

# Graft Copolymerization of Lignosulfonate and Styrene

R. CHEN, B. V. KOKTA, and J. L. VALADE, *Centre de Recherche en Pâtes et Papiers, Université du Québec à Trois-Rivières, Trois-Rivières, Québec, Canada G9A 5H7*

## Synopsis

A study was made of the graft copolymerization of calcium lignosulfonate with styrene. Heterogeneous copolymerization were carried out with methanol as swelling medium, using ferrous ion as catalyst, and ozone and/or hydrogen peroxide as initiator. When using peroxide alone as initiator, monomer conversion was low; after ozonization of lignosulfonates, monomer conversion increased considerably and the grafting efficiency, as well as degree of lignosulfonate grafted, was improved. At 55°C, a 10-fold increase in conversion was observed for reactions with ozone-pretreated lignosulfonates. The investigated factors that affected the graft copolymerization were: the amount of peroxide and ozone charged, the reaction temperature and the ratio of styrene/methanol.

## INTRODUCTION

Lignin is one of the most abundant natural polymeric products. Its content in wood ranges from 20 to 30% on a dry weight basis. In most pulp mills, however, it has been considered as a byproduct, having little economical value, from the delignification processes of chemical digestion and bleaching. Only an extremely small portion of this "byproduct" has been recovered and used, taking advantage of its colloidal properties, in fields such as emulsification, deflocculation, adsorption, elastomer reinforcement, etc. Lignin in pulping effluent is usually handled in two ways: either discarded into a receiving water or burned in a furnace to recover its heat energy. From the concepts of better resources utilization and environmental protection, the first one is unquestionably out of date, since it not only wastes material, but results in stream pollution as well. The second also appears no longer a plausible way of using lignin, because the rising prices of petroleum products and the high energy required in producing synthetic polymers favor the future use of lignin as a raw material in the polymer field. Toward this end, more basic and applied researches are needed so as to gain a better understanding of the compatibility of lignin with other substances in polymer systems.

In recent years, some attention has been attracted to this domain, but not many results have been published. Among those who have published results, Chernyavskaya and Berlin<sup>1</sup> and Nam et al.<sup>2</sup> studied the grafting of methylacrylate onto hydrolyzed wood lignin and onto lignosulfonate, respectively; both used hydrogen peroxide as an initiator. Phillips et al.<sup>3</sup> investigated the radiation-induced graft copolymerization of styrene and various kraft softwood lignins. Naveau<sup>4</sup> obtained methacrylic derivatives of acid-hydrolyzed lignin through esterification. Several works were done on the copolymerization of hydrochloric acid lignin and vinyl monomers, initiated by radiation,<sup>5-7</sup> peroxides,<sup>8-10</sup> and azodiisobutyronitrile.<sup>9-11</sup> Graft copolymerization of ozone-activated hydrochloric acid lignin with styrene was reported by Katuscak and coworkers.<sup>8,12</sup>

In this work, calcium lignosulfonate (Ca-LS) was used as the backbone polymer whereon styrene was grafted. Copolymerization was redox initiated using hydrogen peroxide and ferrous ion. In addition, ozonization was also applied to create active sites on lignin macromolecules. Polymerization was carried out in heterogeneous systems by suspending lignosulfonate in methanol, which dissolves the styrene monomer. It was reported that methanol possesses two functions: (1) swelling the lignosulfonate to increase the accessibility of monomer to the interior of lignin macromolecules<sup>8,13</sup> and (2) trapping radicals in the precipitating polymer coils, thus decreasing the rate of the normal bimolecular termination.<sup>14,15</sup>

