Modification of Oxidized Lignins with Styrene

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Synopsis

The effect of original and ozonized lignins upon the polymerization of styrene was investigated. It was found that the unoxidized lignin prepared by hydrolysis of spruce wood meals with 42% HCl retards the thermal polymerization of styrene. The ozonization of HCl–lignin leads to its chemical transformation during which two types of functional groups are formed: those inhibiting and those initiating the polymerization of styrene. Moreover, the polymerization of styrene in the presence of oxidized HCl–lignin affords both homopolymer and grafted copolymer. The amount of the grafted copolymer depends upon the concentration of active oxygen in lignin formed during oxidation, upon the temperature of polymerization, and, finally, upon the kind and concentration of the solvent used in the polymerization system.

INTRODUCTION

The most studied method to modify lignin with vinyl monomers is the direct radiation-induced grafting.[1–4] The grafting of a peroxidized HCl–lignin prepared by irradiation in air has also been studied.[5] Transfer reactions were used to graft HCl–lignin as well. Dibenzoyl peroxide, cumene hydroperoxide, and α,α'-azobisisobutyronitrile were used as initiators.[6] Grafted lignins can be prepared by thermal decomposition of diazo derivatives of lignin.[7,8] A further method for grafting lignins with vinyl monomers is the modification of lignins activated by ozone.[9–11]

EXPERIMENTAL

HCl–lignin for experiments was prepared by hydrolysis of spruce wood meals with 42% HCl at 0°C according to references 9 and 10. The HCl–lignin contained 15.4% methoxy groups. The empirical formula of its fundamental structural unit was $C_9H_{8.80}O_{2.48}(OCH_3)_{0.92}$.

Styrene was purified by rectification at 53°C and 30 torr in a nitrogen atmosphere, the stabilizer being first removed. It was stored under nitrogen at −30°C.

Oxygen from the nitrogen used in the experiments was trapped by passing through copper turnings.[12] Other chemicals mentioned in this paper were either of analytical grade or purified by distillation.

Lignin was activated in the suspension in methanol by ozone at $-30°C$.[9] The active oxygen content (P_x) in original and oxidized lignins was determined iodometrically. The oxidation of lignins and the estimation of active functional groups are described in more detail in references 9 and 10.

The modification of activated lignin preparations with styrene was carried out in sealed ampoules in a thermostated water bath at 70 rpm. The lignin-to-styrene ratio in the system to be polymerized was 1:10. The content of the ampoules was precipitated with slightly acidified (HCl) methanol after the polymerization was finished. The samples were dried to constant weight, weighed, and homogenized. One part of the sample was used for determination of the overall conversion, the other was extracted with hot benzene, filtered, and washed with the same solvent. The sample was then dried and homogenized, and the content of the grafted polystyrene was estimated.

The overall conversion of styrene and the amount of the grafted polymer were determined by gas chromatography of the pyrolytic products.[13,14] The following conditions were used for the estimations: temperature of the pyrolysis oven, $575 \pm 2°C$; carrier gas, 35 cm³/min N_2; column, 1 m × 10 mm with packing consisting of 15% diethylene glycol succinate on Chromaton N-AW (0.16–0.20 mm). Very good separation of styrene from other pyrolytic products was achieved using the conditions mentioned above.

RESULTS AND DISCUSSION

Lignins differ from other macromolecular substances mainly in their phenolic character, their more or less crosslinked structure, and in the variety of arrangement and representation of functional groups and structural units.

The phenolic hydrogen in substituted phenols is able to take part in radical reactions, thus forming phenoxy radicals.[15,16] It could therefore be assumed that lignin also as a substance containing phenolic units can influence the radical polymerization of styrene; this was proved by the ability of lignin to form stable free radicals.[17,18] To prove this influence, a thermal polymerization of styrene in the presence of HCl–lignin and also of styrene itself has been carried out at 70–97°C (Fig. 1). From the course of the kinetic curves, it is evident that lignin in the above-mentioned temperature range preponderantly retards thermal polymerization of styrene, whereas its inhibitory effect is quite low. The rate of thermal polymerization of styrene in this temperature range is 1.2–1.7 times lowered by HCl–lignin. The retardation effect of HCl–lignin has been observed also in the case of polymerization of styrene initiated with benzoyl peroxide (Fig. 2).

