may be inhibited and retarded during grafting onto lignin and lignified materials (58,65,89,103). This inhibiting effect has been found to vary according to the conditions of the grafting medium, the type of lignin present, and the monomer used. Koshijima and Muraki (63) proposed that gamma-irradiation grafting of styrene proceeds first through the addition of poly(styrene) radicals to the lignin aromatic nuclei, and in latter stages branches propagate from the aliphatic part of the lignin, where C-H bond scission had been caused by irradiation. They explained the retardation of grafting onto birch lignin by the fact that the 5-position of the syringyl groups were not available for reaction. Recently, during a quite advanced stage of this work, Phillips <u>et al</u>.(89,90) emphasized the chain transfer reactions of poly(styrene) radicals with lignin.

The main objective of the present study is to advance understanding of the inhibition mechanism(s) of methyl methacrylate (MMA) polymerization by lignins originating from different woods. In order to dissociate

the influence of these wood origins, investigations were done with a series of appropriately substituted phenols used as lignin model compounds (LMC).

It is proposed to evaluate the chain transfer reactions of poly(MMA) radicals with LMC, in vacuum and in the presence of oxygen, and to relate the results to the inhibitions and retardations observed. It is expected that findings will relate well with actual experiments with coniferous and pored wood kraft lignins.

## 2.0 LITERATURE REVIEW

#### 2.1 Free Radical Reactions

Free radicals may be defined as chemical species having one or more unpaired electrons. Free radicals may be produced by: (i) cleavage of covalent bonds; or (ii) reduction-oxidation reactions. Covalent bonds may be broken by thermal, photochemical, or mechanical processes.

The kinds of reactions in which free radicals participate are quite limited. They can be classified either as radical-propagating reactions, or radical-destroying reactions. In radical-propagating reactions, free radicals react in either a bimolecular way with a substrate molecule or in an unimolecular process producing other free radicals [2-1],

 $C1' + RH \longrightarrow RC1 + H' \dots [2-1].$ 

Radical-destroying reactions are bimolecular reactions of two free radicals yielding products that are not free radicals [2-2],

 $2C1' \longrightarrow C1_2 \dots [2-2],$ 

or disproportionation [2-3],

 $2CH_3CH_2$   $\longrightarrow$   $CH_2=CH_2$  +  $CH_3CH_3$  ..... [2-3].

Appreciation of the factors that affect free radical reactions requires understanding of their resonance, polar, and steric characters.

## 2.1.1 Resonance effect

Ease of radical formation correlates with the bond dissociation energy of the chemical bonds broken in order to form the free radical. The more easily a radical is formed, the more stable it will be (108). Therefore, the ease of formation of free radicals follows the sequence: benzyl >  $3^\circ$  >  $2^\circ$  >  $1^\circ$  >  $CH_3^\circ$  > vinyl. For example, benzyl, styryl or phenoxy radicals are stabilized by resonance because of the possibility of delocalizing an electron in the benzene ring.

Resonance considerations show that radical stability governs the reactivity and the selectivity in many reactions where radicals are formed (95). There is an inverse relationship between selectivity and reactivity of a radical. Thus, very stable phenoxy radicals react preferentially by combination with another phenoxy radical, instead of reinitiating polymerization by reacting with a vinyl monomer, when phenols are used in a retarded polymerization system.

## 2.1.2 Polar effect

Although free radicals are neutral, they have certain tendencies to gain or lose electrons and hence they have the character of electrophilic or nucleophilic reagents (52,95). As a result, a concept of a donor-acceptor polar effect occurs. This concept can be illustrated by a hypothetical, free radical, chain-propagating, displacement reaction between a radical R' and a substrate WY yielding RW and Y' [2-4],

$$R^{*} + WY \longrightarrow [R - - W - - Y] \longrightarrow RW + Y^{*} \dots [2-4].$$

In this reaction there is a transition state in which simultaneous bondmaking between R' and W, and some bond-breaking between W and Y' occur. As seen previously the resonance stabilization of radicals R' and Y' plays an important role in determining the energy of the transition state of this reaction. But this energy could be lowered by allowing a partial separation of charges to appear in the transition state of the reaction [2-4]. The reaction of R' and WY could then involve a transition state in which R' assumes some positive character and X' has a negative character [2-5],

 $R^{\bullet} + WY \longrightarrow [R^{---W^{---}Y}] \longrightarrow RW + Y^{\bullet} \dots [2-5].$ 

Free radicals are called donor radicals when assuming positive character (108). Thus styrene radicals have a tendency to be donor radicals, whereas MMA radicals act as acceptor radicals. A criterion for applying the donor-acceptor polar principle is that there must be a substrate having opposite tendency to that of the free radical.

## 2.1.3 Steric effect

Importance of the steric effect in radical reactions is indicated by the fact that terminal olefins usually react faster and give better product yields than do internal olefins (52). Monomers which possess substituents on both carbon atoms of the carbon-carbon double bond exhibit reluctance in adding to themselves in the growing chain, although they may add to other free radicals quite readily. For example, maleic anhydride reacts with styrene free radicals about twenty times as fast as does styrene, although maleic anhydride will not add to the maleic anhydride radical at all. Another classical example of steric hindrance is the effect of butyl groups on both <u>ortho</u> positions of phenol giving rise to a reduction in the reaction rate with 2,2'-diphenyl-l-picrylhydrazyl (46).

## 2.2 Vinyl Polymerization

Catalyzed vinyl addition polymerization can be initiated by any of three, distinguishable catalyst types: (i) free radical; (ii) cationic; and (iii) anionic (66,85). Generally, monomers with strong electron releasing substituents, which impart a negative polarity to the double bond, respond readily to cationic catalysts; whereas, monomers bearing strongly electron-attracting groups substituted into the vinyl group polymerize with anionic catalysts. Most of the monomers polymerized best by the free radical catalysts have polarities between these two extremes.

Among the various types of polymerization reactions, free radical polymerization of vinyl compounds has received by far the most attention and its mechanism is best understood. The relative simplicity and easy control of free radical polymerization probably account for its early advancement over ionic polymerization. The reactivity characteristics of an olefinic monomer in free radical polymerization can be ascribed usually to the three factors discussed in the preceding section, i.e., resonance, polar, and steric effects, as governed by the nature of the substituents at the carbon-carbon double bond. As in simple organic reactions, these effects influence the transition state for reaction of a monomer molecule in adding to the radical, or in abstracting an atom from the other molecule. If the incoming molecule has a highly resonating functional group capable of conjugating with its double bond, as with styrene, its addition to a radical to form a new radical would be greatly facilitated (76). Conversely, a monomer with a highly electron withdrawing group subsituted at the double bond would have a local positive polarity, thus addition of this species to a radical of the same high positive polarity would be difficult. On the other hand, the addition of this monomer to a radical of negative polarity, such as a styrene radical, would be facilitated. If both the radical and the incoming molecule to be attacked carry a large number of bulky substituents at carbon-carbon double bonds, especially with 1,2-substituted compounds such as maleic anhydride, the approach of one to the other is hindered (1).

## 2.2.1 Q-e scheme

The first two factors of monomer activity have been expressed quantitatively in terms of a free radical stabilization factor (Q) and a polarity factor (e) by Alfrey and coworkers (2,93).

From the results of a large number of vinyl monomer studies, the radical stabilization factor Q has been found to relate directly to the reactivity of the monomer. Values of Q increase when substituents on the monomer vinyl group change through the series -OR,  $-OCOCH_3$ , -COOR, -CN,  $-COCH_3$ , and  $-C_6H_5$  (76). The polarity factor <u>e</u> becomes more negative when the substituent changes from -CN,  $-COCH_3$ , -COOR,  $-C_6H_5$  to -OR (93). It is obvious that the order of product radical stabilization can be correlated with the resonance ability offered by the particular substituent. Further, the order of polarity change can be attributed to the power of these functional groups in donating or withdrawing electrons to or from double bonds.

Table 2.1 gives Q and <u>e</u> values for some common monomers. Styrene was taken as a standard and values of Q = 1.0 and <u>e</u> = -0.8 were assigned to it arbitrarily (94). The value of <u>e</u> may be either positive or negative for a given monomer, while the Q value for any monomer is always positive.

2.2.2 Mechanism of free radical vinyl polymerization

Mechanisms of free radical polymerization have been exhaustively studied, and good reviews are found in texts prepared by Flory (35) and later Chapiro (26) among others.

Factors of particular interest are: (i) the basic chemical mechanism involved; and (ii) the stationary state kinetics.

2.2.2.1 Free radical mechanism

Free radical induced vinyl polymerizations are generally accepted as proceeding by a chain mechanism. Chemical steps of initiation, propagation, and termination are thus involved (35,108).

The three basic reactions of radical induced polymerization may be represented by:

Initiation	Rate Law	
$I_2 \longrightarrow 2I^{\cdot}$	$R_d = 2k_d f[I] \dots$	[2-6]
$I^{\bullet} + M \longrightarrow IM^{\bullet}$	$R_{i} = k_{i}[I'][M]$	[2-7]
Propagation	· .	
$IM' + M \longrightarrow P_2'$		
$P_n^{\bullet} + M \longrightarrow P_{n+1}^{\bullet}$	$R_{p} = k_{p}[P'][M] \dots$	[2-8]

Termination

$$P_{n}^{*} + P_{m}^{*} \longrightarrow P_{n+m} \qquad R_{tc} = 2k_{tc}[P^{*}]^{2} \dots \qquad [2-9]$$

$$P_{n}^{*} + P_{m}^{*} \longrightarrow P_{n} + P_{m} \qquad R_{td} = 2k_{td}[P^{*}]^{2} \dots \qquad [2-10]$$

In general

m

$$P_{n}^{*} + P_{m}^{*} \longrightarrow P \qquad R_{t} = 2k_{t} [P^{*}]^{2} \dots [2-11],$$

(I) represents the initiator; (I') the primary radical; Where: (f) the fraction of initiator that initiates polymerization; (M) the monomer; (P') in the rate law expressions, a polymer radical independent of chain length; and  $(P_n^{*})$  a polymeric radical with (n) monomer units in the chain. There are two termination reactions but both are governed by the same kinetic laws, whereby, a generalized equation can be written. Also, the simplifying assumption is made that the rate constant is independent of the chain length of the polymeric radical taking part in the reaction. This has been implied in Equations [2-8] and [2-11].

## 2.2.2.2 Stationary state equations

In deriving expressions for the overall polymerization rate, the usual steady state assumption is made in regard to the free radical concentration. Therefore, the rate of radical formation equals the rate of radical destruction as [2-12],

$$2k_{d} f[I] = 2k_{t} [P']^{2}$$

$$[P'] = ((k_{d} f[I])/k_{t})^{1/2} \dots [2-12].$$

By neglecting the monomer units consumed in the initiation [2-7] the rate of monomer disappearance in a polymerization system is given according to [2-13],

$$-d[M]/dt = R_{p} = k_{p}[P^{*}][M]$$
 ..... [2-13].

Combining equations [2-12] and [2-13] and considering a steady state for the initiator radical (I'), one obtains an expression for the propagation rate such as [2-14],

$$R_{p} = \frac{k_{p}}{(2k_{t})^{1/2}} [M] (R_{1})^{1/2} \dots [2-14].$$

This equation has been shown to fit results of many experiments, thereby validating the assumptions made above (6).

The ratio between propagation and termination rate constants  $k_p/(2k_t)^{1/2}$  represents monomer polymerizability; large values indicate that a given amount of initiator will produce more polymer in a given time.

Another parameter often used in polymer chemistry is the average kinetic chain length (v). It is defined as the average number of monomers reacting with an active center from its initiation to its termination (35). It can be expressed as the ratio of the rate of

propagation to the rate of initiation ( $\nu = R_p/R_1$ ). Under the steady state assumption, the rate of initiation is equal to the rate of termination. Thus, the average kinetic chain length can be expressed as  $R_p/R_t$ .