## EXPERIMENTALS

### Materials

The lignin material used in this work was a commercial Ca-LS, designated as Toranil B, provided by the St. Regis Paper Co. (Lake States Division). Its lignosulfonate content, determined in our laboratory by ultraviolet absorption at 280 nm, was 86.8% with reference to the purified material. Purification was made by ultrafiltering a 2% aqueous solution with a set of immersible molecular separators (supplied by Millipore). The solution was then dried in a vacuum oven at about 60°C. This operation not only eliminated the impurities (e.g., carbohydrates and pulping chemicals), but also removed most of the low molecular weight lignosulfonates. The lignosulfonate as received, having a methoxyl group content of 8.8%, had a multimodel curve in its molecular weight distribution, as shown by the gel-permeation chromatogram in Figure 1. Low molecular weight lignosulfonates, the total of which was about 16% by weight as estimated from this figure, might have a greater inhibitory effect on the polymerization of styrene compared to the ones with high molecular weight. Through ultrafiltration, the amount of undesired lignosulfonate was reduced to about 6%.

Polymerization-grade styrene was purchased from the Fisher Chemicals. Stabilizer was removed by distillation under vacuum; the central cut was collected in dark bottles and stored in a refrigerator. Methanol of ASC reagent grade from

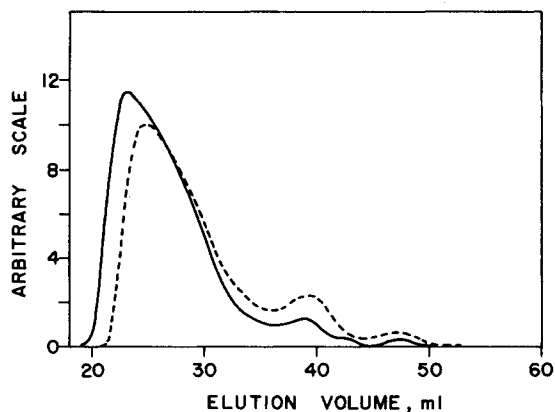


Fig. 1. Gel-permeation chromatogram of calcium-lignosulfonate samples before (---) and after (—) ultrafiltration.

the Anachemia Chemicals was also purified by distillation. All the other chemicals were of reagent grade and used without further purification.

### Ozonization

Ozone was generated using a laboratory ozonator, model 03V9-AR, fabricated by the Ozone Research & Equipment Corp. Compressed dry air was fed to this apparatus to produce ozone in a capacity up to 4.5 g/hr. The ozone content of the gas-stream throughput was regulated by changing the input electrical power to the apparatus. Lignosulfonate to be ozonized was suspended in methanol in a three-necked flask (reactor) kept in actone at  $-30^{\circ}\text{C}$ , which was controlled by the addition of dry ice. Ozone was fed to the flask through a 3-mm O.D. Teflon tube. This tube, whose outlet end touched the center of the flask bottom, was so installed that during ozonization the input gas bubbles could provide good mixing to the reaction system. After a given period, the amount of ozone absorbed by the methanol-lignosulfonate system was determined from the difference between the quantity of ozone generated in this period and that collected in a waste receiver containing a 2% KI solution. The quantity of ozone was determined iodometrically.

### Copolymerization

Figure 2 shows schematic representation of the procedures involved in the experiments. One gram of Ca-LS was suspended in a given amount of methanol in a three-necked flask. When desired, this mixture was subjected to ozonization as described above before any other subsequent addition of reagents. Otherwise, predetermined amounts of reagents were added to the mixture in the following order: styrene, ferrous chloride dissolved in methanol, and hydrogen peroxide. Then the flask—provided with a condenser, a Teflon stirrer, and an inlet for dry nitrogen—was immediately transferred to an oil bath where the temperature was controlled at 55 or 75 or  $90^{\circ}\text{C}$  depending on the reaction conditions selected. The amount of ferrous catalyst was fixed at 15 mg/g Ca-LS to be copolymerized. Copolymerization proceeded under nitrogen atmosphere and gentle agitation conditions. The use of a condenser was for the purpose of preventing liquid

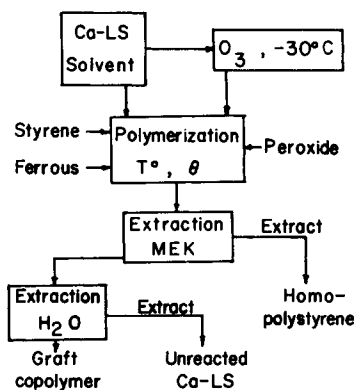


Fig. 2. Schematic diagram of experimental procedures.