When HCl–lignin activated with ozone was used during polymerization of styrene (Fig. 3), a different course of the kinetic curves was found. In the initial stage of the polymerization, significant inhibition periods were

found to be characteristic. After the inhibitiors were exhausted, the polymerization of styrene proceeded faster in the presence of activated HCl–lignin than its thermal polymerization at the same temperature.

One can see from the kinetic curves (Figs. 1 and 3) that the ozonization of HCl–lignin leads to its chemical transformation during which two types of functional groups are formed: those inhibiting and those initiating the polymerization of styrene.

Besides the original lignin phenolic structural units, quinone structures and stable free radicals would also have an inhibitory effect in ozonized lignin. It has been ascertained that the concentrations of both quinone
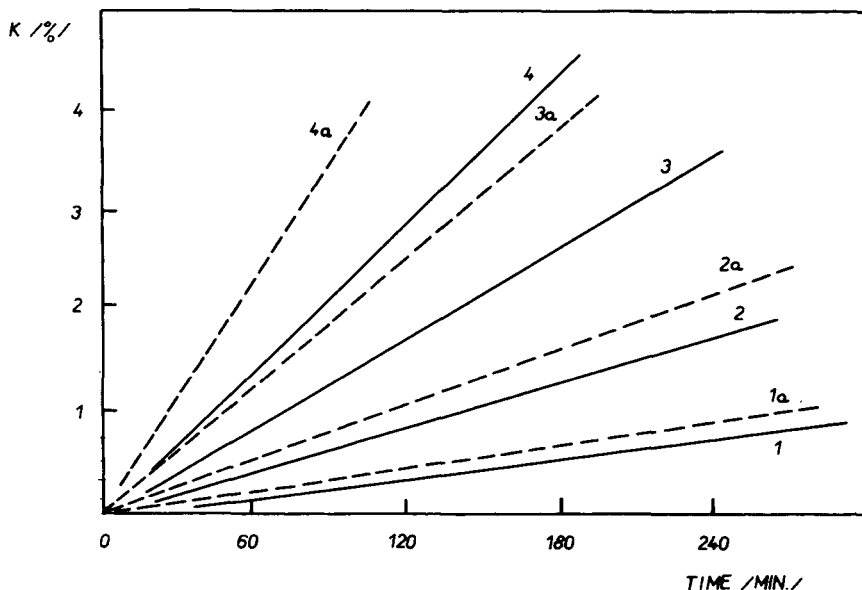

Fig. 1. Effect of HCl–lignin on thermal polymerization of styrene at 70-97°C. Subscript a designates conversion curves of polymerization of styrene itself: (1, 1a) 70°C; (2, 2a) 80°C; (3, 3a) 90°C; (4, 4a) 97°C.

functional groups and stable free radicals increased during the ozonization of lignin.[9,10,18]

On the other hand, the increased polymerization rate proves the formation of peroxide compounds arising from the ozonization of lignin macromolecules. The structure of the peroxide compounds has not been elucidated. It can, however, be presumed that the most probable form of those peroxide compounds are the hydroperoxide derivatives.[10]

