

Thermal Decomposition of Phenol Formaldehyde Resins Modified with Cyanuric Acid

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Synopsis

The thermal decomposition of cured cyanurophenol-formaldehyde oligomers (CPFR) was studied by derivatography, IR spectra and EPR spectra. During the heating of CPFR, processes of restructuring and decomposition take place. Up to 330°C the weight losses of CPFR are smaller compared to those of phenol-formaldehyde oligomers (PFR), while above 330°C the opposite is true. Under these conditions the isocyanuric ring is destroyed. The carbonyl absorption sharply decreases at 400°C, and at 500°C there is practically no absorption. This reduction is probably a result of rearrangement of the isocyanuric rings to a secondary polymer in which nitrogen is combined in the form of cyanic links. The energy of decomposition as determined from the thermogravimetric curve is 17 to 24 kcal/mole. On the basis of the EPR spectra and the low activation energy of destruction, we propose that radical processes play an important part during the process of curing and thermal decomposition of CPFR.

INTRODUCTION

In recent years great attention has been paid to the study of processes taking place when polymeric materials are heated^{1,2} and to the study of thermal decomposition by thermal analysis in particular.³⁻⁵ The combination of the methods of differential thermal analysis and thermogravimetric analysis makes possible some comparative estimations of the thermostability of polymers. For the purpose of improving their properties, the phenol-formaldehyde resins are often modified with chemical compounds of different nature.⁶ From this point of view the modification with cyanuric acid is of great interest.⁷⁻⁹ The latter is prepared easily by pyrolysis of urea.¹⁰ During several years we have been carrying out systematic studies on the synthesis and investigation of polymeric materials prepared on the basis of cyanuric acid.^{7-9,11-16}

EXPERIMENTAL

For the purposes of the investigation, a resol-type cyanuro phenol-formaldehyde resin (CPFR) was prepared^{15,16} by polycondensation of 1 mole cyanuric acid and 3 moles phenol with 6 moles formaldehyde and hexamethylenetetramine as catalyst. Thus prepared, the oligomers

were cured under the following conditions: 50 hr at 70°C, 5 hr at 100°C, and 5 hr at 130°C.

In order to increase the number of the methylene bridges, we tempered the said materials for 6 hr at 150°C, 8 hr at 170°C, and 8 hr at 200°C.

The thermal analysis was carried out by a derivatograph Paulik-Erdey system¹⁷ with simultaneous recording of change of weight with time (TG), rate of change of weight (DTG), and the differential thermal analysis curve (DTA) characterizing change of enthalpy. Annealed powder of aluminum oxide was used as a reference material at a rate of heating of 6.5°C/min in pure nitrogen or air.^{12,18,19}

The infrared spectra were obtained by a Unicam SP-200 spectrophotometer using samples in the form of KBr tablets. The samples intended for experiments at 250°, 300°, 400°, and 500°C were tempered for 60 min in a thermostat.

The (EPR) spectra were obtained by a Japanese apparatus (IEC, 3-BS-x) with DPPHC (1,1-diphenyl-2-picrylhydrazine) as reference material.

The activation energy of destruction was calculated from the thermogravimetric curves (TG) using Doyle's approximate equation.²⁰ The elemental analysis was carried out by the methods described by Kasterina et al.²¹

RESULTS AND DISCUSSION

Some results from the DTA of polymers cured at 130°C and tempered at 150° and 200°C are given in Figures 1 to 3.

The endothermal peaks observed at temperatures between 115° and 138°C are probably a result of the different thermal capacity and thermal conductivity of the systems studied and the reference material²² and also of the influence of the physically combined water and other low molecular products. At higher temperatures a uniform raising of the DTA curves was observed, ending in clearly marked exothermal peaks with maxima at 218°–283°C for PFR and 328°–348°C for CPFR, depending on the curing conditions and the atmosphere. It is interesting to note that in a nitrogen atmosphere the maxima on the thermograms were observed at higher temperatures and were considerably reduced. For this reason we assume that oxygen influences the processes taking place at those temperatures, i.e., it catalyzes oxidation. On the basis of the shape of the DTA curves we conclude that in the temperature range between 115°–348°C two contrary processes take place and that the resulting one influences the DTA curve. On the one hand, free phenol and water, obtained during the process of condensation, are released and on the other hand, this water and the low molecular products lead to the formation of additional crosslinks, i.e., a more intense crosslinking is obtained. Obviously the first process is endothermal, which is confirmed by the endothermal peak on the DTA curve (115°–138°C). The second process,

