

# Synthesis and Polymerization of Lignin Macromonomers.

## II. Effects of Lignin Fragments on Methyl Methacrylate Radical Polymerization\*

C. DA CUNHA, A. DEFFIEUX,<sup>†</sup> and M. FONTANILLE

Laboratoire de Chimie des Polymères Organiques,<sup>†</sup> Université Bordeaux 1, Institut du Pin 351, Cours de la Libération, 33405-Talence Cédex, France

### SYNOPSIS

In the course of a study on the synthesis and polymerization of lignin macromonomers, the effect of lignin fragments and acetylated lignin ones on the radical polymerization of methyl methacrylate has been investigated. Kinetics show that lignin moieties act first as inhibitors of the MMA polymerization. The inhibition process has been attributed to the phenolic groups, which primarily react through hydrogen transfer with free radicals issued from benzoyl peroxide dissociation, thus leading to a series of lignin free radicals inactive towards ethylenic groups. The derivatization of lignin hydroxyl groups into ester groups totally suppresses the inhibition process. Besides, it was also shown that both lignin and acetylated lignin units act as chain limiting agents towards MMA polymerization. As indicated both by the chemical composition of the polymers produced and the kinetic data, the latter process might involve the formation of a new type of lignin free radicals, able to initiate MMA polymerization. A reaction scheme is proposed.

### INTRODUCTION

The possibility of using lignin residues as prepolymers in the synthesis of thermoplastics and thermosetting resins has been studied for a long time. Two general approaches have been developed to this end: radical grafting of vinyl monomers either from or onto lignin derivatives and condensation type reactions from hydroxy groups.<sup>2</sup>

To start with, both methods were applied directly to nonmodified lignin fragments obtained as by-products of the paper industry or—more recently— from the flash hydrolysis process of lignocellulosic materials. However, grafting efficiency and mechanical properties of the resulting material are poor. In order to get a better control of the reactivity of lignin residues<sup>1</sup> and also to fit the lignin structure

to the suitable chemical composition and thermo-mechanical properties of the resulting materials, modified lignins are often preferred.<sup>3-5</sup>

The possibility of synthesizing “linear random” copolymers from ethylenic monomer and modified lignin residues by free radical copolymerization has been studied. The method consists in anchoring polymerizable double bonds on lignin fragments.<sup>1</sup> Then, “linear random” copolymers of lignin macromonomers with ethylenic monomers can be expected from chain polymerization.

There are some relevant but incomplete literature data on the effect of lignin derivatives on radical polymerization processes.<sup>6-12</sup> However, studies were generally performed in heterophasic conditions with insoluble lignin fragments and the experimental results are difficult to interpret. Therefore, prior to going further in the synthetic route considered, the behavior and the effects of unmodified and modified lignin residues in the homogeneous radical polymerization of methyl methacrylate (MMA) has been first examined in details; the corresponding results are presented and discussed in this paper.

\* Part I, see Ref. 1.

<sup>†</sup> To whom correspondence should be addressed.

<sup>‡</sup> Unit associated with CNRS and ENSCPB.

## EXPERIMENTAL

### Chemicals

Methyl methacrylate (Aldrich) and tetrahydrofuran were distilled before use over drying agent. Benzoyl peroxide (Janssen) was dissolved in  $\text{CHCl}_3$  and dried on  $\text{MgSO}_4$  before use.

### Extraction and Purification of Lignin

The flash hydrolysis of lignocellulosic materials was used to destroy the lignin original network. Wheat straw pretreated in acidic media (pH 3) was pressurized at 2 MPa and 180°C and exploded by fast deflating of pressure. The resulting mixture was then enzymatically hydrolyzed at pH ca. 5. The lignin fraction, insoluble in water, was separated from the osidic fraction by filtration. Lignin was then submitted to further purification and fractionation before use: Carbohydrates, enzymes, and minerals were eliminated by repeated washing with distilled water.

The lignin residues obtained after this treatment are only partly soluble in organic solvents.

After drying, lignin was fractionated by THF extraction of the soluble fraction, in a Soxhlet. About 45% (in weight) of the total lignin was then recovered after this treatment.

