Synthesis and Polymerization of Lignin-Based Macromonomers. III. Radical Copolymerization of Lignin-Based Macromonomers with Methyl Methacrylate

C. DA CUNHA, A. DEFFIEUX,* and M. FONTANILLE

Laboratoire de Chimie des Polymères Organiques,† ENSCPB-Université Bordeaux-1, 351, cours de la Libération, 33405 Talence Cedex, France

SYNOPSIS

The radical copolymerization of methyl methacrylate (MMA) with lignin fragments (resulting from flash hydrolysis) functionalized by polymerizable groups is investigated. To transform lignin fragments into macromonomers, the anchoring of styrenyl and methacryloyl groups has been first studied; the optimal conditions for an etherification or an esterification of hydroxy functions in lignin residues, by chloromethylstyrene and methacryloyl chloride leading to lignin-macromonomers of controlled size and functionality, have been investigated. The influence of experimental conditions on both the degree of substitution and the characteristics of functionalized lignin fragments is discussed; linear and cross-linked lignin–MMA copolymers have been prepared. The accurate control of the number of anchored polymerizable groups per lignin fragment is a determining step that establishes the dimensionality of the chains and therefore the processability of the prepared copolymers. "Linear" lignin–MMA copolymers containing up to 40% in mass of lignin have been obtained and some structural aspects of the corresponding materials are examined.
© 1993 John Wiley & Sons, Inc.

INTRODUCTION

The behavior and effects of unmodified and modified lignin residues on the radical homopolymerization of methyl methacrylate (MMA) were examined in a previous paper.[1] In agreement with earlier works, it was observed that unmodified lignin fragments inhibit the radical polymerization of MMA; this was attributed to the fast abstraction of hydrogen from lignin phenolic groups by primary free radicals leading to the formation of nonreactive phenoxy radicals.[2,3] To allow the polymerization to proceed, it was necessary to generate excess primary free radicals with respect to the total number of the phenolic lignin functions present in the systems; this could be achieved either by using a large amount of radical initiator or by protecting the phenolic groups by

acetylation. In such conditions, lignin–MMA copolymers were obtained; however, the incorporation of lignin moieties into the polymeric chains resulted mainly from a transfer reaction process. Therefore, only copolymers with a very low lignin content (one to two lignin fragments per chain) could be prepared.

To synthesize copolymers with a higher lignin content, polymerizable groups had to be anchored on lignin moieties in order to incorporate them into the chains by subsequent copolymerization. The synthesis and polymerization of lignin derivatives with acrylate functions were first reported by Naveau.[4] Lignin methacrylate macromonomers were prepared by reacting either methacrylic anhydride or methacryloyl chloride with a Kraft lignin to obtain multifunctional derivatives; according to the experimental conditions, 20–70% of the lignin fragments could be functionalized by methacryloyl groups. The copolymerization with MMA gave cross-linked networks.

Another route to acryloylation of lignin fragments has been recently described by Glasser and Wang.[5]

---

* To whom correspondence should be addressed.
† URA-CNRS.

It is based on the use of an acrylic monomer with an isocyanate group. The latter gives a urethane linkage by reaction with lignin hydroxyls; model molecules of lignin derivatives were functionalized in this way. Their reactivity in copolymerization with MMA and styrene was then examined: A trend toward an alternating placement was observed. Acrylic lignin derivatives were also copolymerized with vinyl monomers yielding networks.[5]

The aim of the present paper was to examine some functionalization routes of lignin fragments by polymerizable groups and to study their copolymerization with MMA in order to prepare processable linear lignin–MMA copolymers with a higher content in lignin moieties.

RESULTS AND DISCUSSION

To obtain "monodimensional" lignin–MMA copolymers, the major problem is to control the average functionality of polymerizable lignin derivatives to avoid cross-linking; to achieve this, it is preferable to use original lignin fragments with relatively homogeneous structure and molecular weight.

These lignin fragments were obtained from flash hydrolysis of wheat straw and extracted by THF. Only the THF soluble fraction was used as starting material. Its structural characteristics, i.e., average molar mass, molar mass distribution, and functionality in hydroxy groups of the lignin moieties, have been reported in a previous paper[1]; they are given in Scheme 1.

Functionalization of Lignin Fragments by Polymerizable Groups

The phenolic and aliphatic hydroxy groups of lignin moieties (see Scheme 1) were used for the anchoring of polymerizable functions. Their relative reactivity toward nucleophilic substitution by methacryloyl chloride and chloromethylstyrene has been examined.

1. Synthesis of a Methacrylic Lignin Macromonomer (Noted Macromonomer I)

$$n1 = 0.50 \pm 0.03$$
$$n2 = 0.80 \pm 0.02$$
$$n3 = 0.37 \pm 0.03$$
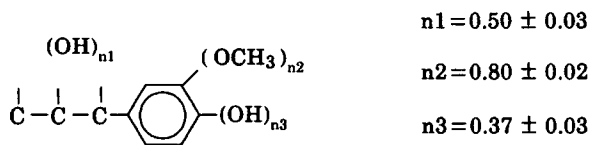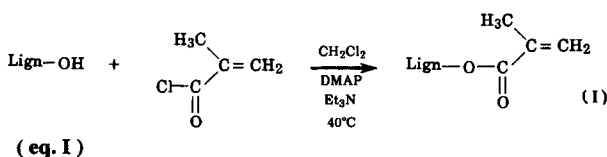
$$M_{n\,SEC} = 900 \quad M_w/M_n \simeq 3$$

$$820 < M_{n\,VPO} < 980$$

Scheme 1 Average structural characteristics of lignin moieties used.

Though starting in heterophasic conditions since lignin fragments are not soluble in CH_2Cl_2, lignin functionalization by methacryloyl groups can be achieved under mild conditions by reacting methacryloyl chloride and lignin in the presence of dimethylaminopyridine (DMAP) and triethylamine. Lignin acylation proceeds rapidly and results in fast and complete solubilization of acylated lignin in the reaction medium.