reagents from escaping through evaporation. After copolymerization, 20 mg hydroquinone was added to destroy any remaining radicals. The reacted mixture was then dried under vacuum at 50°C. The dry solid so obtained was extracted repeatedly with methyl ethyl ketone to remove completely the homopolystyrene formed during the reaction. The residue was further extracted many times with water until no unreacted Ca-LS was detected in the extract. After extraction, the water-insoluble material was the grafted product.

In the present paper, the terms used to interpret copolymerization results were defined as follows:

$$\text{Total conversion, \%} = [(TS - WL)/M] \times 100$$

$$\text{Grafting efficiency, \%} = [(TS - WL - KE)/(TS - WL)] \times 100$$

$$\text{Degree of liginosulfonate grafted, \%} = [(WL - WE)/WL] \times 100$$

where WL stands for the liginosulfonate used in the reaction; M, the styrene monomer; TS, the total solid obtained after reaction; and KE, the ketone-extractable, and WE, the water-extractable fractions. All these symbols have the same weight unit.

## RESULTS AND DISCUSSION

The inhibiting effect of lignin, owing to its quinoid structure, on the polymerization of vinyl monomers has been encountered by several workers.<sup>2,8,10</sup> The degree of inhibition varied in different cases, depending on the lignin preparation, the monomer involved, and the reaction conditions. In the present work it was found that liginosulfonates effectively inhibited the thermal polymerization of styrene; no formation of styrene polymer could be detected after 24 hr of reaction at 75°C. In the case of redox-initiated polymerization, this effect was diminished but not completely eliminated. Figure 3 shows the conversion of styrene against

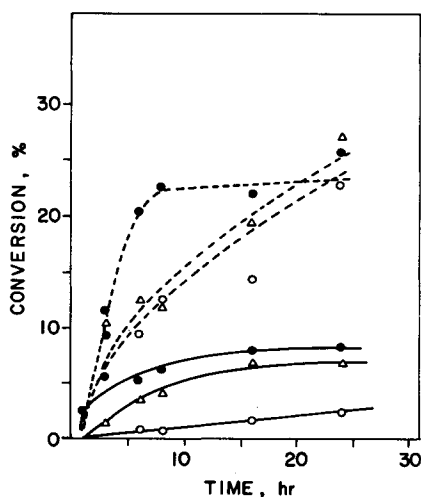


Fig. 3. Variation of the total monomer conversion with reaction time at 90, (●), 75 (Δ), and 55°C (○) with (---) and without (—) ozone treatment. Conditions: LS:MeOH:styrene, 1:10:5; H<sub>2</sub>O<sub>2</sub>, 30 mg (3% LS); FeCl<sub>2</sub>, 15 mg; O<sub>3</sub>, 100 mg, 15 min.

reaction time at three temperatures. The induction periods observed were about 50, 35, and 30 min for the reactions carried out at 55, 75, and 90°C, respectively. Once the inhibiting effect was exhausted, the monomer conversion began to increase, more or less, depending on the reaction conditions; it then proceeded at a very slow or moderate rate (again, depending on the reaction conditions) as the reaction progressed. This indicated that after initiation the polymerization consisted of two periods. In the first period (e.g., when reaction time was less than 6 hr), there was essentially a propagation of polymer chains, thus demanding a fast consumption of monomers. These chains consisted of those grafted on Ca-LS and those suspended freely in the bulk solution. In the second, the termination of polymer chains began to take place, wherein chain radicals vanished gradually and the reaction rate decreased accordingly. One exception is shown by the lowest line in this figure for the reaction at 55°C, where the reaction rate appeared to be constant throughout the polymerization. For this case, it was considered that the termination had not begun within the period of observation. In general, reaction rate was higher at higher temperature.