### Characterization of Lignin S.

- Elemental analysis: C 65%, H 7%, O 27.5%.
- Hydroxyl content: the percentage of phenolic groups was measured by conductimetric titration in aqueous solution by NaOH. The total amount of hydroxyls (phenolic + aliphatic hydroxyls) was determined by addition of excess acetic anhydride in the presence of *N*-methylimidazole and back titration of the nonreacted acetic acid, by conductimetry.
- Methoxyl content: an improved Zeisel gas chromatography technique has been developed for the determination of the methoxyl content. The method uses hydriodic acid to catalyse the cleavage of the alkoxy groups quantitatively to their corresponding alkyl iodides. These iodides are separated and titrated by gas chromatography.<sup>13</sup>

### Acetylation of Lignin

It was achieved by reacting acetic anhydride in the presence of *N*-methylimidazole as a catalyst, in  $\text{CH}_2\text{Cl}_2$ , at 45°C.<sup>14</sup> After 20 min, the reaction medium was acidified by HCl (2*N*) and washed with a

saturated  $\text{NaHCO}_3$  solution. Lignin AC solubilized in  $\text{CH}_2\text{Cl}_2$  was precipitated in *n*-hexane, filtered off, and dried under vacuum. The amount of remaining hydroxyls was checked and was found to be close to zero.

### Copolymerization

Copolymerizations of MMA with lignin S or lignin AC were performed under vacuum or  $\text{N}_2$  atmosphere in a schlenk apparatus. A dioxane solution of lignin, MMA, and benzoyl peroxide in dioxane solution were respectively added in the apparatus and the temperature was raised to 90°C. For kinetic determinations, sampling of the reaction medium was performed with a syringe through a septum. Monomer conversions were determined by gas chromatography. At the end of the reaction, the reaction medium was filtered and the soluble part poured into methanol. The precipitated polymer part was then filtered off and dried under high vacuum. Polymer yields were determined by gravimetry.

### Characterization of the Polymers

SEC analyses were performed on a Varian Vista 5500 apparatus equipped with 4 TSK microstyragel columns.

- 1% polymer solutions in THF were used.
- UV detection was performed at 280 nm.

The amount of lignin in the polymers was determined by UV spectrometry at 280 nm on the basis of the absorption maximum extinction coefficient of lignin *organosolv* ( $\epsilon = 3900 \text{ mol}^{-1} \text{ cm}^{-1}$ ).

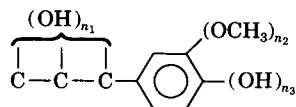
## RESULTS AND DISCUSSION

### Origin and Characteristics of Lignin Used

This study has been performed on lignin wheat straw fragments obtained by flash hydrolysis under high pressure, according to a procedure developed by AS-CAF Cy and presented in the experimental section.

The THF soluble fraction (45% in weight), denoted lignin S, was used as the starting material. The composition and structure of lignin S fragments were established by elemental analysis, acid-base titration of phenolic and aliphatic hydroxy groups, and determination of the methoxy content according to Zeisel procedure.<sup>15</sup> Assuming, as an elemental building unit of lignin S, the phenyl propane moiety,

analytical data indicate the predominance of guaiacyl type structures with the average following composition:



$$n_1 = 0.50 - 0.03, n_2 = 0.80 - 0.02, n_3 = 0.37 \pm 0.03$$

Average molar masses and molar mass distribution of lignin S samples have been determined by SEC (polystyrene calibration) and Vapor Phase Osmometry (VPO).

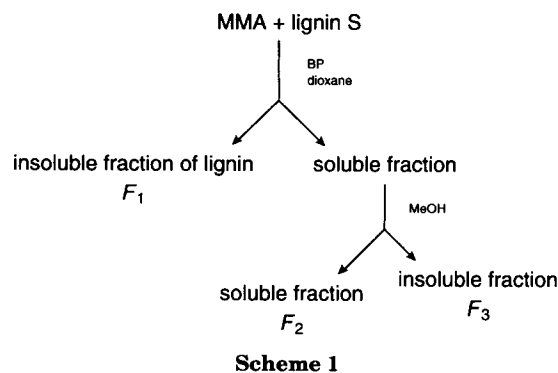
$$\bar{M}_{n \text{ SEC}} = 900 \quad \text{and} \quad \bar{M}_w / \bar{M}_n \approx 3$$

$$\bar{M}_{n \text{ VPO}} = 1150 \pm 100$$

The experimental values correspond to an average of five to six phenyl propane units per lignin S fragment.