Grafting of ozonized HCl–lignin with styrene at a constant content of active oxygen $P_x = 0.25$ mole/kg at 58° and 70°C reveals the kinetic relationships shown in Figure 4. Grafting of ozonized HCl–lignin starts from the beginning of the polymerization of styrene, as shown in Figures 3 and 4.
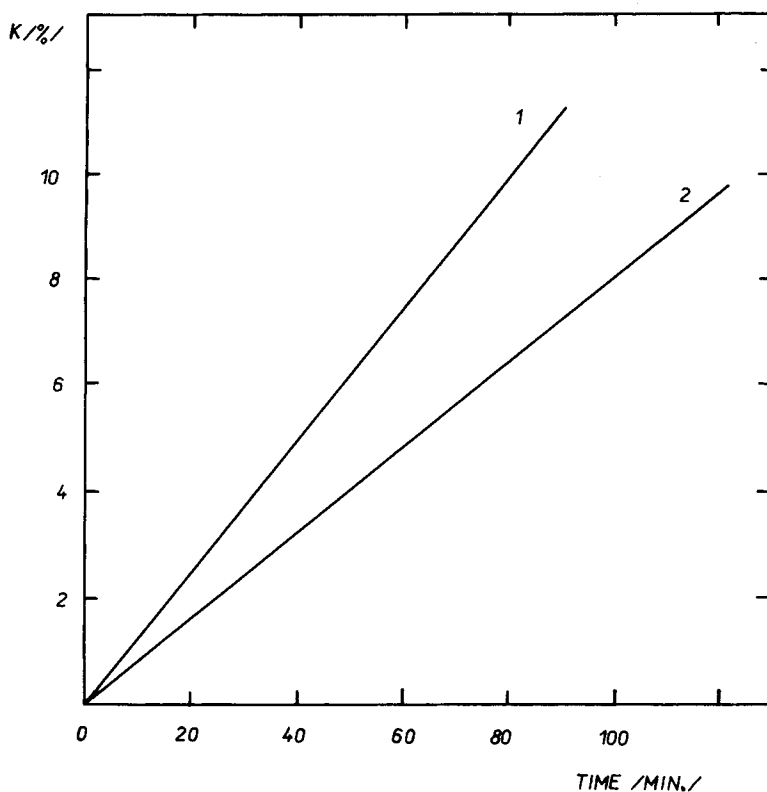
Fig. 2. Effect of HCl–lignin on polymerization of styrene initiated by benzoyl peroxide (0.1 g/100 ml) at 80°C: (1) styrene; (2) styrene + HCl–lignin (10% w/w of lignin in styrene).
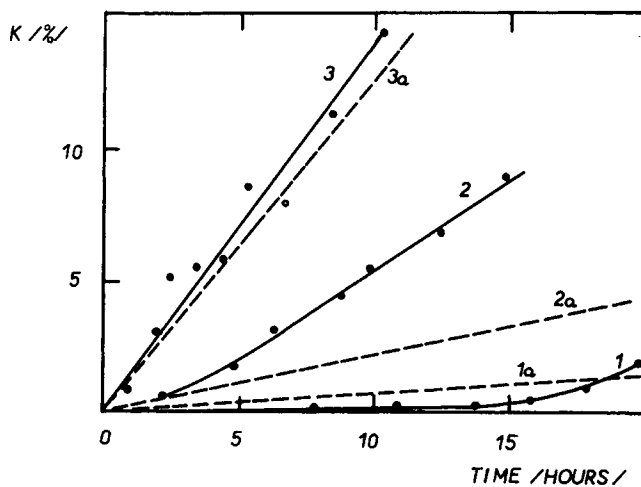

Fig. 3. Effect of oxidized HCl–lignin (P_x = 0.25 mole/kg) on polymerization of styrene at 58–90°C: (1, 1a) 58°C; (2, 2a) 70°C; (3, 3a) 90°C. Subscript a designates conversion curves of thermal polymerization of styrene.

TABLE I
Relationship Between the Efficiency of Grafting η_g and Concentration of
Active Functional Groups P_x in HCl–Lignin After 24 Hours of Modification at 70°C

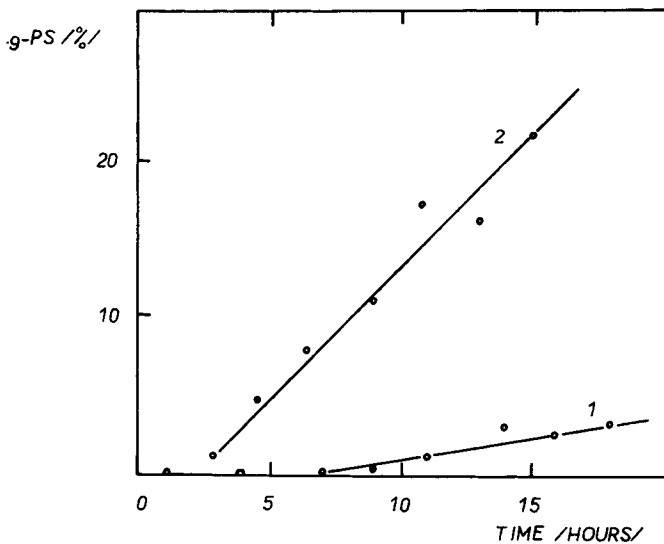| P_x, mole/kg	0.05	0.10	0.15	0.20	0.25	0.30
η_g, %	6.8	8.8	11.8	15.8	20.7	26.3

Fig. 4. Grafting of ozonized HCl–lignin ($P_x = 0.25$ mole/kg) with styrene at 58°C (line 1) and 70°C (line 2).

Table I lists the efficiencies of grafting (η_g) of lignin with styrene at different concentrations of active oxygen (P_x). The lignins used for the grafting were ozonized in methanol at $-30°C$ during different periods of time.[9] It can be seen from Table I that the efficiency of lignin grafting with styrene increases with the concentration of active oxygen in lignin.