2.2.3 Chain transfer reactions

The term chain transfer was introduced by Flory (34) in 1937. The chain transfer reaction was proposed to explain the fact that products from solution polymerizations had lower molecular weights than those from bulk polymerizations.

If the previous reactions are expanded to include transfer to a transfer agent (SH), the following may be added:

$$P_{n}^{*} + SH \longrightarrow P_{n} + S^{*} \qquad R_{tr} = k_{tr}[P^{*}][SH] \dots \qquad [2-15]$$

$$S^{*} + M \longrightarrow SM^{*} \qquad R_{a} = k_{a}[S^{*}][M] \dots \qquad [2-16].$$

Where (S') represents a radical derived by the abstraction of a hydrogen atom from the transfer agent to participate in the propagation reaction in such a way that the overall kinetics are not affected. The degree of polymerization will, however, depend on chain transfer.

If Reaction [2-16] is not competitive with the propagation Reaction [2-8], a decrease in the rate of polymerization will result. Parameters

identified as influencing reactions of free radicals (Section 2.1) will be of importance in determining the rates of Reactions [2-15] and [2-16].

The ratio of the specific rate constants  $k_{tr}/k_p$  is called the chain transfer constant (C<sub>t</sub>).

2.3 Retarded and Inhibited Vinyl Polymerization

The distinction between retarded and inhibited polymerization reactions is primarily one of degree (6). Both effects are caused by the presence of small quantities of substances which react with polymer radicals to yield products of reduced reactivity, thus causing a diminution of the polymerization rate. Substances which may prevent chain growth are often classified on the basis of their effectiveness in so doing. Inhibitors effectively stop the growth of all chains until the inhibition agent is consumed. Retarders, which are less effective than inhibitors, merely slow rather than stop the polymerization process.

The apparent differences between the two classes, and their effect upon the thermal polymerization of styrene are shown in Fig. 2.1. This was abstracted from the original work of Schulz (101) by Walling (108). Curve I represents the thermally initiated polymerization of pure styrene at 100°C. In the presence of 0.1% benzoquinone, a typical inhibitor (Curve II), an inhibition period was followed by polymerization at essentially the same rate as for pure stryene. No inhibition

period is observed in the presence of 0.5% nitrobenzene (Curve III), which is a good example of a retarder. Instead, the reaction rate is reduced to approximately one third its normal rate throughout the entire period of measurement. Nitrosobenzene (Curve IV) is an inhibitor. However, after the inhibition period, the polymerization is still slower than normal. Apparently, reaction products of the initial inhibition reaction act as retarders.

As noted earlier, however, it should be emphasized that differences between inhibitors and retarders are of degree rather than mechanism. For example, a large quantity of retarder may completely stop a polymerization reaction. Also, more sensitive measurement techniques might detect polymerization proceeding during an apparent inhibition period.

Reactions which occur can be accounted for by the following general scheme, as identified by Flory (35):

 $Z' + M \xrightarrow{k_{zp}} P' \dots [2-18]$ 

In this particular scheme it is assumed that the retarding species (Z) combines with the polymer radical (P<sup>\*</sup>) and that copolymers may subsequently be formed. Reaction [2-17] may also proceed by chain transfer (35,66). In either case, the kinetic results are equivalent. From this scheme, it is clear that the inhibitor efficiency is dependent on the ratio of  $k_z/k_{zp}$ , as well as on the absolute value of  $k_z$ , with higher values of both leading to more efficient inhibition.

In some cases the products of Reaction [2-17] will be totally inert. For example, this will occur when the retarding species is itself a free radical, such as diphenylpicrylhydrazyl. Bamford <u>et al</u>. (7), have also reported that ferric chloride directly terminates growing polymer chains. In both of these cases, retardation occurs by linear termination of the kinetic chains, and the retardation scheme becomes simply,

2.3.1 Retardation of vinyl polymerization by phenols in vacuum

As described earlier, reactions of chain transfer compete with the addition step in vinyl polymerizations. Assuming that abstraction of hydrogen atoms does not occur elsewhere in the molecule other than on the phenolic hydroxyl, evaluation of chain transfer constants for a phenol series yields information on the relative lability of phenolic hydrogens. If the resultant phenoxy radical is less active than the growing polymer radical, then the presence of the phenolic compound will retard the polymerization reaction by reducing the number of radicals active enough to initiate a new chain. Previous studies of the retardation of vinyl polymerization by phenols have yielded a variety of results. For hydroquinone retardation, Price (93) proposed a mechanism in which a hydrogen atom was abstracted from hydroquinone, eventually yielding benzoquinone. Benzoquinone reacted further with the growing chain, and as it is a much stronger retarder than hydroquinone, its presence was expected to profoundly affect the degree of retardation. Breitenbach (21) believed that the semiquinone formed by hydrogen atom abstraction reacts differently with another growing chain.

Edwards <u>et al</u>. (32) studied a series of phenols as retarders in thermal polymerization of styrene. They clearly observed chain transfer reactions with a definite retarding effect. Caldwell and Ihrig (23), in their experiments with hydroquinone and 1,4-naphthalenediol also noted a chain transfer mechanism. They deduced from experimental results that the initial step in retardation mechanisms is not a hydrogen atom abstraction, as usually assumed; but rather formation of some undescribed addition complex. Their kinetic results did not allow a decision as to the nature of this complex. Such an addition complex had been suggested previously by Hammond <u>et al</u>. (44) to account for the kinetics of phenolic antioxidant behavior, and by Mayo (72) to account for his observations concerning chain transfer via aromatic halogen compounds.

Other results are not concordant. For example, Dolgoplosk and coworkers (29,31) found no retarding effect for hydroquinone in the polymerization of MMA or styrene, but some slight effect in the polymerization of more active monomers such as vinyl acetate.

Several studies dealing with evaluation of phenol chain transfer constants have been reported. Most of the constants obtained prior to 1965 are listed in the Polymer Handbook (20). Among the most pertinent studies are those of Russell and coworkers (9,15,16,39,40), who evaluated chain transfer constants for several phenols with poly-(styrene), poly(MMA), and poly(vinyl acetate) radicals. They also looked at polymerization retardation effects of these phenols. An important conclusion from their work is that most simple alkyl phenols do not retard the polymerization reaction effectively, at least when low transfer constant values are obtained.

The influence of polar and steric effects were also studied by these authors when investigating effects of substituents on phenols. The rate of phenolic hydrogen atom abstraction was dependent upon the substituents and their position on the phenol. Reduced abstraction rates were observed in the presence of bulky alkyl substituents in the two <u>ortho-positions of phenol (39,40)</u>. Literature (9,16,39) on the topic is summarized in Table 2.2.

In the case of styrene, phenols with transfer constants less than 0.008 do not retard the polymerization significantly. However, phenols having higher transfer constants such as 1-naphthol and 4-methoxyphenol decrease the rate and degree of polymerization to an intermediate extent, while catechol, <u>t</u>-butylcatechol, and pyrogallol act as fairly strong retarders with transfer constants approaching 1.0 (39).

As seen in Table 2.2, chain transfer constants in the polymerization of MMA are small compared with the corresponding chain transfer constants

with styrene. Results of similar experiments with vinyl acetate provide information concerning the extent to which polar factors influence the rate of hydrogen abstraction by polymer radicals. Indeed, phenols act as fairly strong retarders in vinyl acetate polymerization and, as expected, transfer constants are much higher. This is in agreement with the principle that compounds which more readily undergo chain transfer form the more stable radicals. Thus, a point would be reached where a decrease in the polymerization rate occurs because of the relatively greater importance of Reaction [2-15], and the smaller rate  $(k_{a})$  indicated in Reaction [2-16].

In a review paper on the inhibition effects of some aromatic compounds Bagdasar'ian <u>et al</u>. (4) claimed that phenolic hydrogens do not participate directly in reactions with polymer radicals. This was proven wrong subsequently by Bird and Russell (16). Indeed, they observed a large isotope effect showing that poly(vinyl acetate) radicals attack almost exclusively at the OH group.

2.3.2 Inhibition of vinyl polymerization by phenols in presence of air

It is well known that phenols in the presence of air inhibit or decrease vinyl polymerization reaction rates (19). This results from two complementary effects: (i) inhibition properties of oxygen on vinyl polymerization; and (ii) the additional phenol antioxidant properties magnify the oxygen effect.

2.3.2.1 Inhibition of vinyl polymerization by oxygen

Investigations on molecular oxygen inhibiting effects have indicated that the reaction in which the peroxidic radical is formed [2-21] is usually quite fast (13,35),

$$P' + O_2 \xrightarrow{k_z} POO' \dots [2-21]$$

and by comparison the radical regeneration reaction [2-22], is quite slow (13,26,66),

Schulz and Henrici (102), and Henrici-Olivé and Olivé (45) have studied the oxygen-inhibited polymerization of MMA and styrene. They assumed an exactly alternating copolymerization of MMA or styrene and oxygen during the inhibition period. The alternation is caused by the fact that oxygen addition on a radical chain end [2-21] occurs with a velocity constant which is much higher than that of the addition of monomer [2-23],

$$\mathbf{P}^{\bullet} + \mathbf{M} \xrightarrow{\mathbf{P}} \mathbf{P}^{\bullet} \qquad [2-23].$$

Therefore, Reactions [2-21] and [2-22] occur alternatively, while

Reaction [2-23] practically does not occur in the inhibition period because  $k_p$  is much smaller than  $k_z$ . Further, they showed that chain termination arose mainly by mutual interaction of peroxy radicals. It was also found that during the inhibition period the kinetic chain lengths were much shorter. They were seven times shorter for poly(styrene) and 66 times shorter for poly(MMA), which explains the fact that the inhibition periods with styrene were substantially shorter than with MMA.

In a more detailed study Mayo and Miller (74) found the same results. They assumed, however, that the sharp change in rate at the end of the induction period was due more to a temporary restraining effect of the cross termination between peroxy radicals and poly(MMA) radicals, than to an abrupt oxygen depletion.

2.3.2.2 Antioxidant effects of phenols

Antioxidant properties of phenols have been studied. The generally accepted mechanism which results from the efforts of many investigators is essentially as proposed by Bolland and Have (18) in 1947. It can be summarized as [2-24] to [2-27],

Initiation:	RH	-	>	Fre	e Radio	cals (R')	••••	[2-24]
	5	~						
Propagation:	<b>R</b> *	+	<sup>0</sup> 2	>	ROO	• • • • • • •		[2-25]

ROO° + RH	→ ROOH	+ R'	• • • • • • • • • • •	[2-26]
-----------	--------	------	-----------------------	--------

In the presence of a stabilizer (SH), in this case a phenol, the inhibition of the chain reaction occurs as a result of [2-28] and [2-29],

$$R' + SH \longrightarrow RH + S' \dots [2-28]$$

 $ROO' + SH \longrightarrow ROOH + S' \dots [2-29].$ 

The structure of the stabilizer (SH) was found to be of prime importance in determining whether the resultant phenoxy radical (S') would be effective in preventing additional propagation reactions or termination. As discussed earlier (Section 2.3) an inhibitor is considered as strong when Reaction [2-29] is much faster than Reaction [2-26].

Many workers (28,48,79,98) have investigated the antioxidant effects of substituted phenols in great detail and have observed that inhibition of the oxidation reaction depended markedly on phenol structure. It was recognized that antioxidant efficiencies increase as the S-H bond becomes weaker, and therefore that the stability of the resultant radical (S') increases. Electron-donating substituents always increase the inhibition power by lowering the energy of the transition state (48).

