ELSEVIER

Thermochimica Acta 253 (1995) 307–316

thermochimica acta

H_2O_2 catalytic cure of urea formaldehyde resins with different structures ☆

Ye Su *, Ran Quanyin, Wu Weizhong, Mao Xinwei

Research Institute for Chemical Processing and Utilization of Forest Products, Chinese Academy of Forestry, Nanjing, Jiangsu Province 210037, People's Republic of China

Received 6 September 1994; accepted 6 September 1994

Abstract

The H_2O_2 catalytic cure of urea formaldehyde (UF) resins with different structures was investigated by Fourier transform infrared spectroscopy, carbon-13 nuclear magnetic resonance and thermal analysis. The results show that H_2O_2 can be used as an effective curing agent of UF resins. Compared with the traditional curing agent NH_4Cl, with H_2O_2 the curing reaction of the resins takes place at higher temperatures and the exothermal enthalpy is larger; moreover, the pot life of the adhesive systems increases significantly. Scission of the triazinone and uron rings containing –NH– groups appears to some extent during curing.

Keywords: Catalyst; Curing; Hydrogen peroxide; Resin; UF resin

1. Introduction

Urea formaldehyde (UF) resins have great commercial importance, especially as adhesives for wood products. UF adhesives are easy to manufacture at low prices. However, they have a major disadvantage: toxic formaldehyde emission from bonded products. In order to decrease formaldehyde emission, in recent years some researchers have studied the effects of resin structures and curing conditions on

---

* Corresponding author.

☆ Presented at the International and III Sino-Japanese Symposium on Thermal Measurements, Xi'an, 4–6 June 1994.

SSDI 0040-6031(94)02116-3

formaldehyde emission. Tomita and coworkers [1–3] reported a new curing system for UF resins with polyhydrazides. Zileberman et al. [4] proposed hydrogen peroxide as a curing catalyst for UF resins. Thermal analysis is an effective means to investigate the curing reaction of adhesives. However, little has been reported in the way of a more systematic investigation of the new curing systems by thermal analysis. In our previous paper [5], we reported on the NH_4Cl and $(NH_4)_2SO_4$ catalytic curing and cure kinetics of low-toxicity UF resins. In this paper, an attempt is made to study the H_2O_2 catalytic cure of UF resins with different structures using Fourier transform infrared (FTIR) spectroscopy, carbon-13 nuclear magnetic resonance (^{13}C MNR) and thermal analysis.

2. Experimental

Three kinds of UF resins, UF40, UF41 and UF43, were prepared. Their contents of dry resin were 68.4, 65.0 and 63.8%, respectively. The hydrogen peroxide (H_2O_2) used was the commercially available 30% aqueous solution. H_2O_2 dosage was employed based on the weight of dry resin. UF resin and H_2O_2 solution were mixed thoroughly with an electric stirrer. The samples were then placed in a refrigerator (about 5°C). After the samples had been kept cold for 30 min, the thermal analysis was begun.

Thermal analysis curves were recorded using TG–DSC and DSC 8230 of the Rigaku Thermal Analysis Station TAS-100. The sample masses were 4 and 2 mg, and the heating rates were 10 K min^{-1} and 5 K min^{-1}, respectively, unless stated otherwise. Hermetic Al cells were used in all measurements.

The infrared spectra were obtained on a Nicolet FTIR 170SX spectrophotometer using a KBr plate. ^{13}C NMR spectra were obtained using a Bruker spectrometer with the following parameters: SF, 75.469 MHz; HZ/PT, 0.925; RD, 20S; AQ, 1.081S; NS, 1000–3000. Dimethylsulfoxide-deuterated Me_2SO and H_2O–D_2O were used as solvents. The gel time and pot life of the UF resins were determined according to LY 230-83 and LY 231-81, respectively.

3. Results and discussion

3.1. Structural analysis of UF resins

The structure of the UF resins depends on the formaldehyde-to-urea mole ratio and the reaction conditions. Three kinds of UF resins with different structures, UF40, UF41, and UF43, were prepared by means of different synthetic technologies. Their FTIR and ^{13}C NMR spectra are presented in Figs. 1 and 2, respectively.