The effect of solvents upon the modification of oxidized HCl–lignin is given in Table II. The solvents influence both the degree of conversion and that of grafting. The effect of methanol was examined in a wide range concentration (Figs. 5 and 6). Figure 5 shows the relationship of the total conversion of styrene and Figure 6, the relationship between the per cent of polystyrene grafted to lignin and the concentration of methanol. A characteristic feature of this polymerization system is that both the dependence of total conversion of styrene and the amount of grafted polystyrene reveal significant maxima at the same concentration of methanol, $x_{CH_3OH} = 0.33$. The effect of methanol on the polymerization of styrene in the presence of oxidized HCl–lignin is probably due to the increase in polarity of the polymerization system, thereby making lignin capable of being more swollen and styrene to be transported to the lignin macromolecules. The increase of the inner surface of the solid phase in the heterogeneous polymerization system results in an increased rate of the

heterogeneous processes by which, in turn, the grafted copolymerization and homopolymerization is controlled. A similar course of these relationships is encountered also with radiation-induced modification of lignin with styrene in the presence of various solvents.[2]

TABLE II
Effect of Solvents on the Modification of Oxidized HCl–Lignin[a] at 70°C and Constant Reaction Time (24 Hours)

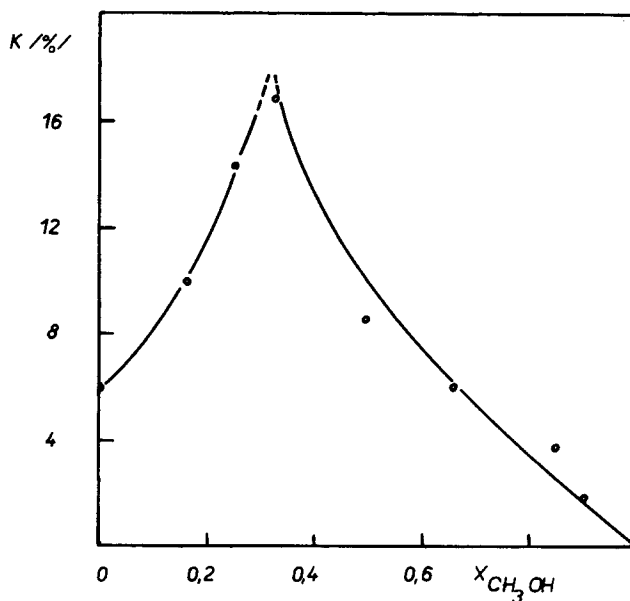| Solvent	Solvent addition to styrene, %	Conversion, %	Polystyrene grafted to lignin, %
No solvent	0	8.0	24.0
Methanol	3	8.0	24.0
	100	8.0	35.0
Dioxane	3	16.0	24.3
	100	25.0	68.5
Dimethyl sulfoxide	3	3.9	2.9
	100	6.3	17.4
Dimethylformamide	3	3.1	2.5
	100	2.4	9.8
Chloroform	3	3.8	2.2
	100	—	—
Benzene	3	1.1	3.4
	100	2.2	1.3

[a] $P_x = 0.25$ mole/kg.

Fig. 5. Relationship between conversion after 24 hr of polymerization of styrene at 70°C in the presence of ozonized HCl–lignin ($P_x = 0.25$ mole/kg) and the concentration of methanol. x_{CH_3OH} is mole fraction of methanol in styrene–methanol mixture.