Because of the relatively high catalytic activity of DMAP compared to pyridine toward the acylation of hydroxy groups, complete substitution of phenolic and aliphatic hydroxy was obtained. The ^{13}C-NMR spectrum of lignin moieties fully substituted by methacryloyl functions is presented in Figure 1. The characteristic resonance peaks of the methacryloyl groups are indicated on the spectrum. For an average anchoring of one methacryloyl group per lignin fragment, partial substitution of hydroxy groups can be easily achieved by adjusting the relative amount of reactants.

Average molar masses of lignin–acrylate fragments have been measured by VPO and SEC. An SEC chromatogram of lignin moieties before and after acryloylation is presented in Figure 2. As can be seen in Table I, acryloylation results in a marked increase in molar masses of lignin moieties that cannot be completely explained by the anchoring of methacryloyl groups, suggesting some coupling of lignin residues during the reaction.

2. Synthesis of a Styrenyl Lignin Macromonomer (Noted Macromonomer II)

The anchoring of styrenyl groups onto lignin was attempted by reacting chloromethylstyrene (CMS) in the presence of a phase transfer catalyst (TBAB) [eq. (IIa)].[6,7] This reaction has been first investigated on model compounds[8] with satisfactory results. However, though the hooking of styrenyl units on lignin moieties could also be achieved, the rather
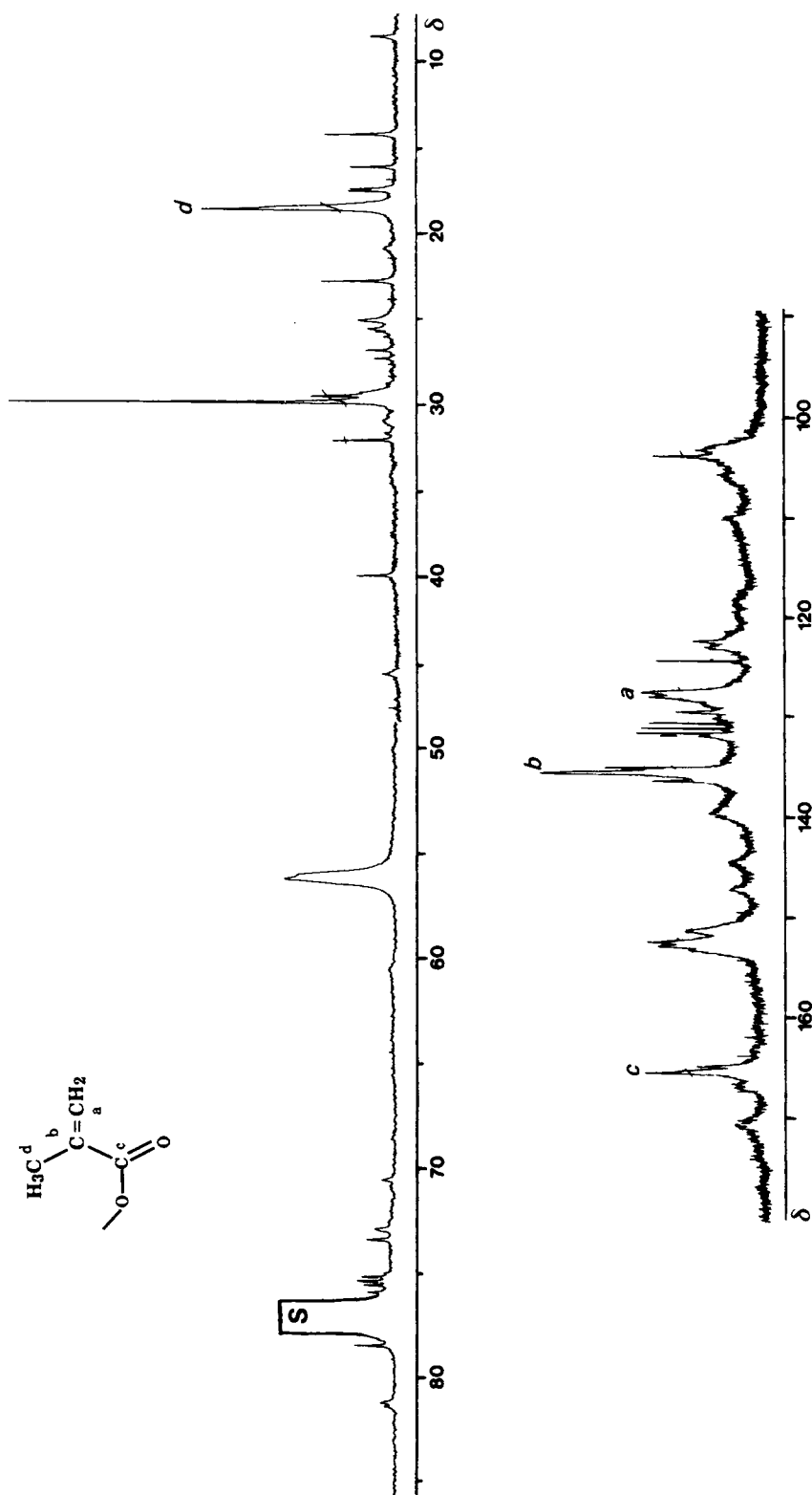
Figure 1 ^{13}C-NMR spectrum of lignin fully substituted by methacryloyl groups. Solvent CDCl$_3$.
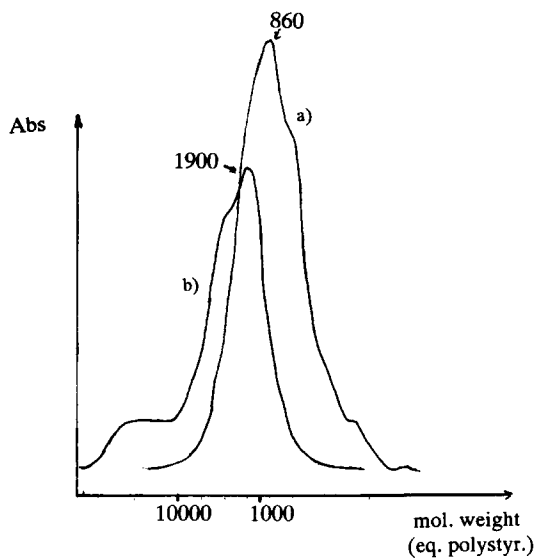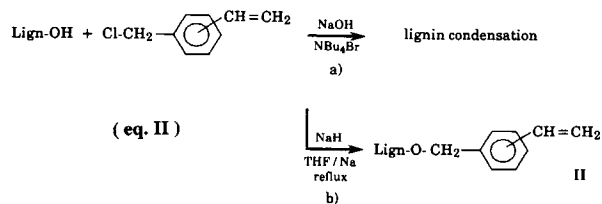
Figure 2   SEC chromatograms of lignin fragments: (a) before modification; (b) substituted by methacryloyl groups.