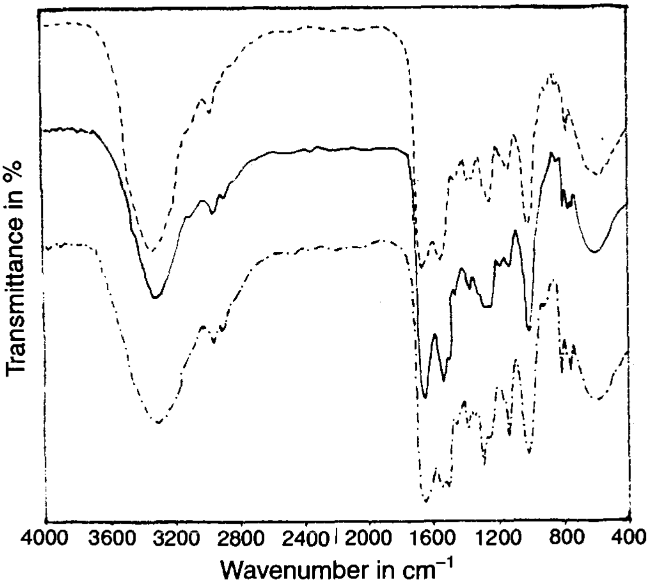


Fig. 1. FTIR spectra of UF resins with different structures: – · – · –, UF40; ——, UF41; – – –, UF43.

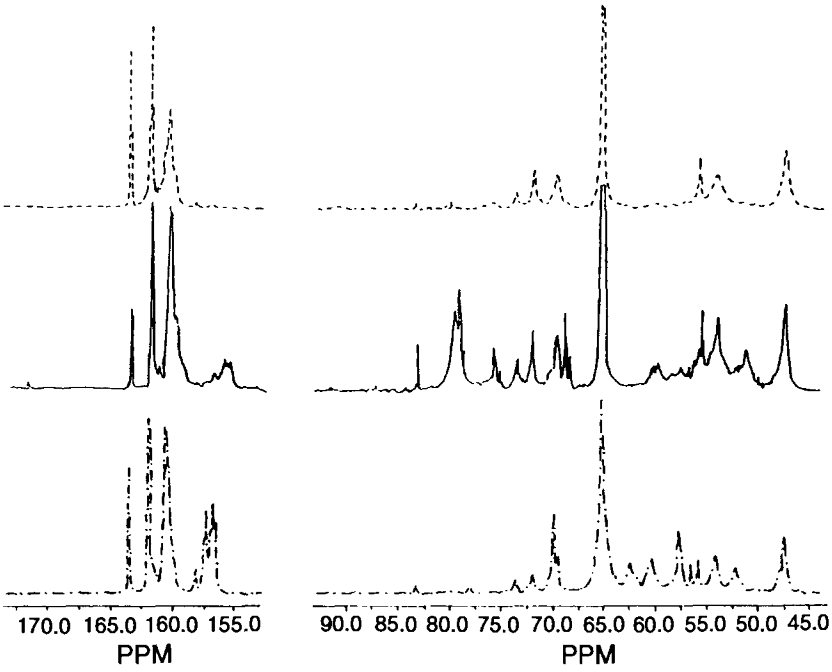
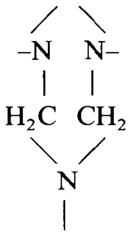


Fig. 2. ^{13}C NMR spectra of UF resins with different structures: – · – · –, UF40, ——, UF41; – – –, UF43.

3.1.1. *UF40 with triazinone rings*

The FTIR spectrum of UF40 in Fig. 1 clearly exhibits the linear amide II peak at 1548 cm^{-1} and the cyclic amide II peak at 1511 cm^{-1}. The appearance of the band at 1511 cm^{-1} is ascribed to the symmetric substitution of nitrogen atom into the urea fragment which causes the amide II band to shift towards the lower frequency region. Moreover, other characteristic bands of the triazinone ring are observed: the band at 1297 cm^{-1} assigned to amide II in the ring, the band at 810 cm^{-1} assigned to skeletal vibration of the cyclic structure, and the band at 757 cm^{-1} assigned to the stretching vibration for C=O in the ring. In its ^{13}C NMR spectrum the chemical shifts of the carbonyl carbon in mono-, di-, and trisubstituted triazinone were observed at 158.2, 157.3–157.5 and 156.6–156.8 ppm, respectively. It follows that UF40 contains various substituted triazinone cyclic structures:



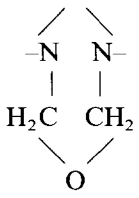
The triazinone content of UF40 is found to be 28.79 mol% of total urea by ^{13}C NMR spectrometry.