# 2.3.2.3 Inhibition of vinyl polymerization by phenols in presence of air

Two theories have been advanced to explain the role of oxygen during the inhibition period; (i) phenols act as inhibitors by formation of oxidation products which inhibit polymerization; or (ii) polymer radicals react very quickly with oxygen to form peroxy radicals, which in turn react with oxygen and thus inhibit the reaction. In the latter case, phenols play the role of antioxidants as seen in Section 2.3.2.2.

## 2.3.2.3.1 Inhibition by phenol oxidation products

It is believed that phenols are oxidized to quinonoid products that can inhibit polymerization. Breitenbach <u>et al</u>. (22) were the first to put forward the hypothesis that polymerization inhibition is related to the oxidation of hydroquinone to quinone. Walling and Briggs (109) gave the same explanation, and finally Dolgoplosk and coworkers expanded this theory in a series of papers (29,30,31). They established, from experiments with styrene and MMA (29,31), that the actual inhibitors were quinone derivatives and not the phenols themselves.

The inhibiting action can be observed in the presence of oxygen or metal salts of variable valence order, which oxidize polyphenols into the corresponding quinones (29). They proposed a cyclic process, whereby phenols are oxidized to quinones that react with polymer radicals and form hydroquinones, which in turn are oxidized back to quinones by oxygen or metal salts (29,30). The cycle is repeated, as confirmed by lengthening of the inhibition period in the presence of oxygen or metal salts, until the benzoquinone is completely consumed or the oxygen or metal salt is exhausted (30).

## 2.3.2.3.2 Phenols acting as antioxidants

The antioxidant theory for the inhibition mechanism of phenols in presence of oxygen was first proposed by Boardman and Selwood (17). They demonstrated that the rate of styrene oxidation is decreased by addition of phenolic antioxidants. They assumed that phenols act as antioxidants during the oxidation of styrene.

Caldwell and Ihrig (24) extended this hypothesis, and emphasized the role of oxygen in the inhibition process. In their study with MMA, they proposed that an oxidation chain-carrying peroxy radical reacts with a phenol to produce a new radical which then terminates another oxidation chain. Thus two kinetic chains, which normally would have used up many oxygen molecules, have been broken.

As discussed in Section 2.3.2.2, structure of the phenols involved is of prime importance because of influences on resonance, polar, and steric effects during the reaction transition state (24,80).

2.4 Grafting onto Lignin and Lignin-Containing Pulps

Research on grafting onto lignin was only initiated a few years ago, with the hope that lignin utlization, and wood and fibre properties
could be greatly improved by adding synthetic polymers to the basic materials. Due to its polyfunctional character, lignin was expected to respond in a multitude of ways to the graft copolymerization with vinyl polymers.

2.4.1 Nature of lignin

Lignin was first recognized as a chemical entity by Payen in 1838 (86) when he obtained it as a residue following reaction of wood with nitric or sulphuric acids. Subsequently it has been the subject of extensive chemical investigations. Since wood is used increasingly as a source of paper fibres, the production of lignin as a waste product also increases.

The structure of lignin is not yet completely known; as a result exact definitions are difficult. For example, Freudenberg (88) derives a definition first of all from its morphology:

> "Lignin is a substance which permeates the membranous polysaccharides and the spaces between the cells, thereby strengthening them. Its presence brings about a physiological death of the tissue. It is a functional component of wood, and it occurs in mature wood as a preformed, completed substance."

On the other hand, as lignins in native form are closely associated with other constituents in wood, it is practically impossible to isolate them without some degree of degradation. Therefore, there is a distinction between lignin in wood and lignin which has been isolated from wood.

The chemistry of lignin is very complex. Lignin is generally defined as a three-dimensional polymer primarily composed of phenylpropane units. These units are linked to one another, possibly by several different types of linkages varying in reactivities. From studies on lignin degradation products, two basic phenylpropane derivatives have been isolated from different wood sources (88,100). Coniferous wood lignins contain exclusively guaiacylpropyl units (I), whereas pored wood lignins contain both guaiacyl and syringylpropyl moieties (II).

For many years lignin chemists have been trying to determine the ways in which phenylpropane units are combined in the lignin macromolecule. In spite of the considerable efforts devoted, lignin structure has not yet been fully revealed. The combination of phenylpropane units can occur either through ether linkages and/or by carbon-to-carbon linkages (37).

In order to identify the structure of lignin, many analytical methods have been used. A most rewarding method has been the synthesis of lignin building blocks from coniferyl alcohol (III) under the influence of a phenol dehydrogenating enzyme (37). When coniferyl alcohol is dehydrogenated, it loses its phenolic hydrogen atom to form initially an aroxyl radical (IV), which is present as the mesomeric radicals (V), (VI), and (VII). Any of these radicals can couple to form several types of lignin linkages.

It has been found for spruce lignin that about 30% of the gualacylpropane units contain a free phenolic hydroxyl group, while the

remaining 70% are probably connected by phenol ether linkages (37). An ether linkage is assumed to happen very often via the phenolic hydroxyl and a carbon in the side chain of another phenylpropane unit. This allows, for example, formation of guaiacylglycerol- $\beta$ -aryl ether structures (VIII). Carbon-to-carbon linkages are formed when two benzene rings are combined through 5,5'-positions (IX). Linkage may be formed also between the side chains, thus giving an  $\alpha, \alpha'$  linkage (X), or even  $\beta,\beta'$  bond. In addition, two phenylpropane radicals can combine in such a way that an ether and a carbon-to-carbon bond are formed in the same structure thus giving a benzofuran (XI), or two phenyl propane radicals can combine with the formation of a  $\beta,\beta'$  carbon bond and two ether bonds between the  $\gamma,\alpha'$  and the  $\alpha,\gamma'$  carbon atoms, thus giving a pinoresinol (XII).

From these combinations of structures, and from independent elemental and functional group analyses, Freudenberg has proposed a constitutional structural scheme for coniferous wood lignin as shown in Fig. 2.2 (37). This hypothetical structural formula for the lignin molecule was presented with reservations, and is subject to frequent revisions as more data become available.

### 2.4.2 Definition of grafting

A graft copolymer may be defined as a high polymer, composed of at least two polymeric sections of different composition, chemically linked together. In the context of this discussion, a lignin graft





II







IX



Х









XIII

ş

copolymer (XIII), might consist of polymerized vinyl monomer (M) chemically attached to a lignin molecule (L) (10).

Graft copolymers containing lignin as the backbone molecule can be prepared by at least two grafting methods: (i) free radical formation on the polymer chain; and (ii) by potential free radical initiator.

2.4.2.1 Grafting by free radical formation on the polymer chain

There is a variety of methods for producing free radicals on existing polymer molecules. Ultraviolet and gamma-irradiation have been particularly successful (105) in this respect. Cobalt-60 gammairradiation, for instance, produces free radicals in the lignin structure to which monomers such as styrene and MMA may be grafted (59).

A vinyl monomer may also be grafted to lignin through a free radical formed by a chain transfer reaction occurring probably at the phenolic or at the benzylic hydrogen of the phenylpropane unit (89). The growing poly(vinyl) radical chain is terminated, but the free radical activity is transferred to the lignin. In this way a number of chains of reduced chain length are formed from each initiator fragment.

2.4.2.2 Grafting from a potential free radical initiator

Graft copolymerization may be initiated also by thermal or redox activation of hydroperoxidic groups obtained by oxidation of the polymer backbone (56). Another possibility for initiating free radicals on polymers containing hydroxyl groups, is by treatment with ceric ions (83). Ceric ions produce free radical sites along the existing chain backbone to which vinyl monomers may be grafted.

## 2.4.3 Grafting onto lignin

Although a lot of work has been related to grafting vinyl monomers onto wood carbohydrates (82), very little has been done on grafting to lignin. In fact, only three groups of workers have considered this problem. Koshijima and Muraki (58) started grafting vinyl monomers to pine wood hydrochloric acid lignin in 1964, and have since published a systematic series of papers on the topic (57,59,60,61,62,63,64,81). Simionescu and Anton have published a single paper (103), and lately Phillips <u>et al</u>. (89,90) extended and reinterpreted the initial results of Koshijima and Muraki.

In their first paper Koshijima and Muraki (58) described the graft copolymerization of MMA and other vinyl monomers onto both pine and birch wood hydrochloric acid lignins under varying gamma-irradiation doses. Grafting rates with MMA were increased by protecting free phenolic groups with acetyl or methyl groups. Because completely methylated or acetylated lignins resisted copolymerization, these investigators concluded that aliphatic hydroxyl groups played an important role in lignin grafting. Some of their results are shown in Fig. 2.3 and 2.4. The same effects were found by Simionescu and Anton (103) in their

studies of grafting acrylonitrile onto reed lignin. No copolymerization took place when the lignin was completely acetylated.

Recently, Phillips <u>et al</u>. (89) gave a reasonable explanation for lack of grafting on completely acetylated or methylated lignin. They assumed that in methylated or acetylated lignins, the formation of benzylic radical is favored over the formation of phenoxy radical. However, the benzylic radical becomes sterically hindered by methylation or acetylation of the hydroxyl group on the  $\alpha$ -carbon, thus reducing the reinitiation reaction in the transfer process. In addition, total lignin methylation or acetylation decreases lignin accessibility to MMA because of the decrease of lignin polarity.

In the case of unmethylated lignin, Phillips <u>et al</u>. assumed that grafting occurred mostly by reinitiation of the phenoxy radical. The latter could result either from irradiation effects on lignin or by a chain transfer reaction. Therefore, the mechanism of grafting is independent of the initiation process for the polymerization, i.e., irradiation or chemical initiator.

Koshijima and Muraki (60) studied solvent effects on the radiationinduced graft copolymerization of styrene onto lignin. Pine wood lignin was methylated with diazomethane and then copolymerized with styrene in the presence of methanol, ethanol, 2-propanol, 1-butanol, <u>n</u>-hexane, and benzene to a 1:10 lignin:styrene system. Methanol markedly accelerated grafting, but benzene did not. Two percent methanol, based on styrene monomer, gave a maximum grafting ratio of 430% which decreased rapidly with increased methanol concentration. With

hexane and benzene, more styrene was converted to poly(styrene) than was grafted onto lignin. With 2% methanol, 40% copolymerized with lignin and only 17% became poly(styrene). They explained this grafting enhancement by low methanol concentrations by the fact that free radicals, formed by methanol radiolysis, probably act upon lignin molecules to increase their number of active centers. Phillips <u>et al</u>., who found the same effect with 2% methanol (89), believed that the addition of methanol increased the swelling of lignin particles and thus a more homogeneous grafting could take place, instead of surface grafting as in a pure lignin:styrene system.

In further studies, Koshijima and Muraki (57,61,63) subjected the graft copolymers to nitrobenzene oxidation, and related vanillin yields to the types of reactions occurring during the grafting process. With grafting ratios up to 100 the vanillin yields diminished proportionately with increasing grafting. At grafting ratios of more than 100 the vanillin yields were constant and independent of the ratios. Gammairradiation of lignin brought about no change in the yields of vanillin. They proposed that radiation grafting onto lignin at grafting ratios of less than 100 proceeded through the addition of poly(styrene) radicals to the lignin aromatic nuclei; then, branches propagated from the aliphatic part of lignin where carbon-hydrogen bond scission had been caused by irradiation. This scheme is in conflict with their own results, since they found the same variations with vanillin by grafting with chemical initiators (61).

Recently, in the graft copolymerization of MMA onto barium lignosulfonate, Nam <u>et al</u>. (81) found that the hydrogen peroxide-ferrous

sulfate redox system was highly effective in giving high yields of graft copolymers. The effect of the peroxide-to-ferrous ion ratio and properties of the lignosulfonate copolymer were studied. A maximum graft add-on was obtained at a 4:1 ratio of peroxide-to-ferrous sulfate, and degree of grafting was governed strongly by the amount of free hydroxyl groups.