basic conditions required led to side condensation reactions of lignin that became insoluble in organic solvents; this route was therefore not suited to control the size and functionality of the modified lignin fragments:

Better results were obtained by first preparing the sodium salt of lignin from NaH in dry THF, followed by addition of CMS to the reaction mixture [eq. (IIb)].

The ^{13}C-NMR spectrum of lignin reacted with CMS is presented in Figure 3. The characteristic styrenyl resonances are indicated, showing the satisfactory anchoring of the polymerizable groups. The molar masses of styrenyl–lignin fragments were found to be in good agreement with the anchoring of one or two styrenic groups per fragment (Table II).

Although the esterification of lignin proceeded up to complete consumption of the phenolic and aliphatic hydroxy, etherification by CMS remained incomplete whatever the amount of the reactant and the experimental conditions used. From selective titration of initial and final phenolic and aliphatic

groups, it has been concluded that CMS reacts only on phenolic hydroxy groups.

3. Acetylation of Macromonomers (I) and (II)

As has been previously mentioned,[1] phenolic groups of lignin inhibit radical polymerization of MMA; their masking was necessary to allow polymerization. In the case of macromonomers **I** and **II**, this has been carried out by acetylating the remaining hydroxy groups of methacryloyl and styrenyl-functionalized lignin fragments, with acetic anhydride in the presence of N-methylimidazole[9]:
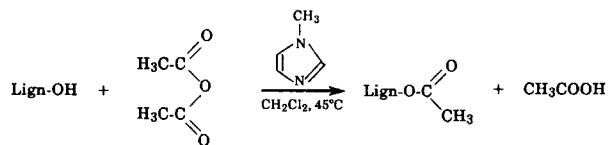
As already mentioned for the synthesis of methacrylated lignins (macromonomer **I**), acetylation of macromonomer **II** results in about a twofold increase of the molar mass of the fragments. This suggests again that some coupling occurs under the relatively basic conditions of acylation. Intermolecular esterification reactions between hydroxy functions and carboxylic groups might be involved in this side process, though their amount in lignin is low.

Radical Copolymerization of MMA with Multifunctional Lignin Macromonomers

Copolymerizations of MMA and lignin–macromonomers (**I**) or (**II**) were performed in conditions similar to those previously reported for radical polymerization of MMA in the presence of nonfunctionalized lignin[1], i.e., dioxane as a solvent, benzoyl peroxide as an initiator and $T = 90°C$.

To control the reactivity of anchored polymerizable functions on lignin fragments, a first series of copolymerization experiments were carried out in the presence of macromonomers with up to five

Table I   Molecular Weights of Lignin S and Lignin–Methacryloyl Fragments

	SEC[a]		VPO
	M_{peak}	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$
Lignin S	860	3.0	880
Methacryloyl lignin	1900	2.8	2050

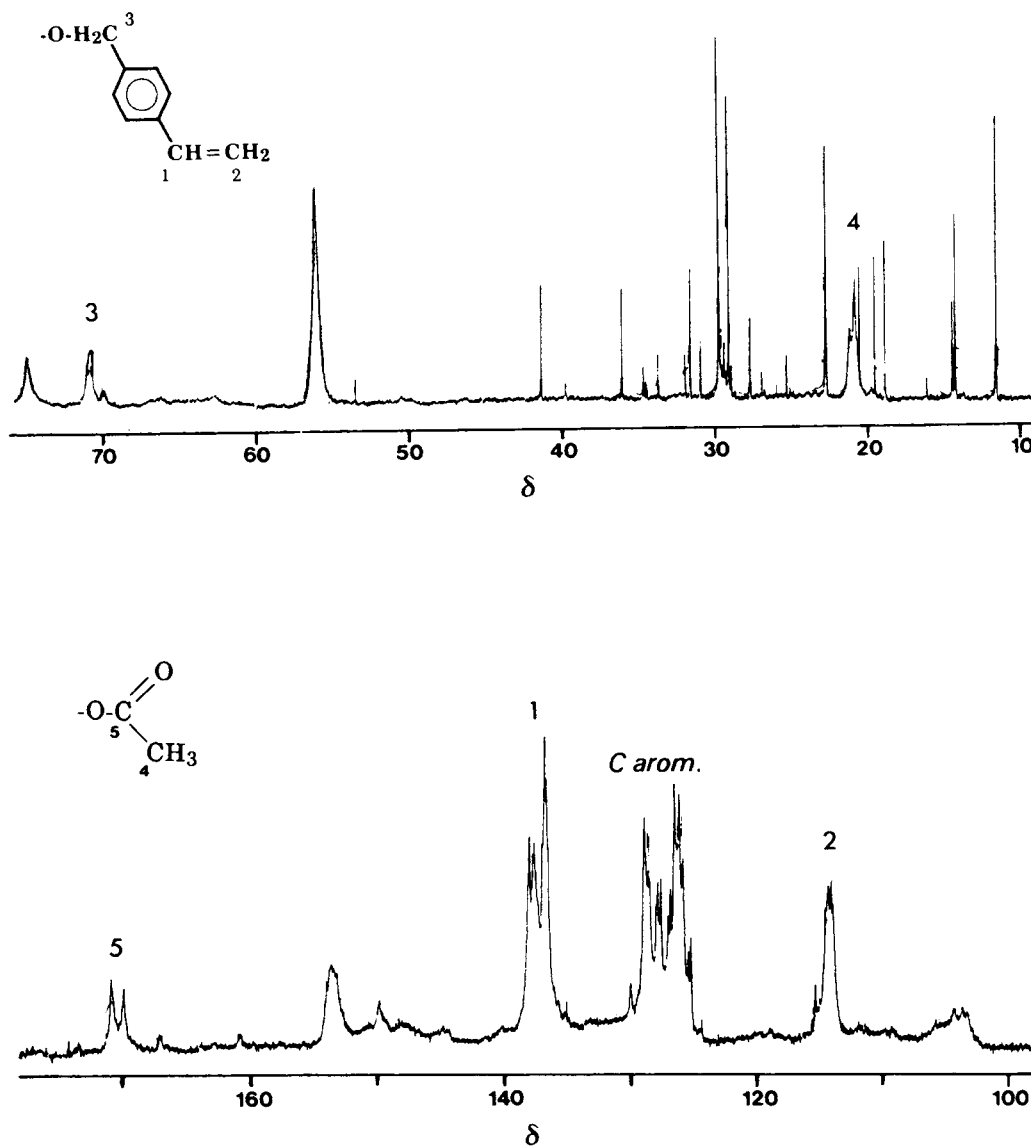[a] On the basis of polystyrene calibration.