In addition to the effect of temperature, the effect of initiator quantity used on the total conversion is demonstrated in Figure 4 for 1 g lignosulfonate reacting with 5 g styrene. In all cases, monomer conversion was a monotonous increasing function of hydrogen peroxide quantity used.

However, an increase in monomer conversion did not always ensure an increase in the other two outcomes of the copolymerization, i.e., the grafting efficiency (GE) and the degree of lignosulfonate grafted (DLG). As can be seen in Figure 5, plotted for reaction at 55°C, both GE and DLG increased with the amount of peroxide only when the initiator was low in quantity. When the amount of peroxide exceeded 60 mg, GE and DLG each approached a plateau at about 18 and 14%, respectively, whereas the total conversion kept increasing. This confirmed the observation of other investigators<sup>1,2</sup> that hydrogen peroxide could initiate the graft copolymerization of lignin, as well as the polymerization of styrene. The initiation of graft copolymerization was believed to occur pre-

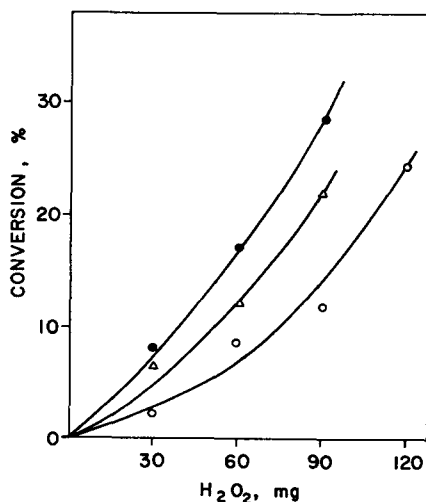


Fig. 4. Effect of the amount of hydrogen peroxide on the total monomer conversion at 90 (●), 75 (Δ), and 55°C (○). Conditions: LS:MeOH:styrene, 1:10:5; 24 hr.

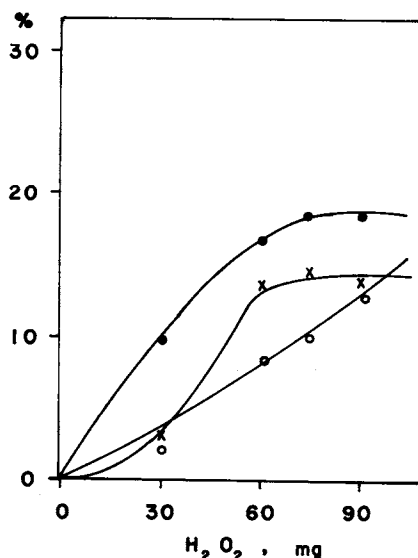


Fig. 5. Copolymerization outcomes as a function of the amount of hydrogen peroxide charged: conversion (O), grafting efficiency (●), and grafted LS(X). Conditions: LS:MeOH:styrene, 1:10:5; 24 hr at 55°C; O<sub>3</sub>, none.

dominately via the reaction of lignosulfonate with the radical formed by the decomposition of the initiator. From Figure 5 it can be noted that both GE and DLG could be controlled by the amount of initiator used, up to a certain limit. Beyond that limit, which could be considered as the saturation point relative to the creation of active sites on the lignosulfonate macromolecules, no further increase in the number of active sites occurred; however, activation of more styrene monomers took place, which in turn produced more styrene homopolymers. As a consequence, either GE or DLG remained unchanged beyond that limit.

In view of the results just mentioned, an attempt was made to improve either GE or DLG by a pretreatment of Ca-LS with ozone. The results after ozonization are shown in Figure 6. It was evident that all three outcomes of copolymerization increased with the amount of ozone absorbed. In the range studied (34–380 mg ozone), a monomer conversion as high as 92% with corresponding GE and DLG of 42.5 and 58% was accomplished. It can thus be concluded that ozonization is a promising way of generating lignosulfonate radicals.