In connection with the inhibitory effect of original and ozonized HCl–lignin on polymerization reactions, it can be assumed that this effect is mainly due to the phenolic units of lignin, which, during lignin isolation and/or ozonization reactions, enable the formation of further possible inhibition centers, such as stable radicals and quinone groups. In order to prove the assumption about the negative effect of phenolic units on the modification of lignin with styrene, modification of CH_2N_2–methylated lignin ozonized under the same conditions as the HCl–lignin used in our experiments was carried out. The content of active oxygen in the ozonized methylated HCl–lignin was $P_x = 0.41$ mole/kg, while the active oxygen content of the equally ozonized HCl–lignin was $P_x = 0.25$ mole/kg. The
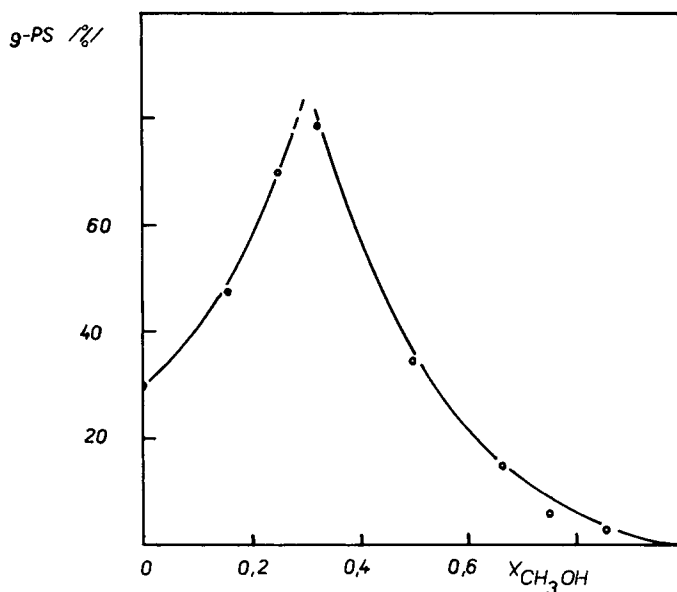

Fig. 6. Relationship between per cent of polystyrene grafted to lignin after 24 hr of modification of ozonized HCl–lignin ($P_x = 0.25$ mole/kg) at 70°C and the concentration of methanol. x_{CH_3OH} is mole fraction of methanol in styrene–methanol mixture.

differences between modification of methylated and nonmethylated HCl–lignin would give us a view of the effect of the lignin phenolic units in the modification process (lignin activation by ozonization + grafted polymerization of lignin with styrene).

Kinetic curves of styrene polymerization in the presence of ozonized CH_2N_2–methylated HCl–lignin ($P_x = 0.41$ mole/kg) at 45°–90°C are listed in Figure 7. It can be seen that also during polymerization of styrene in the presence of methylated lignin below 90°C, measurable inhibition periods appear which are markedly shortened by rising temperatures. After overcoming these inhibition periods, the conversion curves turn to linear ones.

TABLE III

Influence of Temperature on Length of Inhibition Periods of Styrene Polymerization in
the Presence of Ozonized HCl–Lignin or Ozonized Methylated HCl–Lignin

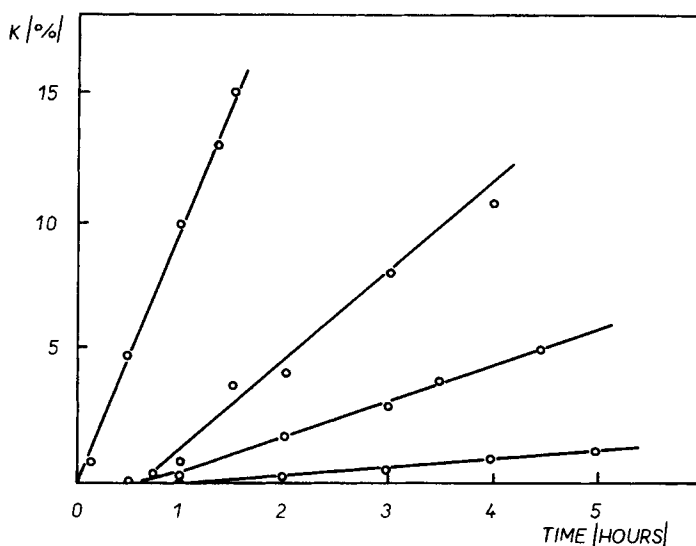|	HCl–lignin (P_x = 0.25 mole/kg) Inhibition periods, min		Methylated HCl–lignin (P_x = 0.41 mole/kg) Inhibition periods, min	
Temp., °C	Polymerization	Grafting	Polymerization	Grafting
45	1800	1800	90	90
58	600	600	45	45
70	120	120	30	30
90	0	—	5	0

Fig. 7. Conversion curves of polymerization of styrene in the presence of ozonized
CH₂N₂–methylated HCl–lignin (P_x = 0.41 mole/kg) at 45–90°C: (1) 45°C; (2) 58°C;
(3) 70°C; (4) 90°C.

Basically, the same course shows kinetic curves of grafting of ozonized
CH₂N₂–methylated HCl–lignin (Fig. 8). Length of inhibition periods as
well as the rates of polymerization and grafting are listed in Tables III
and IV. The rates were calculated from the linear part of the kinetic
curves in Figures 3, 4, 7, and 8.