Figure 3 ^{13}C-NMR spectrum of lignin substituted by styrenyl groups. Solvent CDCl$_3$.

methacryloyl groups per fragment. In this case, a drastic increase in the viscosity of the reaction medium, followed by the formation of a network was observed; this behavior was expected and is in agreement with the incorporation of multifunctional lignin units in the growing chains by means of their

Table II   Molecular Weights of Lignin S, Lignin–Styrenyl, and Lignin–Styrenyl–Acetylated Fragments

	SEC[a]			
	M_{peak}	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	VPO $\bar{M}_n$
Lignin S	860	880	3	880
Styrenyl–lignin	980	920	3	—
Acetylated styrenyl–lignin	2300	2150	2.8	2900

[a] On the basis of polystyrene calibration.
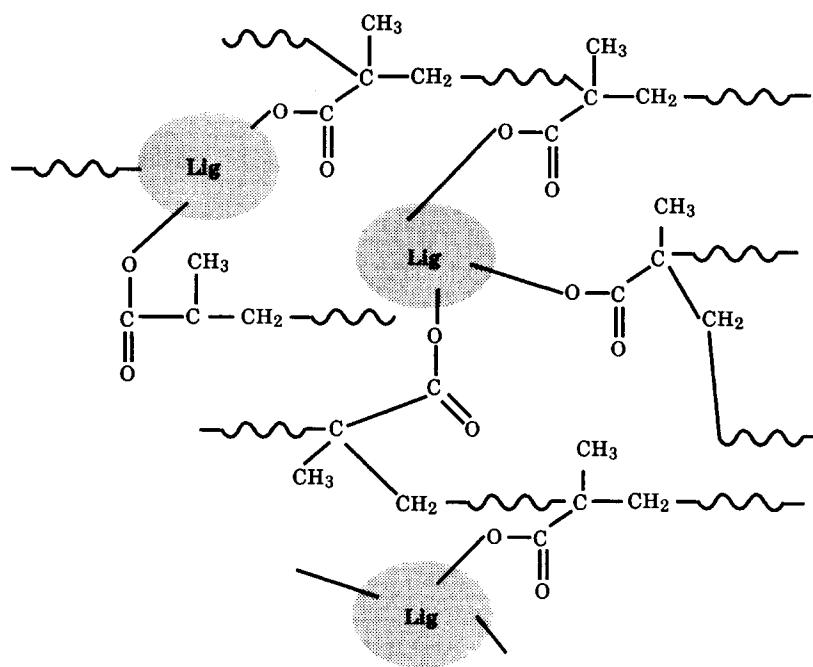
Scheme 2

polymerizable groups (Scheme 2) and not only through a transfer process as already noticed in the case of nonfunctionalized lignin moieties.

Radical Copolymerization of MMA with "Monofunctional" Lignin Macromonomers

The preparation of a soluble and processable uni-dimensional polymer theoretically implies the absence of multifunctional molecules in the monomer feed. The conditions for anchoring an average num-

ber of polymerizable groups per lignin moieties as close as possible to one have been investigated. To this end, the initial ratio between reactants ([methacryloyl chloride]/[lignin fragments]) were varied from 3.8 to 0.8 and the resulting macromonomer was checked in copolymerization with MMA. The corresponding experimental results are collected in Table III.

Even with a stoichiometry corresponding to about one polymerizable group per lignin fragment, the mass proportion of anchored functions ($< 10\%$) is

Table III   Synthesis of Lignin–MMA Copolymer with Macromonomers (Type I) of Various Functionality : Influence on the Copolymer Structure

$R = \dfrac{[\text{Acylation Reagent}]_0}{[\text{Lignin Fragment}]_0}$	[MMA] (mol L^{-1})	$\dfrac{[\text{BP}]}{[\text{MMA}]} \cdot 10^2$	Lignin MMA (% Weight)	Copolymer		$\Phi_p{}^b$ Swelling Ratio
				Network Fraction	Soluble Fraction[a]	
3.8	4.3	0.2	5	95	5	15.5
1.2	4.3	0.2	5	93	7	18.3
0.8	3.3	0.2	5	0	100	—
1.5	2.5	0.8	30	100	0	7.6
1.2	2.5	0.8	30	90	10	8.8
1.0	2.5	0.8	30	89	11	9.2
0.9	2.5	0.8	30	0	100	—

Initiator: benzoyl peroxide; solvent: dioxane; $T = 90°C$; time = 6 h; acylation reagent: methacryloyl chloride.
[a] Precipitated in MeOH.
[b] Measured on network in toluene.

very low and no quantitative measurement can be effected. However, an apparent average functionality of the macromonomers can be deduced from the dimensionality (mono- or tri-) of the copolymers obtained.

Fully soluble monodimensional copolymers were obtained only for initial molar ratio R = [methacryloyl chloride]/[lignin fragment] lower than 1; surprisingly, solubility in the reaction medium was observed for R values up to 0.9. For this upper limit value, the amount of lignin incorporated into polymer, without gel formation, can be expected to be optimal since it corresponds to the presence of a minimal proportion of nonfunctionalized lignin fragments.