3.1.2. *UF41 with uron rings*

In the FTIR spectrum of UF41, a small shoulder peak at 1511 cm^{-1}, assigned to the ring amide II, appears near to the band at around 1548 cm^{-1} for the linear amide II. The characteristic absorption (1187 cm^{-1}) of the –CH$_2$–O–CH$_2$– group and the band at 807 cm^{-1} for symmetric cyclic methylene ether groups (–C–O–C–) in six-membered rings were observed.

Its ^{13}C NMR spectrum shows the following chemical chifts: 155.7–157.2 ppm, which is characteristic of carbonyl carbon in uron rings, and 78.9–79.7 ppm assigned to –N–CH$_2$–O– in the ring, as well as 68.5–68.9 ppm, which is the signal for methylol on uron.

This indicates the UF41 contains various uron rings:



The uron content of UF41 is found to be 18.92 mol% of total urea by ^{13}C NMR spectrometry.

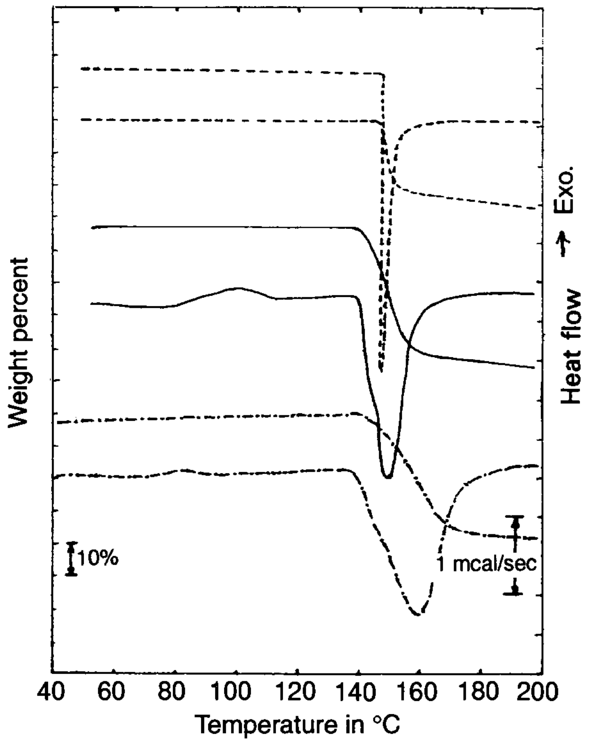


Fig. 3. TG–DSC curves of UF40: – – –, UF40; ——, UF40 + 1% H_2O_2; – · – · –, UF40 + 1% NH_4Cl.

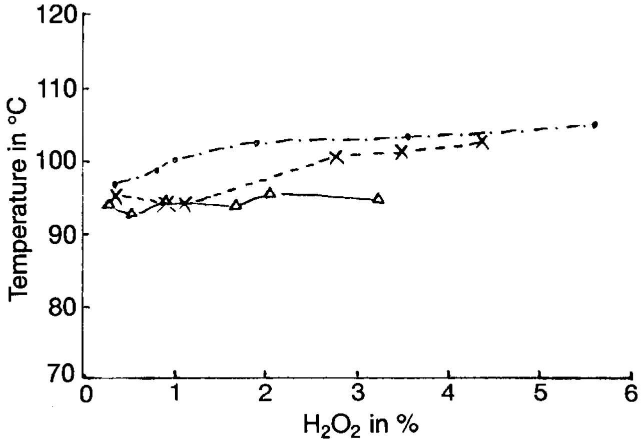


Fig. 4. Effect of H_2O_2 dosage on exothermic peak temperature: –●–·●–, UF40; △ — △, UF41; × – – ×, UF43.