### Polymerization of Methyl Methacrylate in the Presence of Lignin S

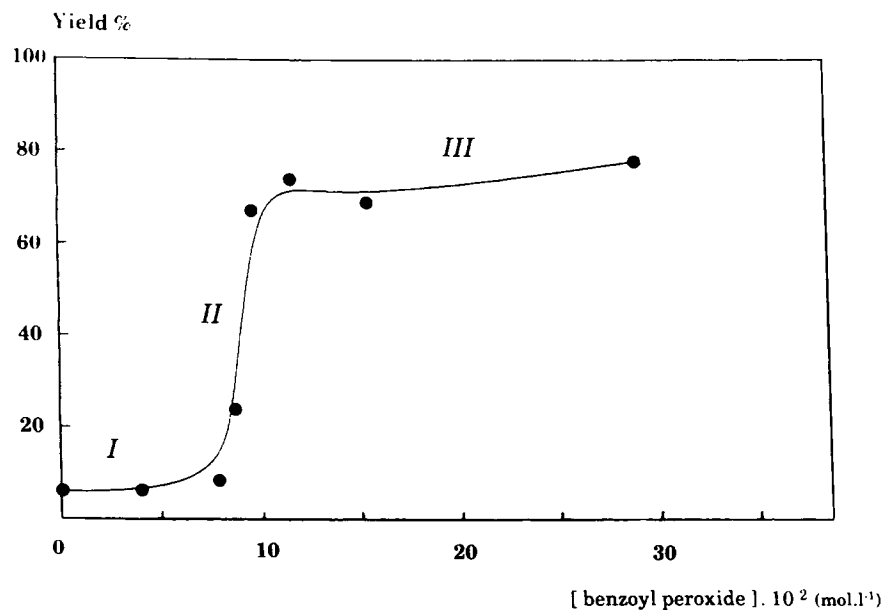
Polymerizations of MMA in the presence of variable amounts of lignin S have been performed in dioxane, a solvent in which the whole of lignin S is soluble.



Benzoyl peroxide (BP) was used as an initiator. The polymerizations were stopped when at least 99% of BP was decomposed.<sup>16</sup>

In all experiments, partial insolubilization of lignin S was observed during the reaction; the insoluble fraction ( $F_1$ ) was recovered by filtration; the soluble fraction was then precipitated by methanol, allowing the fractionation between ungrafted lignin ( $F_2$ ) (dioxane soluble + methanol soluble parts) from poly(methyl methacrylate-*g*-lignin S) and/or homopoly(methyl methacrylate) ( $F_3$ ). The fractionation breakdown is represented in Scheme 1.

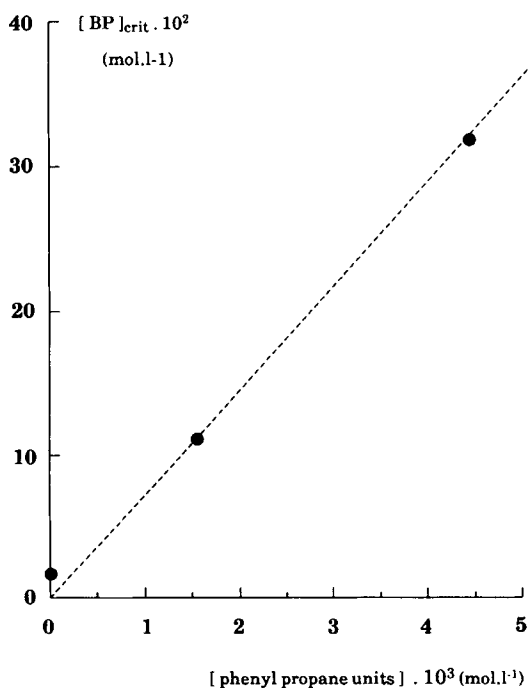
In a first series of experiments, polymerizations were performed using constant lignin S and MMA initial concentrations and increasing amounts of the



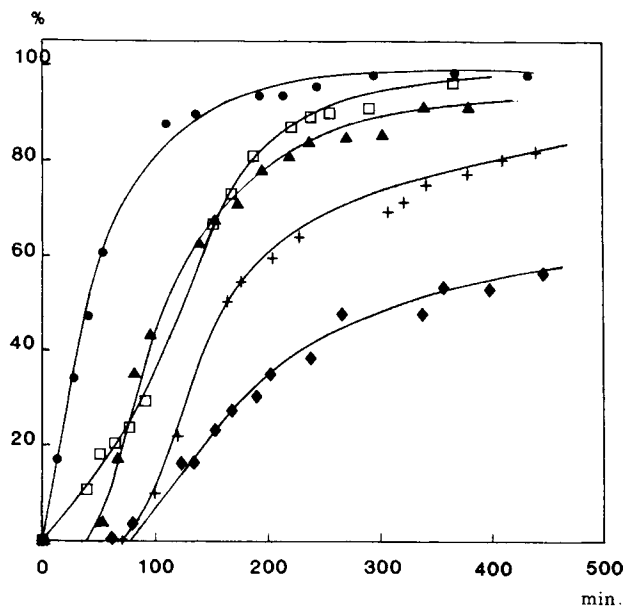
**Figure 1** Influence of the initial concentration of benzoyl peroxide on the polymerization of MMA, in the presence of lignin S: [MMA] = 3.9 mol L<sup>-1</sup>, [lignin]/[MMA] = 14% in weight; solvent, dioxane;  $T = 90^\circ\text{C}$ , reaction time 6 h.