However, it should be emphasized that, owing to the presence of approximately two reactive phenoxy groups as well as several other hydroxylic functions on lignin moieties, the formation of multifunctional macromonomers might also occur. This is shown in the following example in which both equireactivity of phenoxy groups was assumed and the contribution of aliphatic hydroxy with lesser reactivity was disregarded. If P is the reaction probability of a phenol group, the probability to form a difunctional macromonomer is equal to $2P^2$; for a ratio R = 0.9 and a complete reaction of methacryloyl chloride, this would lead to about one-third of difunctional macromonomer in the monomer feed.

Therefore, the absence of any detectable gel fraction in the lignin/MMA copolymers cannot be explained by accurate control of the functionality of lignin fragments alone. The formation of relatively low molar masses copolymers and the incorporation of a small number of macromonomer units per chain (*vide infra*) might contribute to limit cross-linking to chain extensions.

To differentiate between the lignin–MMA copolymers and unreacted lignin macromonomers, a fractionation of the polymerization mixture was performed by precipitation of the polymer into MeOH; in this solvent, the lignin macromonomers are soluble, whereas the copolymers precipitate. The amount of lignin incorporated into the PMMA chain was thus determined by UV titration on the basis of the absorbance of phenylpropane units (λ = 280 nm; ε = 3900 L mol^{-1} cm^{-1}); the corresponding number of lignin fragments per chain was determined from the molar masses of the copolymers, estimated from SEC; results in Table III show that copolymers obtained from this procedure contain several lignin fragments per chain (3–4).

It should be noticed, as shown in a previous paper,[1] that the incorporation of some lignin fragments may result from a transfer process to lignin structure; this reaction leads to an average number of 1–1.5 fragments per PMMA chain, which is not negligible in the present case. The contribution of the two processes in the incorporation of lignin in MMA copolymer will therefore lead to a chain structure tentatively represented in Scheme 3.

Results corresponding to copolymers obtained for R < 1 for two different initial ratio [macromonomers I or II]/[MMA] are collected in Table IV.

For R > 1, the average functionality of lignin moieties is higher than 2 since partially or totally cross-linked materials are obtained. For various values of R, measurements of the swelling ratio ϕ_p in toluene show that densification of the networks increases when

• R increases and
• the amount of incorporated lignin increases.
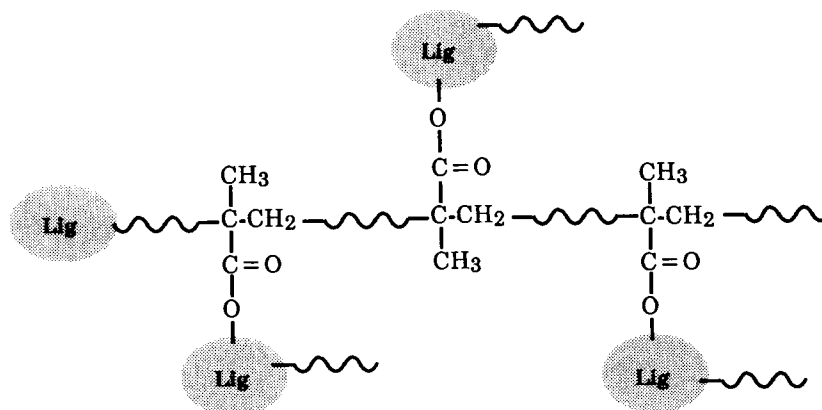
Scheme 3

Table IV   Influence of Reaction Parameters on the Characteristics of Lignin–MMA Copolymers and on the Number of Incorporated Lignin Fragments Per PMMA Chain;
[Phenylpropane Unit] = 0.4 mol L^{-1}; [MMA] = 2.5 mol L^{-1}

	$[PB] \cdot 10^2$ (mol L^{-1})	Polymer Yield[a]	Amount of Incorporated Lignin[b] (% Weight)	M_{peak}	Lignin Fragment / PMMA Chain
Macromonomer I	0.84	57[c]	10	75,000	3.8
	0.74	25	43	33,000[d]	7.0
	2.1	44	14	53,000	3.7
	2.7	46	25	25,000	3.1
	4.9	59	21	32,200	3.4
Macromonomer II	2.0	17	44	17,000	3.7

[a] Recovered by precipitation in MeOH after 6 h reaction.
[b] (Incorporated lignin mass)/(copolymer mass); UV titration.
[c] [Phenylpropane unit] = 0.1 mol L^{-1}; [MMA] = 3.3 mol L^{-1}.
[d] Very broad distribution: $\bar{M}_n$ value.

Physicochemical Characterization of the Lignin Macromonomers–MMA Copolymers

Glass Transition Temperatures

Glass transition temperatures have been determined by DSC and TMA analysis. As indicated in Table V, no noticeable change in T_g has been observed with the variation of the lignin content in the copolymers. This might result from the relatively small difference in T_g for the corresponding homopolymers [112°C and 142°C, respectively, for the poly(MMA) and the native lignin fragments]; it might also indicate a phase separation between the PMMA sequences and lignin moieties, the T_g of the latter being very difficult to observe. This last hypothesis would mean that the copolymers behave as block-type copolymers rather than as random copolymers.

Table V   Effect of Lignin Content on Thermal Properties of Copolymers

	DSC T_g (°C)	TMA T_g (°C)
poly(MMA)	112	[a]
Polystyrene	100	102
Lignin	142[b]	[a]
Acetylated lignin	Not observed	[a]
Lignin(macromonomer) –MMA copolymer	116	116
Lignin(macromonomer) –styrene copolymer	95	107

[a] Not measured.
[b] Estimated; difficult to observe.

Optical Microscopy Observations

Macromonomer–MMA copolymers were examined by optical microscopy; they are translucent, brown-colored because of the presence of lignin, and exhibit an homogeneous texture [Fig. 4(a)]. Lignin appears homogeneously distributed in the PMMA matrix, with no possibility to distinguish between the two components.