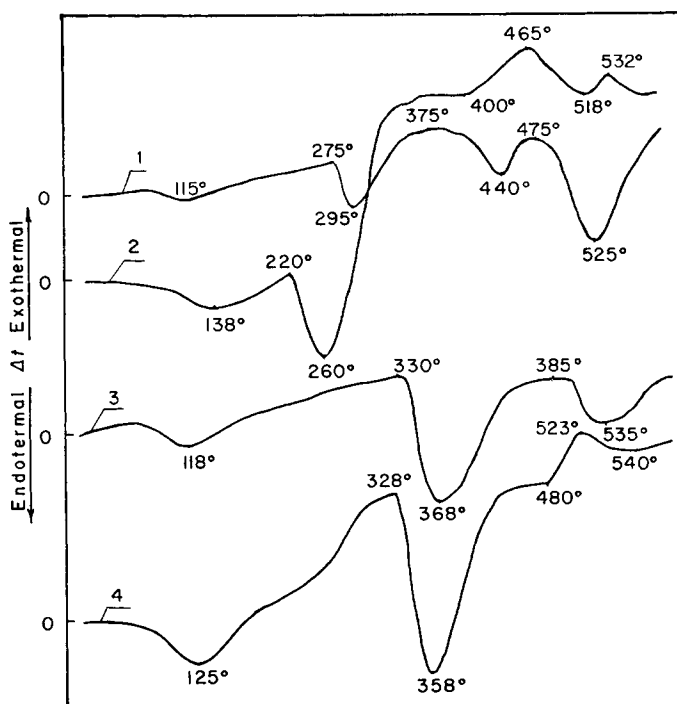


Fig. 1. Thermograms (DTA) of crosslinked polymers, cured at 130°C, obtained in different atmospheres: (1) PFR in nitrogen; (2) PFR in air; (3) CPFR in nitrogen; (4) CPFR in air.

which results in the formation of additional crosslinks, is exothermic and exothermic maxima are observed (218°–348°C) on the DTA curves. It is interesting that up to 330°C the losses of CPFR are considerably smaller compared to those of PFR. The data in Table I indicate that weight losses of CPFR which has undergone thermal treatment at 200°C range from 1.7% to 2.4%, while those of PFR treated under the same conditions range from 8.3% to 8.5%. It has been proved that phenoplastics can be maintained at 175°C for an indefinite time, but for only several hours at 200°C. At a temperature higher than 200°C their strength sharply decreases.⁴ The higher thermostability of CPFR at temperatures to 330°C compared to that of PFR is probably due to the higher thermostability of the cyanuric ring and the higher degree of crosslinking, which is a result of the triple functionality of cyanuric acid.

The exothermic peaks observed at higher temperatures (Figs. 1–3) also depend on the nature of the polymer studied and the atmosphere in which the thermogram is obtained.

The endothermic peaks observed at 260°–370°C and at 505°–550°C are most characteristic since they are a result of the thermo-oxidative destruction of the polymers studied. The character and magnitude of those

TABLE I
Relation of Percentage Weight Loss to Temperature

Poly- mer	Final tempera- ture of curing, °C	Weight loss, % ^a																	
		200°C		300°C		330°C		350°C		400°C		500°C		600°C					
		N	air	N	air	N	air	N	air	N	air	N	air	N	air				
PFR	130	3.32	5.0	8.5	10.0	10.0	10.1	10.6	11.0	13.3	15.0	25.0	26.7	35.0	40.0				
CPFR	130	2.0	5.0	5.0	6.67	6.0	7.15	12.0	18.3	25.0	28.3	36.0	38.4	44.0	45.7				
PFR	150	3.4	5.0	8.3	8.3	8.6	8.4	9.2	10.0	13.3	13.3	21.7	25.0	33.4	36.0				
CPFR	150	2.5	3.3	5.0	6.7	5.84	7.5	14.2	15.9	25.8	28.4	36.8	36.8	45.2	46.6				
PFR	200	5.0	4.8	6.7	6.3	8.3	8.5	8.4	8.8	11.7	12.5	25.0	25.0	33.5	37.6				
CPFR	200	0.0	1.67	1.67	1.7	1.7	2.4	9.1	9.4	21.7	26.7	32.0	35.4	41.6	41.6				

^a At indicated temperature, in nitrogen or air atmosphere.

peaks depend on the type of the polymer studied and the atmosphere in which the thermogram is obtained.

Probably the isocyanuric ring is linked mainly by ether bridges ($-\text{N}-\text{CH}_2-\text{O}-\text{CH}_2-$) and methylene bridges ($-\text{N}-\text{CH}_2-$).^{15,16} The isocyanuric ring is characterized by a relatively high thermostability, and at 300°C only the methylene ether and methylene bridges are destroyed. Obviously at a temperature range of 330° to 400°C the destruction of methylene bridges and of the isocyanuric ring takes place simultaneously.