initiator. The variation of PMMA yields with respect to BP concentration is presented in Figure 1. The polymerization of MMA does not occur in the lower BP concentration range, whereas, in the absence of lignin S, complete conversion of MMA is already observed for  $[BP] < 15 \times 10^{-3} \text{ mol L}^{-1}$ ; formation of PMMA becomes effective only when higher BP concentrations are used. A fast increase in final polymer yields is first observed (Fig. 1, part II of the curve) until they level off for about 70–80% PMMA recovered from methanol precipitation. It was checked that these yields corresponded to complete MMA monomer conversion. The formation of a low molar mass fraction of polymer soluble in methanol should therefore be taken into account in the reaction balance. The critical BP concentration ( $[BP]_{\text{crit}}$ ) capable of leading to complete conversion, corresponds to a  $[BP]_0/[lignin \text{ units}]_0$  ratio equal to  $0.37 \pm 0.03$ . This value closely fits with the number of phenolic hydroxyl groups found per lignin unit. It should be noticed that a similar polymerization behavior was observed in THF or in bulk.

In order to corroborate the relationship between the number of phenolic functions and  $[BP]_{\text{crit}}$ , experiments were performed in the presence of variable amounts of lignin S. The variation of  $[BP]_{\text{crit}}$  with increasing amounts of lignin S units in the system is shown on Figure 2; an almost linear relationship



**Figure 2** Variants of  $[BP]_{\text{crit}}$  with the initial concentration of lignin units in the reaction medium.



**Figure 3** Conversion-time curves for the polymerization of MMA in dioxane at  $90^\circ\text{C}$  in the absence of lignin S,  $[MMA] = 3 \text{ mol L}^{-1}$ : (●)  $[BP] = 8 \times 10^{-2} \text{ mol L}^{-1}$ . In the presence of lignin S:  $[lignin]/[MMA] = 14\%$  in weight;  $[MMA] = 3 \text{ mol L}^{-1}$ : (◆)  $[BP] = 6.8 \times 10^{-2} \text{ mol L}^{-1}$ ; (+)  $[BP] = 7.3 \times 10^{-2} \text{ mol L}^{-1}$ ; (▲)  $[BP] = 9.6 \times 10^{-2} \text{ mol L}^{-1}$ ; (□)  $[BP] = 12.9 \times 10^{-2} \text{ mol L}^{-1}$ .

is observed, its slope approaching 0.37 and closely related to the number of phenolic hydroxyls per lignin unit. These results therefore support the quantitative reaction of phenolic functions of lignin with benzoyl peroxide or, more likely, with free radicals derived from benzoyl peroxide.

Kinetics of the MMA polymerization in the presence and in the absence of lignin S have been examined and compared. The polymer conversions versus time are plotted in Figure 3 for various experiments. Depending on the  $[BP]/[lignin \text{ S units}]$  ratio, either an inhibition or a retardation process is observed. The retardation process increases with a decreasing  $[BP]/[lignin \text{ S units}]$  ratio, again supporting that, even for high BP concentration in which PMMA is formed, a fraction of primary free radicals is consumed by reacting with lignin S units. This is further confirmed by the values of apparent polymerization rate constants, calculated for various  $[BP]/[lignin \text{ S}]$  ratio assuming as kinetic equation:

$$\frac{-d[MMA]}{dt} = R_p = [MMA] \cdot [BP]_{\text{eff}}^{1/2}$$

$$-\ln [MMA] = k_p \cdot [BP]_{\text{eff}}^{1/2} \cdot t + \text{const}$$

Therefore, the apparent polymerization rate constant is

$$k_{app} = k_p \cdot [BP]_{eff}^{1/2}$$

Data presented in Table I are consistent with [BP] efficiency much lower than that observed in the absence of lignin S and corresponding to

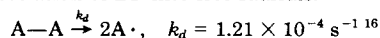
$$[BP]_{eff} = [BP]_0 - [BP]_{crit}$$

or

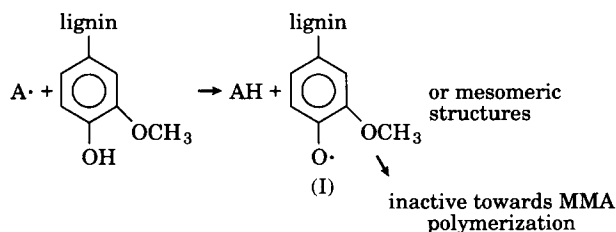
$$[BP]_{eff} = [BP]_0 - [OH]_{phenol}$$

From these results and relevant literature data on the reaction mechanism of phenol<sup>17</sup> with free radicals, a reaction pathway can be proposed (Scheme 2).