To the contrary, the same optical observations performed on both blends (PMMA + lignin fragments) and (lignin–macromonomer MMA copolymer + lignin) [Fig. 4(b)] show the presence of a heterogeneous morphology that reveals large aggregates of lignin fragments scattered in the PMMA matrix.

SEM Observations

In the same way, a comparative observation between a lignin–macromonomer/MMA copolymer and a blend (in the same proportions) of lignin fragments and PMMA was carried out by SEM. The micrographs of both PMMA and lignin fragments are presented in Figure 5. As can be seen, observed morphologies drastically differ: Lignin shows coarse granules whereas PMMA has a leaflike structure.

The corresponding micrographs of a copolymer and a blend of the two compounds with the same chemical composition are shown in Figure 6. In the case of the blend, it is possible to observe the morphology corresponding to lignin fragments, which is very similar to that shown in Figure 5(a). To the contrary, in the copolymer, the presence of lignin domains is not observed and the copolymer mor-
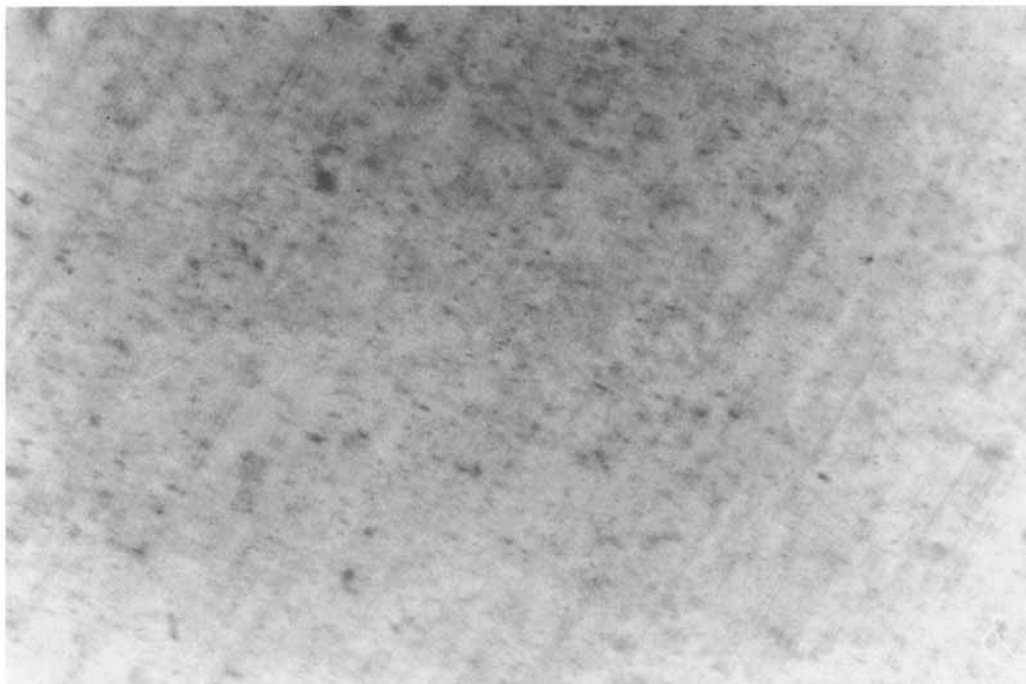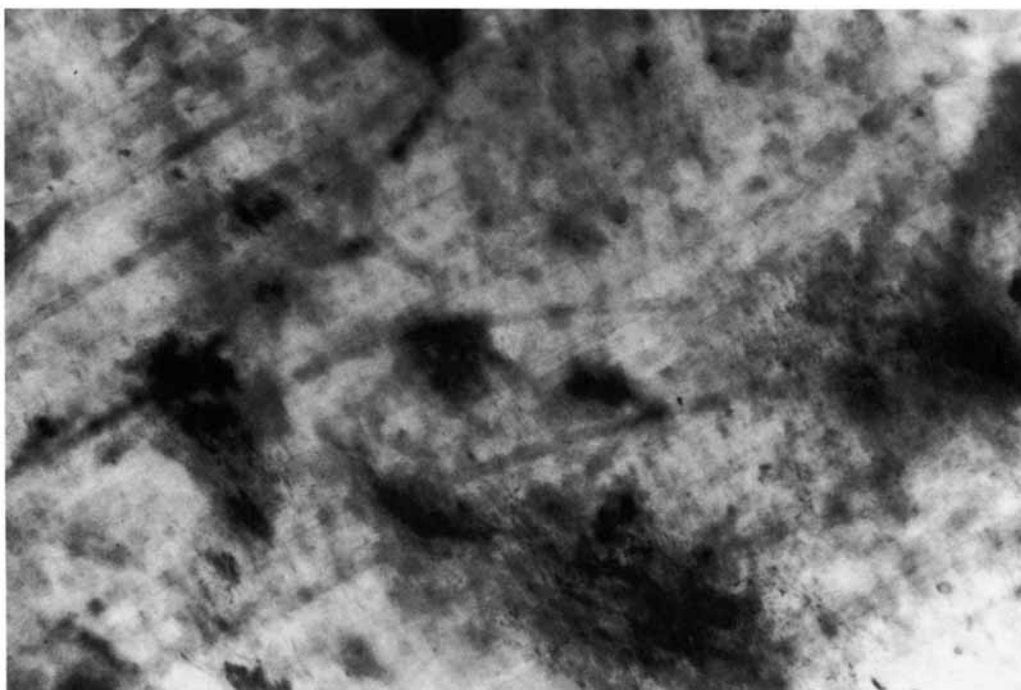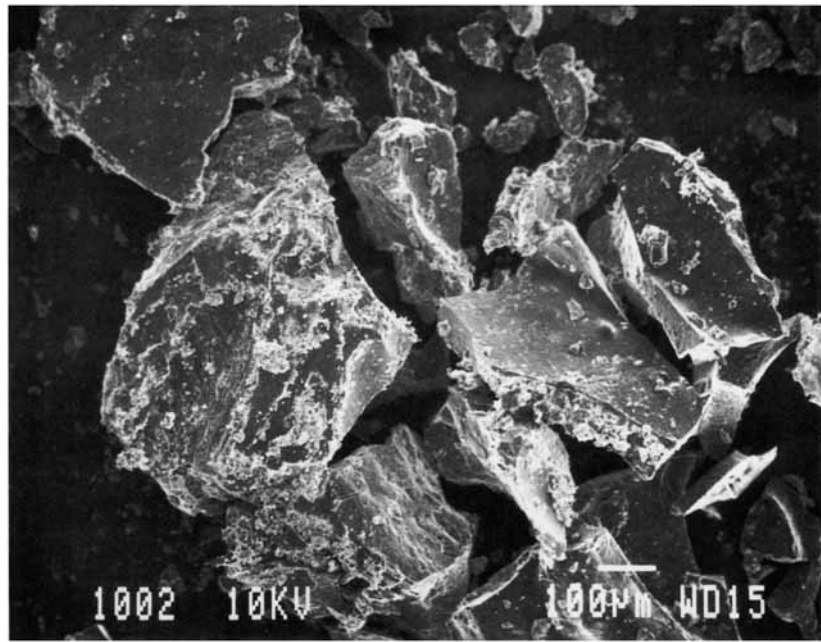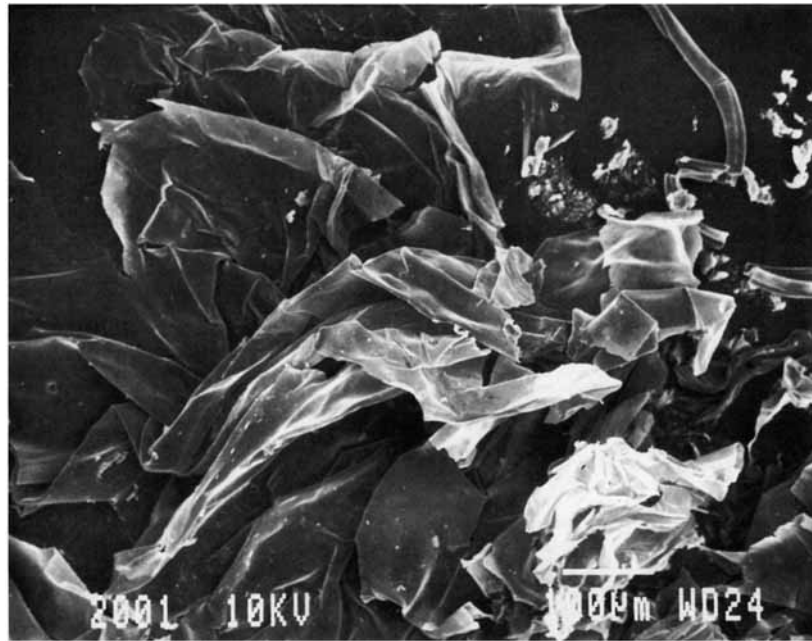
Figure 4 Optical microscopy micrographs obtained by light transmission (×70): (a) lignin/MMA copolymer; (b) mixture (lignin–macromonomer/MMA copolymer + lignin); same micrograph as (b) was obtained with mixture (PMMA + lignin).
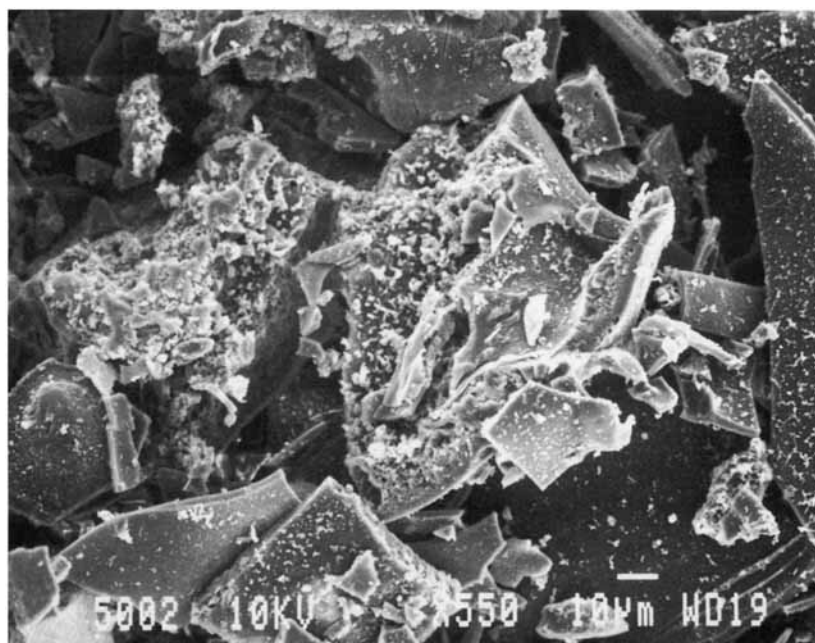
a)