Returning to Figure 3, a comparison can be made of monomer conversion for the reactions carried out with and without ozone pretreatment. When hydrogen peroxide alone was used as the initiator, the reaction rate was very low (see the lower set of curves in Fig. 3). The total conversion after 24 hr was as low as 2.4% for the reaction at 55°C and not more than 10% for that at 90°C. On the other hand, by a pretreatment of lignosulfonate with ozone, both the initial reaction rate and final total monomer conversion were considerably improved. The improvement was more pronounced for reactions at low temperature than at high temperature. For example, at 55°C a 10-fold increase in total conversion, i.e., from 2.4 to 25.7%, was observed. At higher temperature, the extent of improvement decreased, since temperature per se already brought about a positive effect on the acceleration of reaction, e.g., a 3-fold increase in total conversion was found at 90°C compared to a 10-fold increase at 55°C.

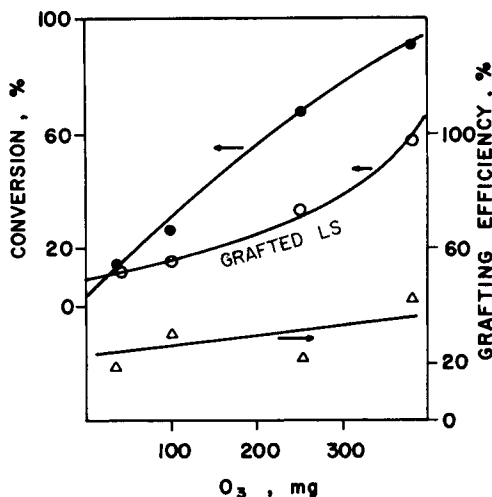


Fig. 6. Copolymerization outcomes as a function of the amount of ozone used; conversion (●), grafting efficiency (Δ), and grafted LS (○). Conditions: LS:MeOH:styrene, 1:10:5; H<sub>2</sub>O<sub>2</sub>, 30 mg (3% LS); FeCl<sub>2</sub>, 15 mg; 24 hr at 55°C.

In the present work, Ca-LS was suspended and ozonized in methanol, which was also used in the subsequent polymerization experiments, in order to avoid unexpected detrimental effects caused by the manipulations that were employed to recover the ozonized lignosulfonates. Figure 7 shows the relationship between the total conversion, as well as GE and the monomer-solvent composition. It is interesting to note that the copolymerization outcomes are not depressed as the amount of methanol increased within a relatively wide range of weight fractions (e.g., 0.3–0.7). Achievement of copolymerization was at its best in this range. Methanol was believed to play an important role in heterogeneous polymerization. It swelled the lignosulfonate particles, thus enhancing the

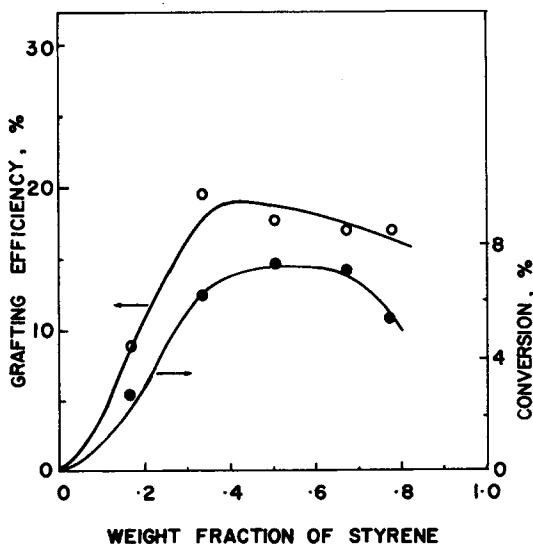


Fig. 7. Variation of the total monomer conversion and grafting efficiency with monomer-solvent composition. Conditions: Ca-LS, 1 g; styrene-MeOH, 20 ml; H<sub>2</sub>O<sub>2</sub>, 30 mg; 24 hr at 75°C.

possibility of monomer and initiator radicals gaining access to the interior of the swollen particles. As polymers of styrene formed, methanol became the non-solvent which precipitated the polymer, resulting in the trapping of polystyrene radicals so that the possibility of normal bimolecular termination was reduced. Similar results have been reported in that using a small amount of methanol was found advantageous in the radiation-induced<sup>3,13</sup> and ozone-activated<sup>8</sup> copolymerization of hydrochloric lignin and styrene.