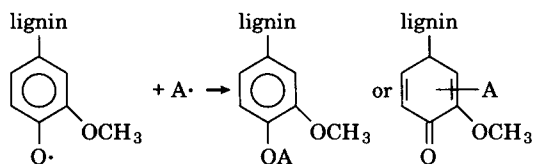
(a) Dissociation of BP into free radicals:



(b) Hydrogen abstraction from phenolic hydroxyls of lignin:



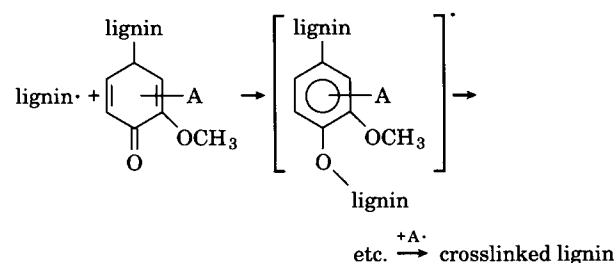
(c) Coupling of lignin free radicals with A· (or A—):



Scheme 2

In this reaction scheme, one BP molecule (two free radicals) is involved per phenolic function, in agreement with experimental data. However, it should be pointed out that this reaction scheme does take the insolubilization process of lignin fragments into account. Experiments performed in the presence of lignin S and BP free radicals (without MMA) result in complete insolubilization of lignin. This was explained by the condensation of lignin fragments.

A possible condensation mechanism might involve the reaction of lignin free radicals (type I) with quinonic structures, prior to deactivation by coupling (c):



The molar masses of polymers obtained with and without lignin S in the reaction medium, are collected in Table II: An important decrease of the  $\bar{M}_n$  of PMMA recovered from methanol as well as an increase of the soluble fraction of oligomers is observed in the presence of lignin S. This might suggest that the termination process discussed earlier is still operative during the polymerization stage. However, since the apparent polymerization rate constant  $k_p$  does not depend significantly on [lignin S] and  $[BP]_{eff}$  it should be considered that lignin units act as transfer agents. Moreover, it can be mentioned that  $\bar{M}_n$  decreases strongly with [lignin S].

Table I Apparent Rat Constant for the Polymerization of MMA in the Absence and Presence of Lignin S, with Variable Amounts of Benzoyl Peroxide<sup>a</sup>

$10^2 \times [BP]_0$ (mol L <sup>-1</sup> )	[Lignin S] $\Phi_{pr}$ <sup>b</sup> Units] (mol L <sup>-1</sup> )	$10^2 \times [OH]_{ph}$ <sup>c</sup> (mol L <sup>-1</sup> )	$10^2 \times [BP]_0 - [OH]_{ph}$ (mol L <sup>-1</sup> )	$10^5 \times k_{app}$ (s <sup>-1</sup> )	$10^4 \times k_p^d$ (s <sup>-1</sup> L <sup>1/2</sup> mol <sup>-1/2</sup> )	$10^4 \times k_p^e$ (s <sup>-1</sup> L <sup>1/2</sup> mol <sup>-1/2</sup> )
8	0	0	8	29.5	10.4	10.4
6.8	0.24	6.1	0.7	5.45	2.1	6.8
7.3	0.23	5.9	1.4	8.7	3.2	7.3
9.6	0.24	6.2	3.4	16.1	5.2	8.7
12.9	0.24	6.1	6.8	21.3	5.9	8.2

<sup>a</sup> [MMA] = 3 mol L<sup>-1</sup>, solvent, dioxane; T = 90°C.

<sup>b</sup>  $\Phi_{pr}$  = phenyl propane (unit mass = 180 g mol<sup>-1</sup>).

<sup>c</sup> ph = phenol.

<sup>d</sup>  $k_p^d = k_{app}/[BP]^{1/2}$ .

<sup>e</sup>  $k_p^e = k_{app}/[BP - OH]_{phenol}^{1/2}$ .