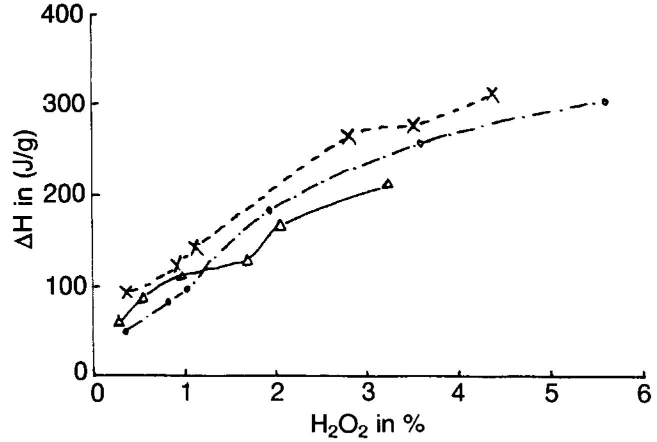
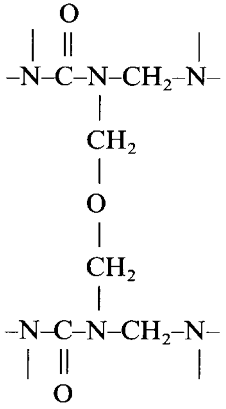


Fig. 5. Effect of H_2O_2 dosage on exothermic enthalpy: ●– · –●– ·, UF40; △ — △, UF41; × – – ×, UF43.

3.1.3. *UF43 with linear-branch structures*

FTIR and ^{13}C NMR spectral analysis show that UF43 has typical linear-branch structures. The characteristic absorption of triazinone was not observed, and the signals of uron were very weak.



3.2. *Curing reaction of UF resins with different structures*

The TG–DSC curves of UF40, UF40–H_2O_2 and UF40–NH_4Cl mixtures are illustrated in Fig. 3. It can be seen that the addition of H_2O_2 results in the appearance of an exothermic peak at 99.3°C, which is not accompanied by weight loss and whose maximum temperature changes with the amount of H_2O_2 and the heating rate. At the end of the exotherm, the sample is found to be in the solid state. Therefore, the peak is due to the curing reaction, indicating that H_2O_2 can be

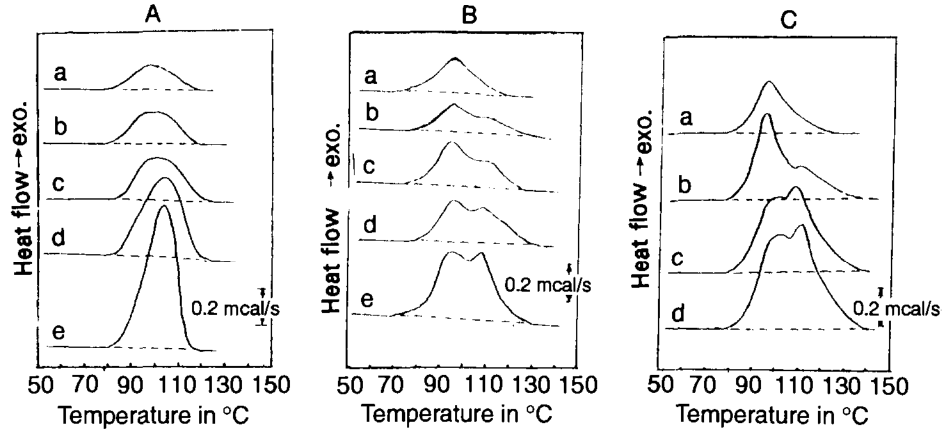


Fig. 6. Effect of the dosage of curing agent on the exothermal peak shape. A. UF40–H_2O_2: a, 0.35%; b, 0.81%; c, 1.01%; d 1.91%; e, 3.57%. B. UF41–H_2O_2: a, 0.27%; b, 0.90%; c, 1.68%; d, 2.04%; e, 3.22%. C. UF43–H_2O_2: a, 0.36%; b, 0.91%; c, 2.76%; d, 3.49%.

Table 1
The gel time and pot life of UF resins

Sample	Gel time in s		Pot life in h	
	H_2O_2	NH_4Cl	H_2O_2	NH_4Cl
UF40	191	85	36.0	19.0
UF41	145	75	21.5	10.5
UF43	135	70	17.0	5.0