Table III shows that the lengths of the inhibition periods of grafting and
of the overall polymerization, respectively, are, equal at the modification
of the ozonized lignins with styrene. This proves that grafting reactions
start from the beginning of styrene polymerization.

In case of the modification of ozonized HCl–lignin, the inhibition periods
are longer than for the ozonized methylated lignin. Inhibition periods
become shorter with increasing temperature and disappear completely at
90°C.

TABLE IV

Influence of Temperature and Type of Lignin on Polymerization and Grafting Rates and Grafting Efficiency During Modification of Ozonized HCl–Lignin and Ozonized CH_2N_2–Methylated HCl–Lignin with Styrene[a]

Temp., °C	Styrene $v_p \times 10^5$	HCl–lignin (P_x = 0.25 mole/kg)			Methylated HCl–lignin (P_x = 0.41 mole/kg)		
		$v_p \times 10^5$	$v_g \times 10^5$	η_g	$v_p \times 10^5$	$v_g \times 10^5$	η_g
45	0.223	—	—	—	0.883	0.586	66.4
58	0.255	—	—	—	3.84	2.93	76.3
70	0.618	1.32	0.428	32.4	9.00	6.58	73.2
90	3.34	3.55	—	—	25.90	14.90	57.5

[a] v_p = Rate of polymerization, mole/kg·s; v_g = rate of grafting, mole/kg·s; η_g = efficiency of grafting, %.
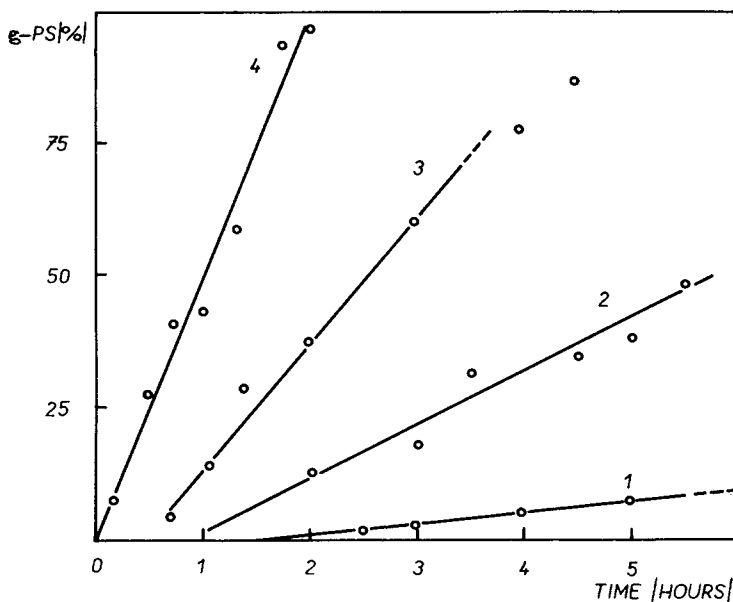

Fig. 8. Kinetics of grafting of ozonized CH_2N_2–methylated HCl–lignin (P_x = 0.41 mole/kg) at 45–90°C: (1) 45°C; (2) 58°C; (3) 70°C; (4) 90°C.

Table IV presents the polymerization and grafting rates when modifying ozonized HCl–lignin and ozonized CH_2N_2–methylated HCl–lignin, respectively. The table presents also polymerization rates of pure styrene at 45°–90°C.

Comparing the rates of polymerization and grafting of both investigated lignins at different temperatures, it is obvious that the polymerization of styrene is more accelerated by ozonized CH_2N_2–methylated HCl–lignin than by ozonized HCl–lignin.

CONCLUSIONS

In the present work it was found that ozonization is a suitable method for preparing centers on the lignin macromolecules which may initiate grafting copolymerization reactions with styrene.

Lignin as the macromolecular substance composed by substituted phenolic units has a week inhibitory and retarding effect on radical polymerization of styrene. Even by increasing the inhibitory effect of lignin by its ozonization, after overcoming the inhibition period, the polymerization of styrene will proceed at a markedly higher rate in the presence of ozonized lignins than the thermal polymerization of pure styrene.

Methylation with diazomethane before lignin ozonization will markedly increase the accelerating effect of the ozonized lignins on radical polymerization of styrene.

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