**Table II** Characterization of PMMA and Poly(lignin-*g*-MMA) Obtained with Various Concentrations of Benzoyl Peroxide

[MMA] (mol L <sup>-1</sup> )	[Lignin Φ <sub>pr</sub> <sup>a</sup> Units] (mol L <sup>-1</sup> )	10 <sup>2</sup> × [BP] (mol L <sup>-1</sup> )	10 <sup>3</sup> × [BP]/ [MMA]	Polymer Yield (%)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
2.8	0	6.15	22	84	17,300	2.4
4.4	0	0.87	2	62	53,000	2
3.9	0	0.47	1.2	32	122,000	2.5
3.9	0.3	8.7	22.3	24	8800	2.2
3.9	0.3	9.7	24.9	67	11,200	3.8
3.9	0.3	11.7	30	74	11,800	3.5
3.9	0.3	15.6	40	69	10,000	3.6
3.9	0.3	19.5	50	61	10,600	2.7
3.9	0.3	29.2	74.9	78	8100	8.5

<sup>a</sup> Φ<sub>pr</sub> = phenyl propane (unit mass = 180 g mol<sup>-1</sup>).

Structure of polymers obtained in the presence of lignin S has been examined by UV spectrometry titration and SEC by using a double detection procedure. Chromatograms of lignin S, PMMA prepared in lignin-free conditions and MMA-lignin copolymers, are presented in Figure 4: Lignin S units and MMA units are sensitive respectively and uniquely to UV or RI detection. Incorporation of lignin S into PMMA chains can therefore be extrapolated from the double UV and RI response of the copolymer. The lignin content of copolymers was then determined by UV on the basis of the absorbance peak at 280 nm ( $\epsilon = 3900 \text{ L mol}^{-1} \text{ cm}^{-1}$ , where mole refers to phenyl propane units of mass 180) of lignin units. Average compositions of copolymers are given in Table III. Results are consistent with an average value of one lignin fragment per PMMA chain.

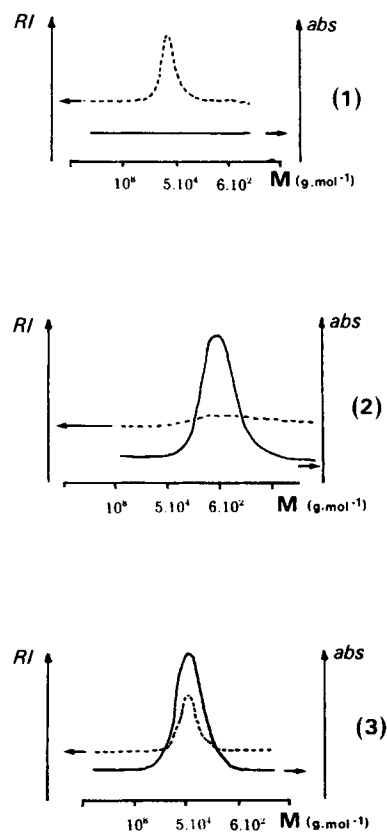
The mechanism of lignin incorporation into PMMA chain will be discussed in the following section.

#### Polymerization of MMA in the Presence of Acetylated Lignin (Lignin AC)

In order to suppress the inhibiting action of phenolic hydroxyl groups, lignin S was converted into the corresponding acetate. Quantitative acetylation of hydroxy functions (both aromatic and aliphatic) was achieved by reacting acetic anhydride in the presence of *N*-methylimidazole. Acetylation conditions and characterization of the products are given in the experimental section.

Polymerizations of MMA, in the presence of acetylated lignin, have been examined with experimental conditions similar to that described in the

previous section. As can be seen in Table IV, the polymerization of MMA proceeds for the whole range of BP concentrations examined, even for very low initiator concentrations. Typical kinetic curves are presented in Figure 5. Neither inhibition nor



**Figure 4** SEC chromatograms of PMMA (1), of lignin S (2), and of PMMA-*g*-lignin S copolymer (3): concentration 1%; elution solvent, THF.

**Table III Variants of the Number of Lignin S Fragments per PMMA Chain for Variable Concentrations in BP<sup>a</sup>**

$10^2 \times [\text{BP}]$ (mol L <sup>-1</sup> )	Polymer Yield (%)	$M_{\text{peak}}$	[Lignin Fragments]/ [PMMA Chain]
3.9	0	—	—
7.8	0	—	—
8.75	24	14,700	1.5
9.75	67	18,600	0.9
11.7	74	20,200	0.9
15.6	69	13,600	0.6
19.5	61	12,600	0.7
29.2	78	13,600	0.7

<sup>a</sup> [Phenyl propane units] = 0.4 mol L<sup>-1</sup>; [MMA] = 3.9 mol L<sup>-1</sup>.