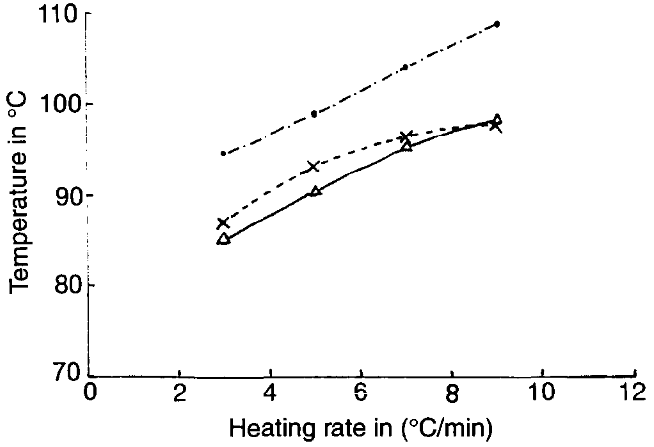


Fig. 7. Effect of heating rate on exothermic peak temperature: •–·–·–•, UF40; △—△, UF41; × — ×, UF43.

used as a curing catalyst for UF resins. The TG–DSC curves for UF41 and UF43 are similar to that for UF40. Compared with the traditional curing agent NH_4Cl, with H_2O_2 the cure temperature of the resin is higher and the exothermal enthalpy is larger. The effects of the dosage of H_2O_2 on the exothermal peak temperature, enthalpy and the peak shape are shown in Figs. 4, 5, 6, respectively.

As the amount of H_2O_2 increases, the peak temperature rises slightly, but the exothermal enthalpy increases significantly. The peak shape for UF40 does not change considerably, while for UF41 and UF43, the peak separates gradually into two peaks, showing that they consist of an overlapping of peaks from two main reactions. H_2O_2 is a strong oxidizer and should lead to the oxidative scission of polymer chains. Consequently, excessive addition is not suitable.

The gel time and pot life of the three UF resins are presented in Table 1. Catalyst levels are 1%. The data in Table 1 demonstrate that the gel times of the resins in the case of H_2O_2 catalysis are longer than that of NH_4Cl catalysis. Thus, if a higher curing rate is required, an increase in curing temperature is necessary. However,

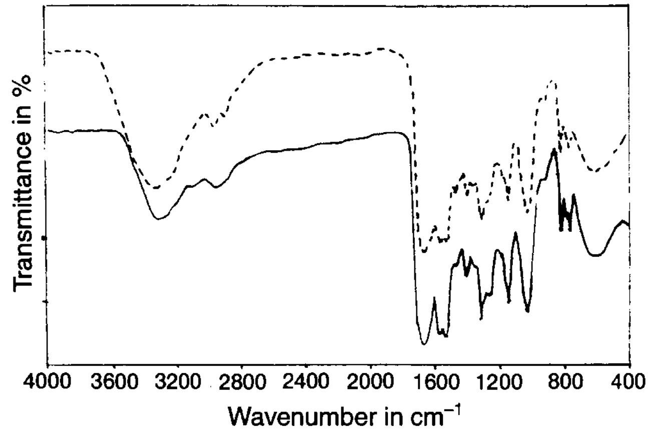


Fig. 8. FTIR spectra of UF40–H_2O_2 system: – – –, unheated; · · ·, heated at 100°C for 1 h.

Table 2
C_1 and C_2 for UF resins before and after H_2O_2 catalytical curing

Sample	Characteristic values	Before curing	After curing
UF40	C_1	0.89	0.88
	C_2	0.91	0.87
UF41	C_1	0.94	0.83
	C_2	0.83	0.68
UF43	C_1	0.99	0.93
	C_2	–	–

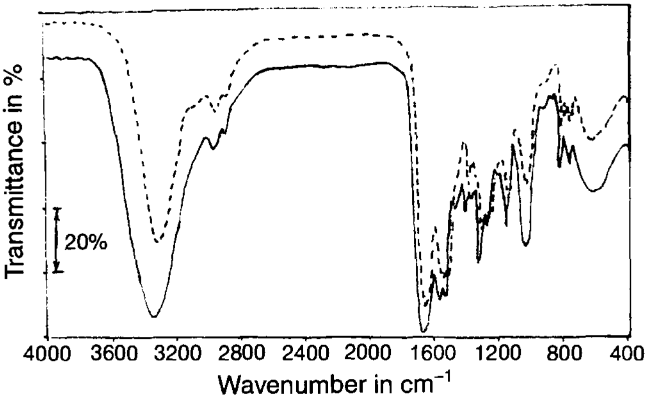


Fig. 9. FTIR spectra of UF40-NH_4Cl system: – – –, unheated; · · ·, heated at 100°C for 1 h.

with H_2O_2 as catalyst the pot lives of the resins are about twice as long as with NH_4Cl; thus H_2O_2 is more suitable. Fig. 7 shows the effects of the heating rate on the exothermic peak temperature. As heating rate increases, the peak temperature for the curing reaction shifts to higher temperatures. The peak temperature of UF40 with triazinone is notably influenced and changes almost linearly with heating rate changes.