$\overline{100\,\mu}$
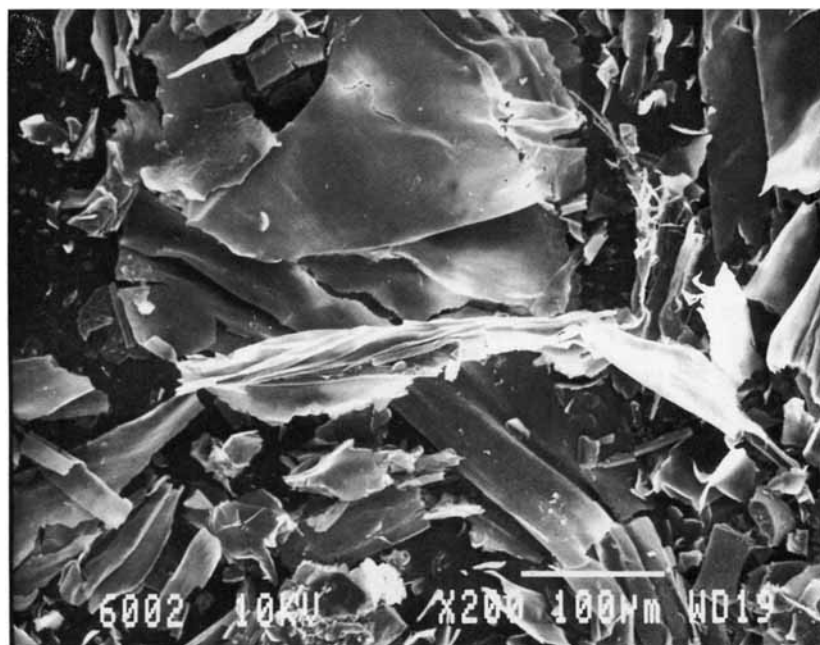

b)

$\overline{100\,\mu}$

Figure 5   MEB prints of (a) lignin and (b) PMMA.

a)

10 μ

b)

100 μ

Figure 6   MEB prints of (a) a mixture (PMMA + lignin) and (b) a lignin macromonomer/MMA copolymer.

phology is close to that of PMMA with increased stiffness in the leaflike structure.