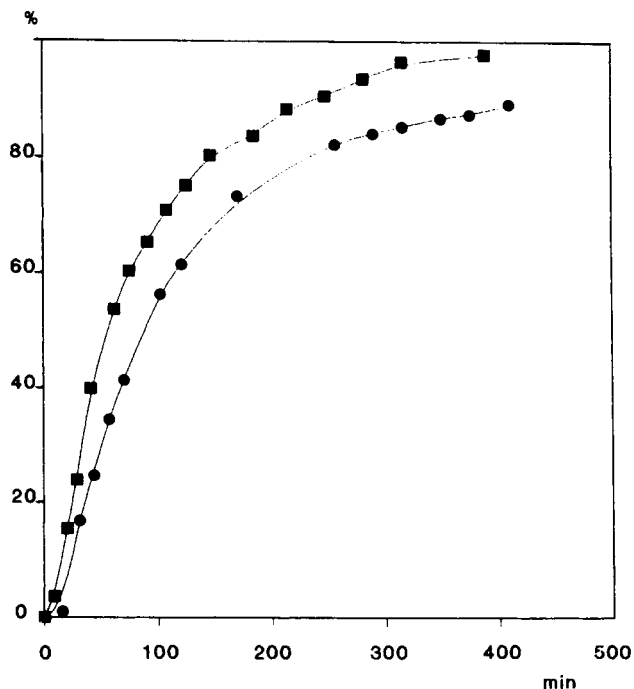
retardation period for MMA polymerization is observed in the presence of lignin AC, supporting again the predominant role of hydroxylic functions in the inhibition process observed with lignin S. Besides, crosslinking of lignin AC was not observed during the polymerization reaction. This suggests, as proposed in Scheme 3, that phenolic structures also play a determining role in the condensation process.

Chemical composition and molar masses of lignin AC-MMA copolymers—determined according to the procedure previously reported—are given in Table IV. Molar masses are intermediate between those of PMMA and lignin S-MMA copolymers. A typical SEC chromatogram of lignin AC-MMA copolymer is given in Figure 6. Chemical composition is again consistent with an average value of 1–1.5 lignin AC fragment per PMMA macromolecule (Table IV). The similar compositions of MMA-lignin S and

**Table IV Variants of the Number of Lignin AC Fragments per PMMA Chain for Variable Concentrations in BP<sup>a</sup>**

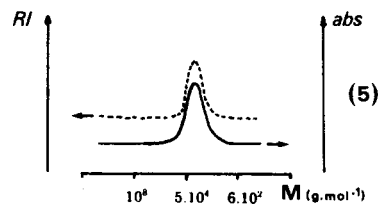
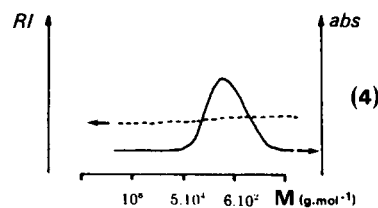
$10^2 \times [\text{BP}]$ (mol L <sup>-1</sup> )	Polymer Yield (%)	$M_{\text{peak}}$	[Lignin Fragments]/ [PMMA Chain]
0.5	23	—	—
1.0	26	43,000	1.5
1.2	25	49,300	1.7
2.9	52	28,100	1.3
4.9	70	26,000	1.0

<sup>a</sup> [Phenyl propane units] = 0.4 mol L<sup>-1</sup>; [MMA] = 2.5 mol L<sup>-1</sup>.



**Figure 5** Conversion-time curves for the polymerization of MMA in dioxane at 90°C in the presence of lignin AC: [lignin AC]/[MMA] = 30% in weight; [MMA] = 3 mol L<sup>-1</sup>; (●) [BP] =  $4.5 \times 10^{-2}$  mol L<sup>-1</sup>; (■) [BP] =  $5.75 \times 10^{-2}$  mol L<sup>-1</sup>.

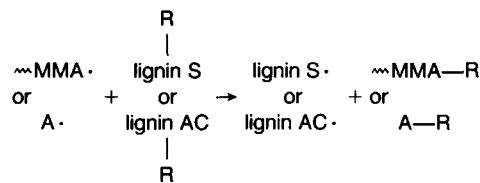
MMA-lignin AC copolymers show that lignin incorporation into polymeric chains does not predominantly result from the coupling termination process between PMMA macroradicals and free radicals de-



**Figure 6** SEC chromatograms of lignin AC (4) and of PMMA-*g*-lignin AC copolymer (5): concentration 1%; elution solvent, THF.