Finally, Simionescu and Anton (103) tried to graft acrylonitrile onto chemically modified reed lignin. They nitrated reed lignin, reduced the nitro groups to amino groups, diazotized the amino groups, and thermally degraded the diazonium salt in the presence of acrylonitrile to obtain a poly(acrylonitrile) grafted lignin. However, the grafted poly(acrylonitrile) yields were quite low, and did not exceed 7 to 8%.

2.4.4 Grafting onto lignin-containing pulps

Mikhailov and Livshits (77,78) investigated the graft copolymerization of birchwood defibrator-type groundwood pulp and a number of its components with MMA in the hydrogen peroxide-ferrous ion redox system. The amounts of grafted poly(MMA) differed according to the material used for grafting. Removal of lignin increased the rate of copolymerization considerably. Grafting of lignin took place only if the lignin was in the wood complex, and experiments with dioxane lignin and sulfuric acid lignin gave negative results. They suggested that the growing chains of poly(MMA) are retarded by chain transfer with lignin molecules. The main poly(MMA) reaction was thought to be grafted onto polysaccharides, and only about 10% onto lignin.

Kubota and Ogiwara (65) studied the effect of lignin in the ceric ion initiated graft copolymerization of MMA onto cellulose. A series of celluloses, prepared from a commercial softwood semichemical pulp by bleaching with acidic sodium chlorite solutions to give lignin contents varying from 0.2 to 20%, were investigated. The copolymerization was carried out under nitrogen at 45°C for 60 min using various ceric ion concentrations. Grafts were characterized by: (i) an induction period during which no grafting occurred. The length of this period increased according to the lignin content of the pulps; and (ii) the fact that ceric ions reacted at a much faster rate with lignin than with cellulose in the wood pulp.

Kobayashi <u>et al</u>. (56) investigated methods of improving the strength of sheets made from high-yield kraft and groundwood pulps by irradiationinduced direct graft copolymerization with acrylamide and styrene. They found that almost no grafting occurred between poly(acrylamide) and kraft pulps, regardless of the conditions of irradiation. Using the technique of pre-irradiation, in the presence and absence of air, substantial amounts of acrylamide could be grafted onto pure cellulose pulps, but even bleached kraft pulp, grafted significantly less than pure cellulose pulps. Other kraft pulps, containing 4-24% lignin, grafted essentially nothing when pre-irradiation was conducted in the presence of air.

The same results, indicating an induction period, were found by Erdelyi and coworker (33,83), who studied the effect of residual lignin on the ceric ion grafting of acrylonitrile onto coniferous and poplar

sulfate pulps. They found for both that the degree of grafting increased with decreasing amounts of residual lignin in the pulps. At equal residual lignin concentrations (1.2%) the induction periods were 3.0 and 5.5 min for coniferous and poplar pulps, respectively. With increased residual lignin content the induction period length increased considerably.

Literature on the modification of pulp and paper by graft copolymerization has been reviewed recently (91), and the deleterious effect of lignin on the grafting of most vinyl monomers has been noted.

#### 3.0 MATERIALS AND METHODS

## 3.1 Materials

Since lignins are regarded as possible inhibitors in vinyl polymerization reactions (Section 2.4), it was deemed of interest to conduct controlled polymerization experiments including additions of lignin model compounds (LMC) in order to study some of the basic aspects involved in graft copolymerization. Results obtained with LMC were also examined in experiments including coniferous and pored wood kraft lignins.

3.1.1 Lignin model compounds

Relatively simple LMC were chosen for this investigation. The intention was to represent the <u>p</u>-hydroxyguaiacyl and syringyl units found in different wood lignins. Compounds were either purchased directly and purified, or they were prepared from readily obtainable materials.

Analytical reagent grade phenol (XIV) was purchased from Mallinckrodt Chemical Works. Veratrole (XV), <u>o</u>-chlorophenol (XVI), guaiacol (XVII), eugenol (XVIII), isoeugenol (XIX), and 4-<u>n</u>-propylphenol (XX) were purchased from the Aldrich Chemical Company. The purification steps involved either sublimation or distillation. After purification, the compounds were stored under nitrogen at  $-20^{\circ}$ C.











CH | 3 CH || CH осн3 I ОН





XVIII

XIX

XX

XXI



XXII

Among nine phenols examined in the study, two were prepared in the laboratory. These were  $4-\underline{n}$ -propylguaiacol (XXI), and  $4-\underline{n}$ -propylsyringol (XII), which were prepared by hydrogenation of isoeugenol and 2,6-dimethoxy-4-allyphenol (Aldrich Chemical Company), respectively (87). Hydrogenation was carried out at 100 psi and room temperature in absolute ethanol medium. Ten per cent palladium on charcoal was used as a catalyst and 1% phenol by weight was present. After evaporation of the solvent, hydrogenation products were isolated by distillation, and the purities were checked by gas liquid chromatography and nuclear magnetic resonance.

## 3.1.2 Kraft lignins

Kraft lignins were kindly donated by Dr. D.V. Braddon of the Westvaco, Charleston Research Center, South Carolina. According to his analysis, the coniferous wood kraft lignin contained 14.2% methoxyl, while the pored wood kraft lignin had 19.8% methoxyl. Both are commercially available and are obtained via a two-step acidification process of kraft black liquor. In 1964, Marton (69) gave an idealized scheme compatible with understanding of pine kraft lignin structure at that time. He noted a high degree of conjugation, and high phenolic content in comparison to spruce milled wood lignin (MWL). Further, the molecular weights were comparatively low for both softwood and pored wood kraft lignins (70).

The ligning were extracted with benzene in a soxhlet apparatus for

24 hours in order to eliminate low molecular weight materials. The pine wood lignin was found to contain 5% and the pored wood lignin 8.5% extractables. The lignins were dried at 50°C under vacuum before use.

3.1.3 Monomer

Methyl methacrylate (MMA) was selected for this investigation because its radical reactivity is intermediate between other common monomers, such as styrene and vinyl acetate. In this regard, see for example Section 2.2.1 and Table 2.1.

Eastman Kodak Company MMA was used and this contained 0.006% hydroquinone as stabilizer. The hydroquinone was removed by washing three times with distilled water. The monomer was then dried over sodium sulfate, and allowed to stand in the refrigerator at least overnight. It was dried again with calcium hydride, before being distilled under reduced pressure in a stream of purified nitrogen. The distillation was performed in an all glass apparatus equipped with a 60 cm Vigreux column. Only the constant boiling middle fraction was collected. The exact boiling point for each distillation depended on rate of nitrogen flow and pressure. The purified MMA was then stored in a Pyrex low actinic glass flask at -20°C until used. At this temperature the purified monomer could be stored up to six weeks without any polymer formation.

## 3.4.1 Initiator

The use of azobisisobutyronitrile (AIBN) as a polymerization catalyst was first noted in 1949 by Lewis and Matheson (67). The compound has since been used and studied in great detail. It has been found to decompose by a strictly first order mechanism (3,13), with rate essentially independent of solvent (13,107). The compound may be decomposed photolytically by near ultraviolet light, as well as thermally [3-1],

$$CH_{3} \xrightarrow[CN]{CH_{3}}_{CN} \xrightarrow[CN]{CH_{3}}_{CN} \xrightarrow[CN]{CH_{3}}_{Or(h\nu)} \xrightarrow{CH_{3}}_{Or(h\nu)} 2 CH_{3} \xrightarrow[CN]{CH_{3}}_{CN} + N_{2} \dots [3-1].$$

The AIBN catalyst has also been used in stationary state polymerization of numerous monomers (13), and in all cases the results were concordant with the free radical polymerization scheme as described in Section 2.2.

The AIBN was purchased from Eastman Kodak Company. This was recrystallized several times from absolute ethanol, being careful not to heat the solution above 50°C, until a constant melting point (103°C) was obtained. After drying in a vacuum desiccator, it was stored in a dark bottle in the refrigerator until used.

### 3.2 Methods

Polymerization experiments were conducted in bulk for LMC studies, whereas dimethyl formamide (DMF)-MMA mixtures were used for lignin investigations.

#### 3.2.1 Polymerization with lignin model compounds

A dilatometric technique was used to investigate LMC inhibition and retardation effects. Determination of LMC chain transfer constants necessitates recovery of polymer, therefore experiments with sealed ampoules were more suitable.

# 3.2.1.1 Determination of lignin model compound inhibition and retardation properties

Because the density of a polymer is usually greater than that of the monomer from which it was formed, the progress of polymerization can be followed by observing the contraction in volume of a fixed weight of monomer as it polymerizes. The sensitivity of the change in specific volume with conversion can be increased significantly if the shrinkage in volume is observed in a tube of very small diameter. A dilatometer is a device constructed with a reservoir to contain a sufficient volume of liquid so as to make the total volume change occurring during monomer conversion meaningful. It is fitted with a capillary tube in order to make the volume change accompanying the conversion discernible.

A detailed sketch of the type of dilatometers used in the present work is given in Fig. 3.1. The dilatometer was essentially a Pyrex glass bulb (A) extended with 15 cm of precision-bore (2.1 mm) capillary tubing. The top of the capillary was equipped with a high vacuum stopcock (B), and a 10/24 standard tapered ground glass joint (C). A mark (D) was made at the beginning of the capillary close to the bulb (A).

The useful length of capillary for polymerization studies was limited to 15 cm. Dow Corning high vacuum silicone grease was applied sparingly to the stopcock and joint when vacuum experiments were done.

## 3.2.1.1.1 Dilatometer calibration

The volume of the dilatometer bulb up to the mark on the capillary, as well as the volume per cm of capillary, was measured by the following method. The bulb was filled with clean mercury at  $20^{\circ}$ C up to the mark, and the dilatometer weighed. It was weighed again with a given length of the capillary filled with mercury. From the data obtained by these measurements, the weight of the empty dilatometer, and the density of mercury at  $20^{\circ}$ C (13.546 g/cc), the volumes were calculated. The capillary diameters were found to be 2.08 mm, and the dilatometer bulb volumes were found to vary between 9.5 and 10.5 ml.

From the data of Fox and Loshaek (36) it was calculated that there would be 24.7% decrease in volume of MMA for 100% polymerization at 50°C. The dilatometers were filled to the mark (D) with monomer at 20°C, and the levels of the liquid after expansion at 50°C were noted. It was calculated that a fall of one cm in the MMA level in the capillary corresponded to  $(S_0)/(0.247 \times V_0)$  per cent polymerization. The symbols  $(S_0)$  and  $(V_0)$  denote the inside area of the capillary in cm<sup>2</sup>, and the volume of the dilatometer up to the expanded level at 50°C in ml.

Representative values for the dilatometer constants were 1.404, 1.529, 1.320 and 1.338% polymerization per cm contraction of MMA level

in the capillary for the four dilatometers used in the study.

## 3.2.1.1.2 Polymerization experiments

The reaction mixture was prepared by weighing a predetermined amount of LMC into a clean, tared 50 ml round-bottom flask. Weighings were accurate to 2 x  $10^{-5}$  grams. An appropriate volume of purified MMA solution with 5 mg/ml (3.04 x  $10^{-2}$  M) of AIBN was pipetted into the 50 ml flask. Following thorough mixing, the solution was introduced into the dilatometer bulb with a syringe equipped with a 30 cm needle.

Polymerization experiments were performed under two different controlled conditions: (i) in vacuum; and (ii) in air. In both cases the level of the monomer solution at 20°C was adjusted to the mark (D) on the capillary.