A few experiments were tried with water as solvent for lignosulfonate, but no polymerization could be initiated by peroxide in this medium. Trials were then directed towards using ozone-pretreated Ca-LS in a hope that polymerization might be activated. Another difficulty arose when carrying out ozonization in aqueous solution, namely, that at the usual ozonization temperature, i.e.,  $-30^{\circ}\text{C}$ , the solution was frozen to a solid state wherein the diffusion of ozone became very poor. If the procedure was conducted at a temperature above the solution freezing point, there was a risk that the ozone would induce ring cleavage of lignosulfonates or the formation of quinoids and epoxides. Both would greatly reinforce the inhibiting effect of lignin and were undesirable in the subsequent copolymerization. The problem of the freezing of the solution during ozonization, when using water alone as solvent, was solved to a certain extent through the use of a methanol-water mixture, but the polymerization outcomes were still not encouraging. As shown in Table I, compared to pure methanol, the methanol-water solvent obviously lowered the total monomer conversion and GE in both Ca-LS that did or did not undergo ozone pretreatment; furthermore, the molecular weight of the homo polystyrene decreased considerably. Referring to experiments A and D, a small increase in the amount of water that accompanied the initiator also exhibited the same type of influence; and employing double the amount of initiator greatly reduced the molecular weight of the polystyrene chains. The data in this table also show that ozonization had an obvious effect on the total conversion and GE but not on the molecular weight of polystyrene. This implies that ozonization merely produced lignosulfonate radicals and had no influence on the degree of styrene polymerization.

The copolymer product obtained in this work was a brownish amorphous solid whose softening point was in the range of  $110\text{--}125^{\circ}\text{C}$ . It was not dissolved in most ordinary organic solvents; as a result, it was impossible at this moment to obtain any information on the molecular weight of this product. Its polystyrene-lignin bond could be cleaved during hydrolysis in 5% NaOH aqueous solution at elevated temperature. Figure 8 shows representively the infrared spectra of the purified Ca-LS and one of the copolymers obtained. Besides the characteristic bands for lignosulfonates in the range  $1220\text{--}1145\text{ cm}^{-1}$  for covalent sulfonates and at  $1265\text{ cm}^{-1}$  for aromatic ethers present in both samples, it was found that the copolymer product had sharp bands at 1602, 1495, 907, and  $700\text{ cm}^{-1}$ , whereas the unreacted Ca-LS showed no such bands. The particular bands are characteristic of aromatic stretching of styrene. On the basis of the infrared spectra B shown in Figure 8, it can be safely said that the lignosulfonate molecules had been grafted with styrene polymer chains.



TABLE I  
Results of Polymerization Under Various Conditions<sup>a</sup>

Experiment	Styrene:Methanol:Water	Reaction temperature, °C	Hydrogen peroxide, mg	Ozone, mg	Total conversion, %	Grafting efficiency, %	$\bar{M}_v$ of polystyrene <sup>b</sup>
A	1:1:(0.007) <sup>c</sup>	55	30	—	2.7	8.8	420,000
B	1:1:(0.007)	55	30	100	22.0	31.0	400,000
C	1:1:0.5(0.007)	55	30	100	17.3	12.5	98,000
D	1:2:(0.014)	75	60	—	12.0	23.5	160,000
E	1:2:1 (0.014)	75	60	—	5.8	13.8	61,000

<sup>a</sup> Fixed conditions: 1 g lignosulfonate; 10 g styrene; 24-hr reaction.

<sup>b</sup> Molecular weight obtained viscometrically in tetrahydrofuran at 25°C.