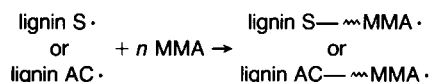
rived from lignin phenolic structures (Step c, Scheme 2). A different lignin incorporation process based on a transfer reaction and common to both lignin S and lignin AC is proposed:

(a) Radical transfer onto lignin fragments:



with R = H or organic radical

(b) Initiation of MMA polymerization:



Scheme 3

Depending on the relative rate of propagation and transfer as well as on the contribution to termination process of either chain coupling or disproportionation, an average value of 0 to 2 lignin fragments per PMMA chain can be incorporated into the macromolecule. Decreases of the  $\bar{M}_n$  of the PMMA in the presence of lignin AC, or lignin S, without any noticeable effect on apparent polymerization rate constants (Tables II and IV) tend to support the hypothesis of a transfer process. However, it must be considered in this case that these lignin free radical intermediates are active initiators for MMA polymerization, suggesting that they are different from those involving lignin phenolic groups (type I, Scheme 2).

## CONCLUSIONS

The radical polymerization of MMA, initiated by benzoyl peroxide in the presence of lignin S or lignin AC has been examined. Results lead to the following comments:

- Unmodified lignin (lignin S) is an inhibitor of MMA radical polymerization and very likely of the polymerization of other ethylenic monomers. Inhibition may be attributed to phenolic groups present in lignin.
- In order to allow radical polymerization, it is necessary to operate with an excess of initiator with respect to the number of phenolic func-

groups by acetylation or any other method.

- In the latter conditions, lignin-MMA copolymers can be obtained. Incorporation of lignin results mainly from a transfer process and therefore copolymers with only a low content of lignin can be expected.

Thus, in order to prepare copolymers with higher lignin content, these observations have led us to study the anchoring of polymerizable groups on lignin moieties. The corresponding results will be reported in a forthcoming paper.

Authors thank A.F.M.E. for its financial support.

## REFERENCES

1. P. Dournel, E. Randrianalimanana, A. Deffieux, and M. Fontanille, *Eur. Polym. J.*, **24**(9), 843 (1988).
2. V. P. Saraf and W. G. Glasser, *J. Appl. Polym. Sci.*, **29**, 1831 (1984).
3. O. H.-H. Hsu, and W. G. Glasser, *Appl. Polym. Symp.*, **28**, 297 (1975).
4. O. H.-H. Hsu, and W. G. Glasser, *Wood Sci.*, **9**(2), 97 (1976).
5. W. G. Glasser and H. Hsu, in *Urethane Chemistry and Applications*, K. Edwards, Ed., ACS Symp. Series. No. 172, Washington, DC, 1981, p. 311.
6. Koshijima and E. Muraki, *J. Polym. Sci.*, **6**, 1431 (1968).
7. Nam, T. Koshijima, E. Muraki, and T. Maku, *J. Polym. Sci.*, **9**, 855 (1971).
8. R. L. Chen, B. V. Kokta, C. Daneault, and J. L. Valade, *J. Appl. Polym. Sci.*, **32**, 4815 (1986).
9. S. Katuscak, M. Mahdalik, A. Hrivik, and V. Minarik, *J. Appl. Polym. Sci.*, **17**, 1919 (1973).
10. R. B. Phillips, W. Brown, and V. T. Stannett, *J. Appl. Polym. Sci.*, **15**, 2929 (1971).
11. R. B. Phillips, W. Brown, and V. T. Stannett, *J. Appl. Polym. Sci.*, **16**, 1 (1972).
12. R. B. Phillips, W. Brown, and V. T. Stannett, *J. Appl. Polym. Sci.*, **17**, 443 (1973).
13. M. Girardin and M. Metche, *J. Chromatogr.*, **264**, 155 (1983).
14. K. A. Connors and N. K. Pandit, *Anal. Chem.*, **50**, 11 (1978).
15. K. L. Hodges, W. E. Kester, D. L. Wiederrich, and J. A. Grover, *Anal. Chem.*, **51**(13), 2172 (1979).
16. J. P. Bop, C. Filliatre, B. Maillard, and J. J. Villenave, *Thermochim. Acta*, **43**, 339 (1981).
17. Y. Minoura, N. Yasimoto, and T. Ishii, *Makromol. Chem.*, **71**, 159 (1964).

Received April 8, 1991

Accepted May 14, 1991