In vacuum experiments, the dilatometer was connected to a high vacuum system by means of the ground glass joint (C). The monomer was frozen by introducing the bulb into liquid nitrogen, and then the system was degassed by the usual freeze-thaw method. The dilatometer was evacuated to a pressure of about  $10^{-3}$  mm Hg. The stopcock (B) was then closed, and the monomer was allowed to thaw permitting the dissolved gases to escape into the dilatometer. The monomer was then refrozen and the dilatometer evacuated again to  $10^{-3}$  mm Hg. This freeze-thaw cycle was repeated five times after which no more escaping bubbles were observed in the monomer. At this stage the monomer was considered to be free of dissolved oxygen. The sealed dilatometer was inserted into a constant temperature water bath maintained at  $50^{\circ} + 0.05^{\circ}C$ .

The water bath was illuminated from the back by a red light. Readings of the capillary meniscus level were taken with a cathetometer through a one cm wide opening in the front side of the thermostat. Meniscus levels were read to the nearest 0.01 cm, and the time of the reading noted. After the reaction had proceeded to about 7% conversion, the dilatometer was removed from the bath, and emptied by inserting a fine intramedic tubing into the bulb through the capillary tube and applying suction.

The empty dilatometer was rinsed twice with chloroform, and then was shaken half filled with chloroform for at least four hours on an automatic shaker. Periodically, a more rigorous cleaning was undertaken. In this procedure dilatometers were filled with a mixture of warm sodium dichromate-sulfuric acid cleaning solution. Following this treatment they were thoroughly rinsed with distilled water and reagent grade acetone.

For polymerizations in air the procedure as described above was used, except that the monomer in the dilatometer was not evacuated by the freeze-thaw method, but instead it was saturated at 20°C with ambient air.

## 3.2.1.1.3 Interpretation of experimental results

A typical inhibition plot is shown in Fig. 3.2. The per cent polymerization was calculated by applying the appropriate dilatometer

constant level changes as described previously. The time zero was taken to be four minutes after immersion of the dilatometer into the thermostat, which was the required time for thermal expansion of the monomer in the dilatometer.

The intersection of the line drawn through the uninhibited portion of the run and the initial base line was used to determine the length of the inhibition period (IP). The slope of the plot for the position of the curve corresponding to the uninhibited part of the run gives the rate of polymerization, in percent/minute, following the inhibition period. When retardation was present, it was given as degree of retardation (DR), and was defined as

## DR = Rate of inhibited polymerization Rate of uninhibited polymerization

## 3.2.1.2 Determination of transfer constants

As discussed in Section 2.2.3, chain transfer reactions occur when vinyl polymerization takes place in the presence of a transfer agent (SH) [2-15]. Polymer technologists have used chain transfer reactions to control the molecular weight of synthetic polymers. Mercaptans, aldehydes, and some hydrocarbons are used routinely in controlling the molecular weights of styrene-butadiene rubbers, polyethylene, and other polymeric materials (108).

The effectiveness of an organic compound as a chain transfer agent can be evaluated if the ratio of  $k_{tr}/k_{p}$  is known,[2-8] and [2-15]. This ratio can be evaluated by means of the Mayo equation, derivation of which is considered in the following paragraphs.

Several investigators have attempted to correlate the kinetic chain length (v) (Section 2.2.2.2) with the average degree of polymerization of the product originating from a polymerization reaction. The average degree of polymerization ( $\overline{P}$ ) is defined as the average number of monomer units per polymer chain, and is calculated from the molecular weight of the polymer.

If reactions other than those considered in Section 2.2.2.1 did not take place to an appreciable extent, there should be a straight relationship between  $\overline{P}$  and  $\nu$  (66). This relationship depends upon the relative importance of chain termination by combination [2-9] and by disproportionation [2-10], the former giving  $\overline{P} = 2\nu$  and the latter  $\overline{P} = \nu$ . When both termination and disproportionation are present, the constant of proportionality would lie between one and two,

$$\bar{P} = kv = k R_p/R_t$$
 [3-2].

Baysal and Tobolsky (12) found that  $\overline{P}$  was very nearly 2v for the polymerization of MMA with certain initiators. Other investigators found that  $\overline{P}$  was not directly proportional to v when polymerization reactions were carried out in solvents (73) or when high concentrations of initiators (55) were used. Thus, when  $\overline{P}$  was not directly proportional to v, it was postulated that other termination reactions were taking place, and that the degree of polymerization could be written as [3-3],

 $\overline{P} = \frac{\text{Rate of polymerization}}{\text{Sum of rates of reactions leading to termination}} \dots \dots [3-3],$ 

The reactions that can lead to termination of the chain reaction are: (i) combination (tc), and/or disproportionation (td); (ii) chain transfer to monomer (tm), polymer (tp), initiator (ti), and transfer agent (tr). By taking the reciprocal of Expression [3-3], 1/P can be expressed as [3-4],

$$\frac{1}{\bar{p}} = \frac{R_{tc} + R_{td} + R_{tm} + R_{tp} + R_{ti} + R_{tr}}{R_{p}} \qquad ..... [3-4].$$

Where: R<sub>subscript</sub> refers to the rate of the reaction involved. Conditions may be chosen such that all other chain transfer reactions, except for chain transfer with a transfer agent (SH), are minimized. This is particularly convenient when a series of additives is considered, since all other termination rates can be assumed to be constant. Under these conditions, Equation [3-4] can be expressed as [3-5],

$$\frac{1}{\overline{p}} = \frac{1}{\overline{p}} + \frac{R_{tr}}{R_{p}} \qquad (3-5),$$

Where:  $1/\overline{P}_{o}$  is the average degree of polymerization when no transfer agent is present. From Equations [2-8] and [2-15] the rates of propagation and termination due to chain transfer can be obtained, and Equation [3-5] then becomes [3-6],

Equation [3-6] can be simplified to yield the Mayo equation (71) as [3-7],

$$\frac{1}{\overline{p}} = \frac{1}{\overline{p}} + \frac{k_{tr}[SH]}{k_{p}[M]} \quad \dots \quad [3-7].$$

The ratio  $k_{tr}/k_p$  is the chain transfer constant (C<sub>t</sub>), as seen previously. Mayo (42) verified this relationship for several aromatic hydrocarbon solvents at low polymer conversion.

## 3.2.1.2.1 Polymerization experiments

Reaction mixtures were prepared as described in Section 3.2.1.1.2. The initiator concentration was 2 mg/ml of monomer  $(1.21 \times 10^{-2} \text{ M})$ except for 4-<u>n</u>-propylguaiacol experiments where 1 mg/ml (6.1 x  $10^{-3} \text{ M})$ was used. The concentration of transfer agents ranged from 0.15-2 x  $10^{-3} \text{ M}$ .

Reactions were carried out in ampoules constructed from 16 x 125 mm ignition tubes. They were thoroughly cleaned, rinsed with distilled water, and dried at 120°C before use. The ampoules were sealed under vacuum, after the same series of freeze-thaw cycles described for LMC.

Reactions were carried out by shaking the sealed ampoules in a constant temperature bath at  $50^{\circ}C$  ( $\pm$  0.05°C) in the dark, for the desired length of time. After the reaction had proceeded beyond 5-8% conversion the ampoules were removed from the bath, cooled, and opened. The polymer was washed out with 20-30 ml of acetone, and precipitated by slowly pouring the solution into 250 ml of cold methanol while stirring with a magnetic stirrer. This solution was filtered using Whatman No. 2 filter paper. The sample was dried in a vacuum oven heated at  $50^{\circ}C$ , until constant weight was obtained (usually 24-36 hr).

The per cent conversion of monomer was taken to be the weight of polymer obtained divided by the weight of the original monomer and multiplied by 100.

3.2.1.2.2 Evaluation of chain transfer constants

Plotting the inverse of  $\overline{P}$  against the transfer agent-to-monomer ratio yields a straight line with the slope equal to the transfer constant, [3-7].

 $\overline{P}$  can be obtained by several techniques. The most common being dilute solution viscometry. In this technique, use is made of the Mark-Houwinsk equation which relates polymer molecular weight to intrinsic viscosity [n] as [3-8],

$$M = K[n]^{\alpha}$$
 [3-8]

by the constants K and  $\alpha$ . The intrinsic viscosity can be determined by plotting the viscosity number  $(n_{\rm sp}^{\prime}/c)$  versus concentration (c), and extrapolating to infinite dilution by means of the Huggins (51) equation [3-9],

$$\frac{\lim}{c \longrightarrow 0} \eta_{sp}/c = [\eta] + K'[\eta]^2 \times c \dots [3-9].$$

A more convenient way is to employ an equation giving intrinsic viscosity from a single viscosity measurement. For this, Equation [3-10] has been chosen (92,84) as,

$$[n] = \frac{n_{sp}}{4c} + \frac{3\ln(n_r)}{4c} \qquad ..... [3-10].$$

The terms used above are defined for capillary viscometers as follows:  $(n_r)$  viscosity ratio, is the ratio between the efflux time for the polymer solution and the efflux time for the pure solvent;  $(n_{sp})$ specific viscosity, is equal to  $n_r$ -1; and (c) concentration in g/100 ml of solution.

Measurements were made at  $20 \pm 0.05$ °C on solutions of polymers in freshly distilled benzene. Two Ubbelohde type (No.1) viscometers having efflux times of 184.6  $\pm$  0.3 and 211.5  $\pm$  0.3 sec for pure solvent were employed. Concentrations not greater than 0.5 g of polymer/100 ml of benzene were used (92). Polymer and solvent in 50 ml bottles were shaken for at least three days to insure complete polymer solution.

Intrinsic viscosity values obtained by use of [3-10] were converted to number average  $\overline{P}$  values by use of equation [3-11] as given (12),

3.2.2 Polymerization with lignins

A solution of monomer and DMF was made in 50:50 (V:V) proportions. Initiator was added to this mixture in order to obtain a solution of 5 mg/ml of AIBN catalyst. A desired amount of dried lignin was placed in an ampoule and a certain volume of MMA-DMF-AIBN mixture was added to give a concentration of 50 mg of lignin per ml of MMA. Under these conditions both coniferous and pored wood lignins were completely dissolved in the monomer-solvent mixture. For polymerization in vacuum, ampoules were attached to the vacuum line, and the contents frozen in liquid nitrogen. The same freeze-thaw cycle technique used for LMC was performed, and finally the ampoule was sealed under vacuum.

The polymerization procedure was the same as that used for determination of transfer constants. After the reaction had proceeded (up to 50% conversion for some experiments), the mixture was cooled and transfered with 20-30 ml of benzene containing a little hydroquinone into a 50 ml beaker. Polymer recovery involved simple evaporation of the solvent and residual monomer. This was accomplished by placing the beaker under an air jet until a viscous mass was obtained, followed by vacuum evaporation at 50°C until no weight change was observed (usually 48 hr).

The techniques for polymerization and recovery when lignins were used in presence of air were the same as those described for polymerization with lignins under vacuum, except that 21 x 50 mm three dram vials were used as reaction vessels. The air was, of course, left in the reaction mixture.

#### 4.0 RESULTS

Results obtained in vacuum with 5 mg/ml  $(3.04 \times 10^{-2} \text{ M})$  AIBN initiated polymerization and low concentration (0.01 M) for five LMC are shown in Fig. 4.1. No inhibition took place, and very little retardation occurred. However, retardation was quite noticeable when isoeugenol was used.

When higher concentrations (0.1-2 M) of two LMC were used, with all other conditions remaining the same, inhibition and slight retardation effects were observed as shown in Fig. 4.2 and 4.3. Straight line relationships are observed between logarithms of inhibition periods and phenol concentrations for the two LMC as indicated in Fig. 4.4. It can be seen that at the same concentration 4-<u>n</u>-propylsyringol inhibited more than 4-<u>n</u>-propylguaiacol. Table 4.1 indicates the respective inhibition periods and polymerization rates resulting from application of these two LMC.