All these observations are therefore consistent with the formation of lignin–macromonomer/MMA copolymers in which the lignin fragments, contrary to that observed in lignin/PMMA blends, are uniformly dispersed in the PMMA matrix, at least at the observation levels used.

In conclusion, the chemical modification of lignin fragments by methacryloyl chloride or chloromethylstyrene leads to functionalized lignin moities that can be copolymerized with MMA in the presence of free radicals. The close dependence of the gel formation on the number of anchored functions per lignin unit indicates that these groups are directly incorporated into the growing chains. In the case of soluble materials, the incorporation of lignin in the poly (MMA) chains was further confirmed by NMR and UV analysis of the polymers.

Besides the differences observed by optical and SEM microscopy between the lignin–macromonomer/MMA copolymers, on the one hand, and blends of lignin fragments and poly(MMA), on the other, suggest distinct morphologies that may be explained by the better dispersion of lignin fragments in the PMMA when they are part of a copolymer.

EXPERIMENTAL

Chemicals

Methacryloyl chloride (> 90%) (Aldrich) and chloromethylstyrene (98%, mixture of m- and p-isomers) (Eastman Kodak) were used without further purification. Methyl methacrylate (Aldrich) and dioxane (SDS) were distilled over drying agents before use.

Preparation of lignin S: the lignin fragmentation was obtained by flash hydrolysis of wheat straw. The crude product was then fractionated in accordance with earlier work.[1] The purification and characteristics of the fraction extracted have been described elsewhere[1]; its number-average molar mass (M_n) is 900 g mol^{-1}.

Macromonomer Synthesis

Reaction of Lignin Fragments with Methacryloyl Chloride

Two grams of dry lignin were dispersed into a mixture of methylene chloride (10 mL) and triethyl-

amine; freshly distilled dimethylaminopyridine (DMAP) (10^{-3} mol) used as an activator was then introduced. Methacryloyl chloride was finally added dropwise at 40°C, under dry nitrogen, up to the quantity defined.

Esterification of remaining lignin hydroxyls was then achieved by adding excess acetic anhydride with respect to free hydroxy groups. Detailed experimental and analytical results for acetylation are given elsewhere.[1] After a 30 min reaction, the mixture was neutralized by HCl 1N, washed several times with NaHCO$_3$, and dried on MgSO$_4$. The macromonomer was then precipitated in hexane and dried under vacuum.

Reaction of Lignin Fragments with Chloromethylstyrene

Dry lignin, 1.5 g, dissolved in 70 mL of freshly distilled THF and 270 mg (9 · 10^{-3} mol) of sodium hydride were introduced in a Schlenk vessel. After a few minutes, 1.4 mL of chloromethylstyrene was added. The mixture was allowed to react at 80°C under dry nitrogen for 20 h and the lignin was precipitated into ethanol, filtered, and washed with ether. The reaction was finally completed by reacting free hydroxy functions with a mixture of N-methylimidazole and acetic anhydride.

Polymerization Procedure

The polymerization and copolymerization reactions were performed according to the experimental procedure described in Ref. 1.

Characterization of Polymers

Measurement of Molar Masses

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 calibration of the columns was carried out by using polystyrene standards.

DSC Analysis

A Mettler differential scanning calorimeter (DSC 30) was used to determine the thermal properties of homopolymers, copolymers, and lignin fragments. A heating rate of 5°C/min was used and the thermal properties were recorded at the second heating cycle.

TMA Analysis

Glass transition temperatures were also measured with a thermomechanical analyzer Mettler (TMA 40). Copolymers were pressed into pellets on a hot press under 22 MPa at 150°C for 5 min. The testing temperature ranged from 20 to 250°C.

SEM Examinations

Surface morphology of lignin and copolymers was examined with a JEOL JSM 840 A scanning electron microscope. All samples were coated with gold on a hummer X sputter.

Optical Microscopy

Copolymers and lignin–MMA mixtures were pressed into a film on a hot press under 22 MPa at 150°C for 5 min and examined with an optical microscope by light transmission.

REFERENCES

1. C. Da Cunha, A. Deffieux, and M. Fontanille, *J. Appl. Polym. Sci.*, **44**, 1205 (1992).
2. R. B. Phillips, W. Brown, and V. T. Stannett, *J. Appl. Polym. Sci.*, **15**, 2929 (1971).
3. R. B. Phillips, W. Brown, and V. T. Stannett, *J. Appl. Polym. Sci.*, **17**, 443 (1973).
4. H. P. Naveau, *Cellulose Chem. Technol.*, **9**, 71 (1975).
5. W. G. Glasser and H. X. Wang, *Lignin: Properties and Materials,* ACS Symp. Ser. 397, American Chemical Society, Washington, DC, 1989, p. 515.
6. E. V. Dehmlow and S. S. Dehmlow, in *Phase Transfer Catalysis Monographs in Modern Chemistry,* H. F. Ebel, Ed., Verlag Chemie, Berlin, 1978, pp. 104–114.
7. W. E. Keller, *Phase Transfer Reactions,* Fluka Compendium-1, Verlag, Stuttgart, New York, 1986 pp. 178–198.
8. P. Dournel, E. Randrianalimanana, A. Deffieux, and M. Fontanille, *Eur. Polym. J.*, **24**, 9, 843 (1988).
9. K. A. Connors and N. K. Pandit, *Anal. Chem.*, **50**, 11 (1978).