The proportion of amide I (1648 cm^{-1}), amide II (1548 cm^{-1}) and amide II (1511 cm^{-1}) in the ring differed somewhat among the three resins, while the characteristic peak at 1015 cm^{-1} for methylol does not alter significantly. Fig. 8 shows the FTIR spectra for UF40–H_2O_2 systems unheated and heated at 100°C for 1 h. According to the procedure proposed by Pshenitsyna et al. [6], the characteristic value C_1 and C_2 can be calculated by the following equations: $C_1 = D_{1548}/D_{1648}$, $C_2 = D_{1511}/D_{1648}$, where D_{1648}, D_{1548} and D_{1511} are the absorption intensities for the bands at 1648 cm^{-1} (amide I), 1548 cm^{-1} (amide II), and 1511 cm^{-1} (amide II in the ring), respectively. Table 2 compares C_1 and C_2 for UF resins before and after H_2O_2 catalytical curing at 100°C for 1 h. For linear resins, C_1 theoretically equals unity; the C_1 value obtained for linear-branch UF43 is close to unit. For UF resins with either triazinone or uron rings, after curing the relative proportion of amide II in the rings decreases. It is obvious that the scission of the rings takes place to some extent during curing. The rings with –NH– groups are subjected to serious destruction, while completely substituted rings do not change significantly. It can be deduced that the partial hydrolytic splitting of the rings with NH–carbamide fragments took place under conditions of curing. The DSC curves for heat oxidation of cured UF40 and UF41 have a small endothermic peak at about 400°C, while for cured UF43 it is absent. This indicates that resins with a cyclic structure after H_2O_2 catalytic curing retain highly substituted rings. FTIR spectra of the three resins before and after NH_4Cl catalytic curing are shown in Fig. 9. It can be seen that the relative intensities of the bands at 1548, 1511 and 1648 cm^{-1} do not change much, while the relative intensities of the methylol at 1015 cm^{-1}, amide III in the rings at 1297 cm^{-1} and linear amide III at 1260 cm^{-1} change significantly. The methylol content clearly decreases after curing. It is quite evident that in the presence of H_2O_2 catalyst, the curing reaction mechanism of UF resins is not totally the same as with NH_4Cl catalyst. It can be suggested that when H_2O_2 is used as a curing agent the curing mechanism of UF resins is as follows: (1) Free formaldehyde present in UF resins as well as from the reverse decomposition of methylol is oxidized to formic acid by H_2O_2. This have been confirmed by TG–DSC studies for H_2O_2 oxidation of formaldehyde which exhibits an exothermal peak temperature of 93.6°C. (2) Formic acid results in the acid-catalyzed polycondensation of UF resins, which occurs between the secondary amide and methylol as well as between two methylols. H_2O_2 is a strong oxidizer and readily gives rise to the scission of weak bonds for UF resins, forming considerable quantities of methylols.

References

[1] B. Tomita, H. Osawa, C.Y. Hse and G.E. Myers, Mokuzai Gakkaishi, 35(5) (1989) 455.
[2] K. Miyake, B. Tomita, C.Y. Hse and G.E. Myers, Mokuzai Gakkaishi, 35(8) (1989) 736.
[3] K. Miyake, B. Tomita, C.Y. Hse and G.E. Myers, Mokuzai Gakkaishi, 35(8) (1989) 742.
[4] E.H. Zileberman, N.N. Furkov, A.A. Smarkov, G.V. Brovkina, E.N. Mizinov, Zh. Prikl. Khim., (2) (1985) 429.
[5] Ye Su, Chemistry and Industry of Forest Products, 11(1) (1991) 77.
[6] V.P. Pshenitsyna, N.N. Smtrnova, L.N. Pukhovits, A.N. Pukhpovitskaya Ye. S. Potekhina and N.D. Eksanova, Vysokmol. Soedin., 26(7) (1984) 1463.