When lower initiator concentrations were used the magnitude of inhibition and decrease in polymerizaton rate for  $4-\underline{n}$ -propylphenol,  $4-\underline{n}$ -propylguaiacol, and  $4-\underline{n}$ -propylsyringol were much higher as shown in Fig. 4.5 and Table 4.2. The solutions contained 2 mg/ml (1.21 x  $10^{-2}$  M) initiator and 0.25 M of phenols.

Figure 4.6 represents plots of the reciprocal of the average degree of polymerization ( $\overline{P}$ ) versus the ratio of the concentration of LMC to monomer. Using the method of least squares, best straight lines were fitted to the data. Slopes of the lines were calculated to give chain transfer constants, as described previously. It can be seen that

for the phenols investigated the slopes increased as the number of substituents increased. These slopes ranged from  $3.2 \times 10^{-4}$  for 4-n-propylphenol to  $54.6 \times 10^{-4}$  for 4-n-propylsyringol. If the phenolic hydroxyl group is blocked as in veratrole, the chain transfer constant drops practically to zero. Values of the chain transfer constants obtained from these trials are summarized in Table 4.3.

When polymerizations were allowed to take place in the presence of air, the results were drastically different. MMA when polymerized with 5 mg/ml of AIBN and at 50°C, either alone or in the presence of veratrole  $(10^{-2}$  M), gives an inhibition period of 12.5 minutes as shown in Fig. 4.7.

Effects of phenols, under the same conditions as applied for vacuum experiments, are shown in Fig. 4.8 through 4.14, and in Table 4.4. Inhibition periods were again found to depend on LMC concentrations; however, LMC concentrations necessary to obtain long inhibition periods (up to 260 min) were found to be quite low  $(10^{-3}-10^{-2} \text{ M})$ . Straight line relationships between the logarithms of inhibition periods and the phenol concentrations were obtained again (Fig. 4.15).

Confirmation of the results found with LMC were obtained by using purified kraft lignins as a source of phenols. The results are shown in Fig. 4.16 for experiments in vacuum and in Fig. 4.17 for experiments in the presence of air. The experimental conditions were described in Section 3.2.2. It can be seen that the inhibition periods were longer with pored wood lignin compared to coniferous wood linin. These results are further summarized in Table 4.5.

## 5.0 DISCUSSION

The failure of various workers (33,56,59,65,77) to obtain acceptable grafting yields of various monomers onto lignins and high yield pulps, which are of considerable importance as commercial products, warranted a closer examination of the reactivity of various phenolic compounds towards vinyl polymers. The results of the present study were analyzed with the objective of contributing to the theoretical base of what seems to be a major practical problem.

## 5.1 Experiments with Lignin Model Compounds

In this work the LMC are referred to as inhibitors of the catalyzed MMA polymerization. Conversion-time plots (e.g., Fig. 4.5) show, however, that polymerization is not completely inhibited during the so-called "inhibition period". A period succeeding suppression of polymer formation is evident in which the rate increases gradually as the inhibitor is removed. This transition leads smoothly into a simple kind of retardation. In this case there is fair degree of competition by the polymer free radical for the monomer or the retarder. When the retarder molecule adds to the radical, growth stops altogether. On the whole, the transition from slow to fast reaction is fairly abrupt, and use of the term inhibitor is therefore justified. It must be recognized, however, that compared with a material such as diphenylpicrylhydrazyl (8), LMC are inefficient inhibitors. The steady rates, in % conversion/min, observed after the inhibition periods, are all slightly less than those observed in uninhibited polymerization (Tables 4.1 and 4.2). The differences can be accounted for in part by the retardation effect of the products formed, and in part by the consumption of initiator during the inhibition period, although the latter may be quite limited. Indeed, approximately 1% of the AIBN added decomposes in one hour at 50°C (11), so that in these experiments (maximum duration of five hours) the amount of initiator could be taken as constant throughout the polymerization experiments.

## 5.1.1 Polymerizations in vacuum

At low LMC concentrations and with 5 mg/ml of AIBN, no inhibition took place, Fig. 4.1. This is in agreement with earlier related studies of Russell and coworkers (9,16,39) who reported on the effects of phenols at low concentrations on various vinyl monomer polymerizations.

Isoeugenol was found to behave differently than other phenols. Although it did not produce an inhibition period, it did decrease the rate of polymerization by 10% (RD = 0.900), Fig. 4.1. This can be explained by the increased resonance stability of the phenoxy radical formed during the transfer reactions. This is expected to take place because of the double bond on the propyl group can be conjugated with the benzene ring. The following resonance structure may be written as (XXIII).



The frequency of reinitiation [2-16] is thus greatly reduced, hence a decrease in the rate of polymerization results. See Section 2.2.3.

The chain transfer constants found at 50°C for different phenols are reported in Table 4.3. They are quite small, but are of the same order of magnitude as those obtained by other workers and reported in the Polymer Handbook (20). The chain transfer constants given in Table 2.2 for MMA have been calculated at 45°C, so they are expected to be smaller than those found in this work at 50°C (25). This suggests that the techniques employed in this study are at least as reliable as those used by other investigators.

The major result of these chain transfer constant experiments is the relatively high constant obtained for  $4-\underline{n}-propylsyringol$  (54.6 x  $10^{-4}$ ) versus the values for  $4-\underline{n}-propylguaiacol$  (8.3 x  $10^{-4}$ ) and  $4-\underline{n}-propylphenol$  (3.2 x  $10^{-4}$ ). The transfer reaction for  $4-\underline{n}-propylsyringol$ is therefore 6.5 times higher than for  $4-\underline{n}-propylguaiacol$ . No retardation was noticed in these experiments. However, it should be noted that phenols having bulky <u>ortho</u> substituents have been found to retard vinyl polymerizations (25,38,47). Equations intended to correct these retardations have been proposed (54), but it was found that

apparent chain transfer constants did not differ greatly from those that were calculated from the Mayo equation (39).

The difference in relative reactivities of poly(MMA) radicals towards different phenols can be interpreted in terms of contributions to the stability of the transition state of polar structures in which an electron has been donated by the radical to the phenol,

The relatively low reactivities found indicate, however, small contributions of polar structures in the transition state (9). In applying the scheme developed by Bamford <u>et al</u>. (7), it can be deduced that phenols appear to belong to the same class of substrates as <u>t</u>-butylthiol and ferric chloride, which are found to be electron-acceptor substrates.

The most likely abstracted hydrogen atom, besides the phenolic hydrogen, would be the benzylic hydrogen. However, it has been reported that the chain transfer constant of poly(MMA) radicals with ethylbenzene at 52°C is  $0.501 \times 10^{-4}$  (25). In addition, the chain transfer constant for veratrole is approximately zero as seen in Fig. 4.6 and reported in Table 4.3. Therefore, it can be assumed that growing poly(MMA) radicals abstract exclusively phenolic hydrogen atoms from the 4-<u>n</u>-propylphenols used. This is in agreement with results derived from isotope studies with different phenols (16,47).

The effect of substituents on the phenols is manifested by the different lengths of the inhibition periods. These follow practically the same pattern found for chain transfer constants. Thus substances

with increasing inhibition periods follow the order:  $4-\underline{n}$ -propylphenol,  $4-\underline{n}$ -propylguaiacol, and  $4-\underline{n}$ -propylsyringol.

The phenol substituents have two main effects: (i) the resonance stabilization of the phenoxy radical is increased, which slows reinitiation [2-16] and increases the inhibition period; and (ii) the transition state of the transfer reaction [5-1] is destabilized by polar effects resulting from the electron-donating substituents. An example of the latter could be the case of 4-<u>n</u>-propylsyringol, wherein the negative charge on the phenolic oxygen cannot be delocalized along the benzene ring [5-2],



According to the consideration of polar effects, the rate of [5-2]should be smaller for  $4-\underline{n}$ -propylsyringol than for  $4-\underline{n}$ -propylguaiacol, which in turn should be smaller than the rate for  $4-\underline{n}$ -propylphenol. However, the chain transfer constants obtained, as seen earlier, show opposite results. This indicates that in the transfer reaction of poly(MMA) radicals to phenols, the resonance stabilization of the phenoxy

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radical is much more important than the polar effect resulting from the electron-donating substituents present. In fact, stability of the phenoxy radicals is known to be increased with either electron-attracting or electron-donating substituents (50).

If higher concentrations of phenols are used, larger inhibition periods are obtained, e.g., Fig. 4.2 and 4.3. As noted previously (Section 2.3), retardation can be transformed into inhibition by high retarder concentrations. The logarithmic plots between the inhibition periods and phenol concentrations are linear as shown in Fig. 4.4 for  $4-\underline{n}$ -propylguaiacol and  $4-\underline{n}$ -propylsyringol. The curves are also parallel and can be represented by the relation

 $IP = K_1 [pheno1]^{0.6}$ 

When lower initiator concentrations were used (2 mg/ml compared to 5 mg/ml), higher inhibition periods were obtained, Fig. 4.5. This is quite normal since the rate of polymerization is proportional to the square root of the initiator concentration (Section 2.2.2) as shown in Fig. 5.1. As the rate of initiation is lowered, the inhibition period is increased since inhibitor molecules will last much longer (13).

5.1.2 Polymerization in presence of air

Before looking at the effect of phenols on vinyl polymerization in presence of air, it will be of value to verify the results obtained
by other workers in studying the effect of oxygen alone. As shown in Fig. 4.7, an inhibition of 12.5 min has been observed when 5 mg/ml of AIBN was used for the polymerization of MMA at 50°C. This turns out to be the same order of magnitude as found by other workers (75, 102). As seen in Section 2.3.2.1 the mechanism must be that proposed by Schulz and Henrici (102), whereby the following (XXIV) MMA-oxygen copolymer of low molecular weight is formed.



When phenols are present in addition to oxygen during the MMA polymerization, peroxy-poly(MMA) radicals have the opportunity of reacting with phenols. The polymerization will be allowed to continue or not according to the stability of the new phenoxy radicals formed.

As shown in Fig. 4.8 through Fig. 4.14, and in Table 4.4, long inhibition periods and sometimes high degrees of retardations were obtained with very small phenol concentrations  $(10^{-3}-10^{-2} \text{ M})$ . Inhibition periods for the same phenol concentration increase in the following order: <u>o</u>-chlorophenol, phenol,  $4-\underline{n}$ -propylphenol, guaiacol,  $4-\underline{n}$ -propylguaiacol, eugenol,  $4-\underline{n}$ -propylsyringol, and isoeugenol. These results are in agreement with the established role of phenols as antioxidants (79,98). The electron-withdrawing chloro-group is seen to

have a deactivating effect relative to phenol, while electrondonating groups in <u>ortho</u> or <u>para</u> positions have the expected activating influence. These results infer that polar effects are important in the transition state of the transfer reaction of the peroxy-poly(MMA) radicals with phenols.

Polar contributions to the transition state of radical displacement have been used in the past to explain anomalous results. For example, Mayo and Walling explained their results in that manner for the chlorination of alkyl halides and aliphatic acid derivatives (76).

One of the most effective techniques for separating polar effects on substituted benzene nuclei from others arising from steric and related factors, is by studying the effects of substituents and treating the results in terms of the Hammett equation (43):

in which (k) and (k<sub>o</sub>) are rate constants for reactions of substituted and unsubstituted benzenes, respectively, in the particular reaction under investigation and the substituents involved; ( $\sigma$ ) is a constant characteristic of the substituent only, for which values have been tabulated for a wide variety of substituents; and ( $\rho$ ) is a constant for all substituents and depends only on the reaction series.

In order to apply this equation to inhibition as indicated by LMC data, the logarithms of the ratios of inhibition periods for substituted phenols to the inhibition period for phenol at the same

concentration were plotted against the sum of the tabulated substituent constants for groups on the phenol. If the electron density of the O-H bond of the phenolic hydroxyl determines the reactivity, then the substituent effect should be correlated with the  $\sigma$  constants, calculated from the ionization of substituted benzoic acids (43,68).