<sup>c</sup> The value in parentheses denotes the amount of water accompanying the amount of the 30 wt % hydrogen peroxide solution used.

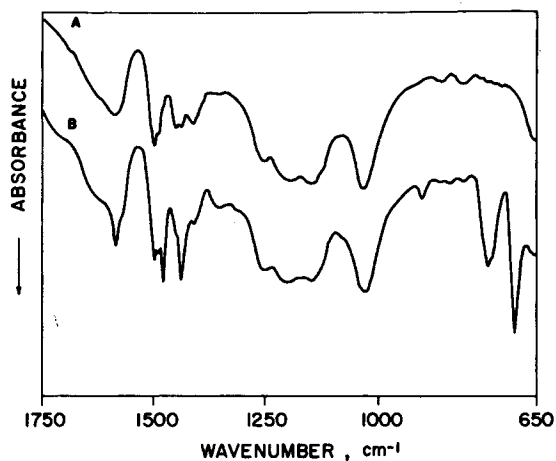


Fig. 8. Infrared spectra of original and grafted lignosulfonate samples in KBr. A, Ca-LS; B, Ca-LS/PS.

### CONCLUSION

Graft copolymerization of Ca-LS and styrene was effectively initiated with a redox system consisting of hydrogen peroxide and ferrous chloride in methanol medium, where a relatively wide range of weight fraction of methanol in a methanol-styrene mixture could be used. Grafting efficiency reached a limit when the amount of peroxide charged increased to a certain value; beyond that, a further increase in the amount of peroxide resulted in no further grafted copolymers but the formation of more styrene homopolymers. The outcomes of copolymerization were considerably improved with the use of ozone-pretreated lignosulfonates but deteriorated under the influence of the presence of water in the reaction system.

The authors gratefully acknowledge the financial assistance received from the National Research Council of Canada and from the Department of Education of the Province of Quebec. The work described in this paper forms part of the research program of the Centre de Recherche en Pâtes et Papiers at Université du Québec à Trois-Rivières.

### References

1. S. B. Chernyavskaya and A. A. Berlin, *Khim. Drev.*, No. 1, 96 (1978).
2. C. Nam, R. Koshijima, and E. Muraki, *J. Polym. Sci., Part A*, **9**, 855 (1971).
3. R. B. Phillips, W. Brown, and V. T. Stannett, *J. Appl. Polym. Sci.*, **16**, 1 (1972); **17**, 443 (1973).
4. H. P. Naveau, *Cellul. Chem. Technol.*, **9**, 71 (1975).
5. R. B. Phillips, W. Brown, and V. T. Stannett, *J. Appl. Polym. Sci.*, **15**, 2929 (1971).
6. T. Koshijima and E. Muraki, *J. Polym. Sci., Part A*, **6**, 1431 (1968).
7. C. Simionescu, A. Cernatescu-Asandei, and A. Stoleru, *Cellul. Chem. Technol.*, **9**, 363 (1975).
8. S. Katuscak and M. Mahdalik, *J. Appl. Polym. Sci.*, **17**, 1919 (1973).
9. T. Koshijima and E. Muraki, *J. Jpn. Wood Res. Soc.*, **13**, 355 (1967).
10. Yu.A. Zoldners, Ya.A. Surna, and Yu.E. Tirzinya, *Khim. Drev.*, No. 5, 116 (1975).
11. Yu.E. Tirzinya, Yu.A. Zoldners, and Ya.A. Surna, *Khim. Drev.*, No. 6, 98 (1975).
12. S. Katuscak, A. Hrivik, and M. Mahdalik, *Pap. Puu*, **53**, 519 (1971).
13. T. Koshijima and E. Muraki, *J. Jpn. Wood Res. Soc.*, **12**, 139 (1966).
14. F. W. Billmeyer, *Textbook of Polymer Science*, 2nd ed., Wiley-Interscience, New York, 1971, p. 357.
15. A. Chaprio, *J. Chim. Phys.*, **47**, 747 (1950).

Received March 16, 1979