The values of the  $\sigma$  constants were added. Since para  $\sigma$  constants were used for non-established ortho substituents, the Hammett coefficients as used here are only estimates. However, the Hammett equation has been applied before with a similar assumption to reaction series of benzene derivatives containing ortho substituents (53,97,104). The reaction constant is identical with that of the corresponding reaction series not containing the ortho substituents. For example, for dissociation of 4-n-substituted-2-chlorophenols (104),  $\rho = 2.22$ , and dissociation of 4-substituted-2-nitrophenols (97),  $\rho = 2.16$ . for Both are in close agreement with  $\rho = 2.23$  for dissociation of substituted phenols (14) which did not contain an ortho group. Finally the propyl group was assigned the same  $\sigma$  constant as the ethyl group. The sum of  $\sigma$  constants for each LMC is shown in Table 5.1. Individual σ values were taken from McDaniel and Brown's compilation (68). Since no appropriate values for the propylene groups of eugenol and isoeugenol could be found, they were not considered.

The relative inhibition periods obtained with different phenols yielded the expression (Fig. 5.2):

The sign and magnitude of the  $\rho$  factor of a reaction series is generally considered to be a measure of the charge separation in the transition state (68). A favorable effect of high electron density implies a negative value of  $\rho$ , with a higher effect resulting in a larger negative  $\rho$  value (99). Although the present application of the technique is no more than semi-quantitative, the pattern of results is quite clear, and indicates a polar effect in attack of the peroxypoly(MMA) radical. The value of  $\rho$  found (-0.83), however, indicates that there is only a moderate degree of charge separation in the transition state. The  $\rho$  value calculated herein is of the order of magnitude derived by Russell ( $\rho = -0.6$ ) in studying the oxidation of toluene derivatives by reaction with peroxy radicals (99).

The great sensitivity of peroxy-poly(MMA)-phenol reactions to substituents on phenol can be ascribed in part to the importance  $\delta + \delta$ of polar contributions of the form  $XC_6H_4OH -$  peroxy to the transition state of [5-5],

 $X-C_{6}H_{4}OH + POO' \longrightarrow X-C_{6}H_{4}O' + POOH \dots$  [5-5].

Indeed, the transition state for this reaction can be considered to consist of three resonance forms

In this, the more electronegative the peroxy radical POO', the more favored form XXVI should become, hence the greater the importance of the

polar effect since the electron-donating substituents can help to accomodate the positive charge on the phenol. According to the Hammond postulate (52), structure XXV which resembles the reactants should occur with a highly reactive peroxy radical, while structure XXVII which resembles the products should occur in the presence of an unreactive peroxy radical. The correlation of the present results with  $\sigma$  constants indicates that structure XXVI contributes to the transition state, but the magnitude of the  $\rho$  factor suggests that there is only a moderate degree of charge separation.

In conclusion, the maximum inhibition period caused by the phenols studied will be achieved when the phenolic substituents have the largest possible negative  $\Sigma\sigma$  value. This means that the efficiency of phenols is increased by an increase in the electron density of the hydroxyl group.

Results from series such as  $4-\underline{n}$ -propylphenol,  $4-\underline{n}$ -propylguaiacol and  $4-\underline{n}$ -propylsyringol can thus be explained by taking into account the polar effect. However, looking at results obtained with the series  $4-\underline{n}$ -propylguaiacol, eugenol and isoeugenol, it is evident that in addition to polar effects there is an important resonance contribution. Indeed, the difference in results obtained (e.g., for a concentration of 3 x  $10^{-3}$  M, IP values were 167, 175, and 260 min, respectively) reveals that a double bond in conjugation with the aromatic ring leads to maximum inhibition activity. Presumably, this is due to the stabilization of the resonating form of the phenolate

ion as seen previously for polymerization in vacuum (XXIII). When the double bond is removed to the  $\beta$ -position as in eugenol, the difference in inhibition, compared to the normal propyl group, is rather insignificant (167 versus 175 min.).

The logarithmic plots between inhibition periods and phenol concentrations were again linear, Fig. 4.15. They were also parallel, with slopes equal to 0.4 for all LMC studied in the presence of air. The relationship can therefore be represented by expression [5-6],

As seen in the vacuum polymerizations, phenolic inhibitors completely lose their activity if the phenolic hydroxy groups are blocked by etherification. Figure 4.7 shows the effect, or rather lack of effect, of veratrole in presence of air; there is practically no distinction from the curve obtained with MMA alone in presence of air.

To justify the results found in these experiments, and to be in agreement with related results found in the literature (23,38,44,80), the proposition is advanced that LMC reactions with poly(MMA) radicals in presence of air are similar to reactions occurring when phenols are used as antioxidants. The mechanism discussed in Section 2.3.2.2 (Reactions [2-24] to [2-29]) applies here, R' being a poly(MMA) radical. The electronegative peroxides formed by reaction of poly(MMA) radicals with oxygen will preferably react with phenols (29), which assume the role of electron-donor substrates. Therefore, phenols

decrease oxygen consumption in the system, hence increasing the inhibition period.

5.2 Experiments with Kraft Lignins

In order to verify the results found with LMC, experiments with kraft lignins were performed. Kraft lignins were chosen because of their low molecular weights, their high phenolic contents, as well as their high percentage of conjugated double bonds in the propyl side chains (Section 3.1.2). It is interesting to note the differences in molecular weight values given by Marton and Marton (70). They found Mn = 1600 for pine kraft lignin and 1050 for the pored wood kraft lignin. Also, the degree of polydispersity was relatively small; the ratio of weight average to number average molecular weight Mw/Mn = 2.2 for coniferous wood kraft lignin and about 2.8 for the pored wood kraft lignin, thus indicating fairly homogeneous materials in both cases.

As seen in Section 2.4.3, grafting onto lignin depends in part on the state of lignin swelling. Wide variations in per cent grafting were obtained when different amounts of methanol were used in reaction mixtures (60,90). This has been explained for grafting with styrene (90) as resulting from a more homogeneous grafting due to improved accessibility of lignin by the monomer.

In order to avoid the introduction of these complicating effects in the present experiments, enough solvent was added so that the lignins were completely solubilized. It was found that 50:50 MMA-DMF mixtures were necessary for complete solubilization of the lignin fraction added. Another detrimental effect avoided by performing experiments with completely soluble lignins was the gel effect. The gel effect results from an increase of the viscosity of the reaction medium with conversion to a point where the radical termination rate constant  $(k_t)$  decreases, and as the propagation rate constant  $(k_p)$  remains constant, the result is an increase in the overall rate of polymerization (66). It has been found that the gel effect for MMA occurs at about 20% conversion (106); however, it could probably occur much earlier in heterogeneous media (110).

The experimental results with lignins are given in per cent conversion. Attempts were made to determine the grafting ratios by extraction of the homopolymer (poly(MMA)) with benzene in a soxhlet apparatus, but no logical results were obtained. In fact, most of the time, lower weights of grafted lignins than the initial weights of lignins were obtained. While the present work was being performed others were faced with a similar problem in styrene grafting to lignin (90). These authors suggested that the graft copolymer chains assume more of the solubility behavior of poly(styrene). The degree of interaction of the chain with solvent molecules should depend on the length of the lignin backbone, as well as the length of the grafted poly(styrene) chain.

5.2.1 Kraft lignins in vacuum

As shown in Fig. 4.16 and Table 4.5, the effect of kraft lignins on the polymerization of MMA in vacuum results in inhibition periods (25 min for coniferous wood, and 50 min for pored wood lignin) and retardations (DR = 0.765 for coniferous wood, and 0.600 for pored wood lignin). From the results seen previously with LMC, it was expected that the additional syringyl groups present in pored wood lignin would inhibit the polymerization to a greater extent than the guaiacyl groups alone as found in coniferous wood lignin. Normally, no inhibition should have taken place for experiments in vacuum. It might be possible, however, that either traces of oxygen remained in the system, or that the concentration of lignin used (50 mg/ml of MMA) was high enough to induce inhibition.

Reactions of poly(MMA) radicals with lignin molecules must occur through chain transfers. The most probable chain transfer reaction will be the abstraction of phenolic hydrogens, as discussed for the polymerization of MMA in presence of LMC.

5.2.2 Kraft lignins in presence of air

The inhibition of MMA alone in this set of experiments was 30 min as shown in Fig. 4.17 and Table 4.5. It can be seen also that inhibition periods in presence of kraft lignins were much longer than when kraft lignins were used in vacuum experiments (175 min for coniferous wood and 250 min for pored wood lignin), although degrees of retardation were

of the same order of magnitude (DR = 0.806 and 0.626 for coniferous wood and pored wood lignins, respectively).

Inhibition by kraft lignins is in agreement with the mechanism proposed previously for the action of phenols in the polymerization of MMA in presence of air. Lignins can be identified as phenolic substances acting as antioxidants. The correlation between model compound experiments and practical results with kraft lignins is rather remarkable.

As described in Section 5.1.2, an important factor influencing grafting of poly(MMA) onto lignins in presence of air is the degree of substitution of the phenolic groups, which relates to wood origin (Section 2.4.1). The rate of MMA conversion is therefore significantly affected by the grafting reaction. Furthermore, in the case of pored wood lignin, much of the polymer formed must be homopolymer. Indeed, the slow reinitiation reactions of the additional syringyl type phenoxy radicals decrease the copolymerization of peroxy-poly(MMA) radicals with lignin molecules (Section 5.1.2).

All these observations are in good agreement with practical results in that grafting of vinyl monomers onto lignin and onto lignified materials is more difficult than, for example, onto pure cellulose (59,65,83,103). In addition, not only are graft yields affected in a differential way with lignins, but notable differences were also reported in curing rates between bulk polymerization and polymerization in the wood complex (5,27). This could be related in part to the inhibiting effect of lignins.

## 6.0 RECOMMENDATIONS FOR FURTHER RESEARCH

The information derived in this study on inhibition of MMA polymerization by lignins gives a firm basis for additional investigations which might include:

1. The effect of Lignin-MMA ratio on inhibition and retardation occurring during grafting.

2. The influence of chemical modifications of lignins caused by isolation methods.

3. Studies on inhibition and retardation with monomer systems of different reactivity.

4. An improvement in separation of lignin-vinyl graft copolymers from the homopolymer fraction.

5. An investigation of lignin-vinyl graft copolymer physical properties.

## 7.0 CONCLUSION

The effects of lignin model compounds (LMC) and kraft lignins on the polymerization of methyl methacrylate (MMA) in vacuum and in presence of air were investigated. The polymerization was followed by a dilatometric method and initiated by azobisisobutyronitrile (AIBN) at 50°C. Substituted phenols were first used as LMC in order to ascertain influences of the methoxyl group number and propyl side chain features found in lignins. Results obtained with LMC were confirmed with coniferous wood and pored wood kraft lignins. The following conclusions are advanced from evidence obtained in this study:

1. For experiments in vacuum with low concentration of LMC  $(10^{-3}-10^{-2} \text{ M})$  and 5 mg/ml of AIBN, neither noticeable inhibition nor retardation was observed. At higher concentration of LMC (0.1-2 M), inhibitions and retardations started to occur. Inhibition periods were found to vary according to the 0.6 power of phenol concentration.

2. Chain transfer constants for poly(MMA) radicals with LMC were  $3.2 \times 10^{-4}$  for  $4-\underline{n}$ -propylphenol,  $8.3 \times 10^{-4}$  for  $4-\underline{n}$ -propylguaiacol, and  $54.6 \times 10^{-4}$  for  $4-\underline{n}$ -propylsyringol. Interestingly, the chain transfer constant for veratrole was practically zero, meaning that growing poly(MMA) radicals abstract mostly phenolic hydrogen atoms.

In these transfer reactions, it is proposed that phenols react as electron-acceptor substrates and the phenoxy radicals formed are greatly stabilized by the <u>ortho</u> and <u>para</u> substituents.

3. In the presence of oxygen, LMC inhibit the polymerization of methyl methacrylate even at very low concentrations  $(10^{-3}-10^{-2} \text{ M})$ . Length of the inhibition period varies according to the 0.4 power of phenol concentration. Inhibition periods are thought to be lengthened because interaction of chain-carrying peroxy radicals with phenols breaks an oxygen-consuming chain reaction which normally occurs in inhibition of vinyl monomers by oxygen. This chain-breaking allows the oxygen concentration to remain at a level high enough to inhibit the polymerization for longer times.

4. The polar contribution in the reaction between phenols and poly(MMA)-peroxy radicals was demonstrated by employing the Hammett equation. The effects of aromatic substituents on the reaction were studied on the basis of the following Hammett equation:  $log[(IP_{substituted phenol})/(IP_{phenol})] = \rho\sigma; \sigma$  is the Hammett polar substituent constant, and  $\rho$  is the reaction constant. The  $\rho$  value was found to be -0.83 indicating that, in presence of air, phenols are reacting as electron-donor substrates.

5. Experiments with coniferous wood and pored wood kraft lignins in vacuum, and in presence of air, confirmed the results found with lignin model compounds. Lignin phenolic groups are thus shown to be responsible for inhibitions observed during polymerization of MMA in presence of lignins. As expected, the inhibition obtained with pored wood lignin was much longer, since the additional syringyl groups delay reinitiation reactions to a greater extent than guaiacyl groups alone.

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Monomer	<u>e</u>	<b>Q</b>
Styrene ,	-0.8	1.0
Methyl methacrylate	0.4	0.74
Acrylonitrile	0.9	0.68
Vinyl acetate	-0.1	0.022
Vinyl chloride	0.2	0.024

Table 2.1. Q and  $\underline{e}$  values for some common monomers (94).

Table 2.2. Chain transfer constants (C<sub>t</sub>) for some substituted phenols with St, MMA, and VA.\*

Compound	St at 60°C C <sub>t</sub> x 10 <sup>4</sup> (39)	MMA at 45°C C <sub>t</sub> x 10 <sup>4</sup> (9)	VA at 45°C C <sub>t</sub> x 10 <sup>4</sup> (16)
Phenol	14		190
4-Methylphenol	39	-	710
4-Methoxyphenol	260	<5	-
2,3,4,6-tetramethy phenol	L- 580	11	940

St: styrene; MMA: methyl methacrylate; VA: vinyl acetate.

\*

Table 4.1. Effect of phenol concentrations on MMA polymerization in vacuum at 50°C; AIBN at 5 mg/ml.

Pheno1	Conc. (molar)	Inhib. period (min)	Rate of polym. (% conv/min)	DR*
None		0	0.140	<del>.</del>
4- <u>n</u> -Propylguaiacol	0.133	2	0.136	0.973
	0.677	5	0.132	0.942
	1.337	7	0.124	0.885
	2.032	9	0.117	0.836
4- <u>n</u> -Propylsyringol	0.1	6	0.139	0.993
	0.2	10.5	0.137	0.978
	0.5	17	0.130	0.928

Table 4.2. Effect of phenol concentration on MMA polymerization in vacuum at 50°C; AIBN at 2 mg/ml.

Phenol	Conc. (molar)	Inhib. period (min)	Rate of polym. (% conv/min)	DR <sup>*</sup>
			· · · · · · · · · · · · · · · · · · ·	
None	-	_	0.093	<b>-</b> .
4- <u>n</u> -Propy1pheno1	0.25	34	0.085	0.914
4- <u>n</u> -Propylguaiacol	0.25	46	0.065	0.699
4- <u>n</u> -Propylsyringol	0.25	140	0.065	0.699

\*

•					
LMC	[SH]/[M] x 10 <sup>2</sup>	[n] (d1/g)	P	1/P x 10 <sup>4</sup>	$C_t \times 10^4$
	0.896	1.844	5254	1.903	· · · · · · · · · · · · · · · · · · ·
4-n-Pronvlahenol	2.020	1.858	5297	1.888	3 0
4- <u>m</u> -rropyrphenor	2.380	1.819	5172	1.933	J•2
· · · · · · · · · · · · · · · · · · ·	2.895	1.787	5068	1.973	
	0.487	2.280	6675	1.498	
k-n-Pronulausissal	0.637	2.319	6807	1.469	83
	1.052	2.228	6505	1.537	0,5
	2.952	2.051	5925	1.687	·
	0.627	1.663	4674	2.139	
4-m-Propyleyringol	0.820	1.606	4494	2.225	54 6
4- <u>11</u> -110py13y111g01	1.399	1.352	3612	2.585	54.0
÷ .	2.112	1.257	3406	2.936	
	0.344	1.908	5460	1.831	
Veratrole	0.797	1.950	5597	1.787	=0
Veracione	2.322	1.904	5447	1.836	-0
	3.598	1.911	5470	1.828	
		· .			

Table 4.3. Determination of transfer constants (C<sub>t</sub>) for some lignin model compounds (LMC) with MMA at 50°C; AIBN at 2 mg/ml.

The initiator concentration was 1 mg/m1.

\*

				*
Phenol	Conc.	Inhib.	Rate of polym.	DR
	(Molar)	period	(% conv/min)	
	$\times 10^3$	(min)		
		· · · · · · · · · · · · · · · · · · ·	···· <u>·</u>	
MMA alone	0	13	0.140	
	1	38	0.131	0.936
Phenol	3	58	0.124	0.885
	10	106	0.117	0.836
	1,5	32	0.127	0,907
o-Chlorophenol	3	× 44	0.121	0.864
-	7	59	0.110	0.786
	1	74	0.130	0.928
4-n-Propy1pheno1	3	117	0.130	0.928
	8	163	0.123	0.878
Guaiacol	3	129	0.132	0.943
	1	106	0.133	0.950
4-n-Propylguaiacol	5	211	0.118	0.842
	8	251	0.104	0.743
	1	142	0.136	0.971
4- <u>n</u> -Propylsyringol	3	232	0.094	0.671
_	5	280	0.073	0.521
	1.5	132	0.133	0.950
Eugeno1	3	171	0.129	0.921
	8	265	0.118	0.842
	0.8	150	0.110	0.786
Isoeugenol	1.5	193	0.098	0.700
	3	260	0.084	0.600

Table 4.4. Effect of various phenols on MMA polymerization in presence of air at 50°C; AIBN at 5 mg/ml.

\* D

DR = (Rate of inhibited polymerization)/(Rate of uninhibited polymerization).

Table 4.5. Effect of kraft lignins on MMA polymerization in vacuum, and in presence of air at 50°C; lignins in 50:50 MMA:DMF mixtures, with 50 ml lignin per ml of MMA; AIBN at 5 mg/ml.

Lignin	Inhib. period	Rate of polym. (% conv/min)	DR <sup>*</sup>
	(min)		
MMA alone	<b>`0</b>	0.145	-
Coniferous wood	25	0.111	0.765
Pored wood	50	0.087	0.600
MMA alone	30	0.150	_
Coniferous wood	175	0.121	0.806
Pored wood	250	0.094	0.626
	Lignin MMA alone Coniferous wood Pored wood MMA alone Coniferous wood Pored wood	LigninInhib. period (min)MMA alone0Coniferous wood25Pored wood50MMA alone30Coniferous wood175Pored wood250	LigninInhib. period (min)Rate of polym. (% conv/min) (% conv/min)MMA alone00.145Coniferous wood250.111Pored wood500.087MMA alone300.150Coniferous wood1750.121Pored wood2500.094

\*

DR = (Rate of inhibited polymerization)/(Rate of uninhibited polymerization).

Table 5.1.	Sum of estimated Hammett substituent constants ( $\sigma$ ) and
	relative inhibition period values (IP/IP) for lignin
	model compounds (LMC).

LMC	Sum of estimated $\sigma$ constants	IP/IP <sub>o</sub> *
o-Chlorophenol	+0.227	0.705
Phenol	0	1.0
4- <u>n</u> -Propylphenol	-0.151	1.685
Guaiacol	-0.268	2.114
4- <u>n</u> -Propylguaiacol	-0.419	2.770
4- <u>n</u> -Propylsyringol	-0.687	3.721
		,

IP = inhibition period for substituted phenol

 $IP_{o}$  = inhibition period for phenol

\*



골목

Figure 2.1. Thermal polymerization of styrene at 100°C in the presence of: I, no additive; II, 0.1% benzoguinone; III, 0.5% nitrobenzene; IV, 0.2% nitrosobenzene (101).



Figure 2.2. Schematic model for the constitution of spruce lignin by Freudenberg (37).



Figure 2.3. Rates of vinyl monomer grafting onto pine and birch lignins by direct grafting with gamma-irradiation (58). N: hydrochloric acid pine lignin; L: hydrochloric acid birch lignin; MMA: methyl methacrylate; VA: vinyl acetate; St: styrene.





91<sub>:</sub>











Figure 4.1. Effect of low lignin model compound concentration (0.01 M) on MMA polymerization in vacuum at 50°C; AIBN at 5 mg/ml.



Figure 4.2. Effect of 4-n-propylguaiacol concentration on MMA polymerization in vacuum at 50°C; AIBN at 5 mg/ml.



Figure 4.3. Effect of 4-<u>n</u>-propylsyringol concentration on MMA polymerization in vacuum at 50°C; AIBN at 5 mg/ml.

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Figure 4.4. Log-log relationship between inhibition periods and phenol concentrations; MMA polymerization in vacuum at 50°C; AIBN at 5 mg/ml.



Figure 4.5. Effect of lignin model compounds (0.25 M) on MMA polymerization in vacuum at 50°C; AIBN at 2 mg/ml.



Figure 4.6. Plot of Mayo equation for chain transfer constant evaluation of lignin model compounds at 50°C; AIBN at 2 mg/ml (1 mg/ml for 4-propylguaiacol).



Figure 4.7. Effect of air on MMA polymerization at 50°C; AIBN at 5 mg/ml.

(100



Figure 4.8. Effect of phenol on MMA polymerization in presence of air at 50°C; AIBN at 5 mg/ml.



Figure 4.9. Effect of <u>o</u>-chlorophenol on MMA polymerization in presence of air at 50°C; AIBN at 5 mg/ml.







Figure 4.11. Effect of 4-n-propylguaiacol on MMA polymerization in presence of air at 50°C; AIBN at 5 mg/ml.



Figure 4.12. Effect of 4-n-propylsyringol on MMA polymerization in presence of air at 50°C; AIBN at 5 mg/ml.



Figure 4.13. Effect of eugenol on MMA polymerization in presence of air at 50°C; AIBN at 5 mg/ml.



Figure 4.14. Effect of isoeugenol on MMA polymerization in presence of air at 50°C; AIBN at 5 mg/ml.



Figure 4.15. Log-log relationship between inhibition periods and phenol concentrations; MIA polymerization in presence of air at 50°C; AIBN at 5 mg/ml.



Figure 4.16. Effect of kraft lignins on MMA polymerization in vacuum at 50°C; AIBN at 5 mg/ml; lignins: 50 mg/ml of MMA; polymerizations performed in 50:50 MMA:DMF mixtures.



Figure 4.17. Effect of kraft lignins on MMA polymerization in presence of air at 50°C; AIBN at 5 mg/ml; lignins: 50 mg/ml of MMA; polymerizations performed in 50:50 MMA:DMF mixtures.



Figure 5.1. Relationship between MMA polymerization in vacuum and square root of initiator concentration.



Figure 5.2. Relationship between relative inhibition period (IP) values and estimated Hammett substituent constants ( $\sigma$ ).