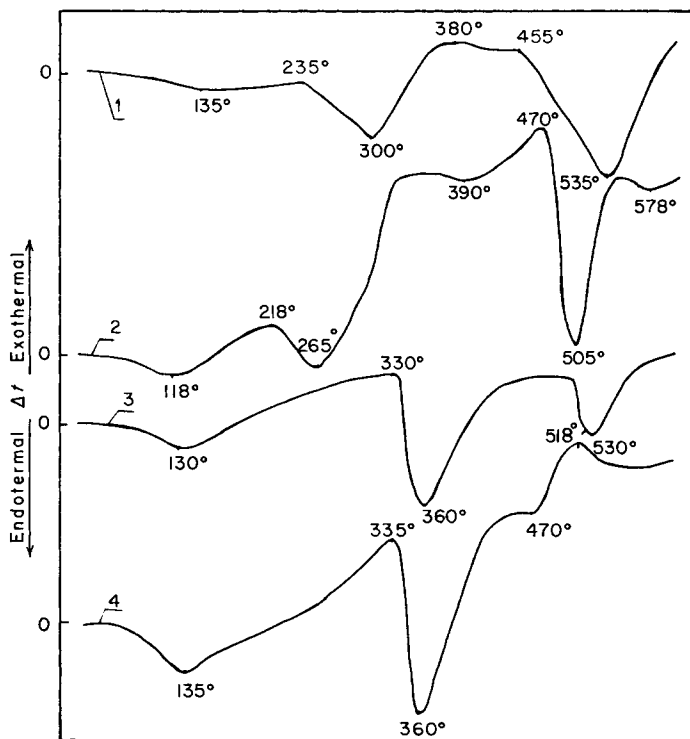


Fig. 2. Thermograms (DTA) of crosslinked polymers, tempered at 150°C, obtained in different atmospheres: (1) PFR in nitrogen; (2) PFR in air; (3) CPFR in nitrogen; (4) CPFR in air.

According to data (Table I) at temperatures higher than 330°C, the weight losses in CPFR are higher compared to those in PFR. That can be explained by the fact that crosslinking by means of C—C bonds is more thermostable than that by means of C—N bonds. It is important to point out that the yield of a secondary polymer (solid residue) depends both on the nature of the polymer and the atmosphere in which the experiment is carried out. Data (Table I) indicate that when the process takes place in air, the yield of a secondary polymer decreases.

Some information on the character of the processes taking place during thermal decomposition can be obtained from elemental analysis (Fig. 4).

The shape of the curves on Figure 4 shows that at 250°C an increase of the oxygen content in the crosslinked polymer is observed. This increase is probably a result of oxidation of methylene ether and methylene bridges in CPFR. These results indicate also that the cyanuric ring is stable at

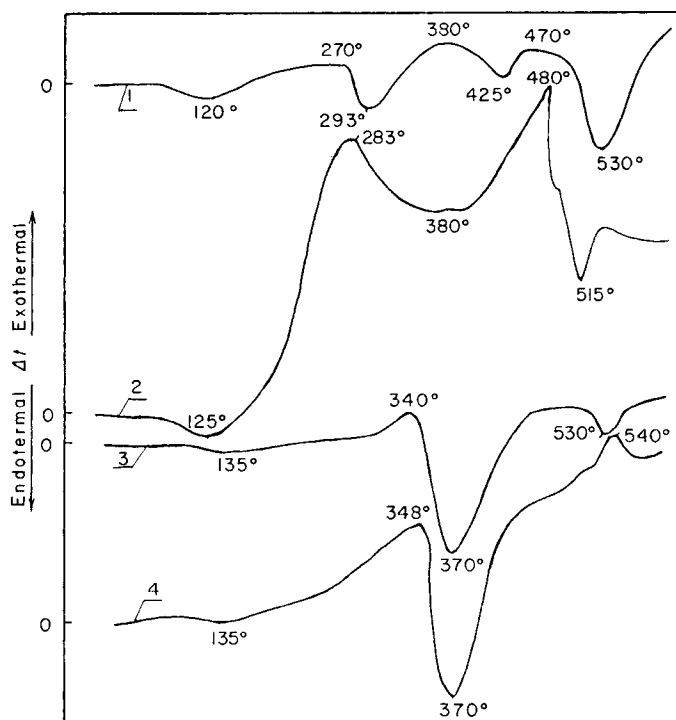


Fig. 3. Thermograms (DTA) of crosslinked polymers, tempered at 200°C, obtained in different atmospheres: (1) PFR in nitrogen; (2) PFR in air; (3) CPFR in nitrogen; (4) CPFR in air.

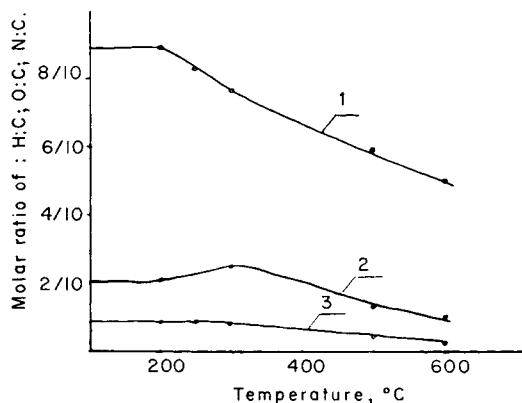


Fig. 4. Change of elemental composition of CPFR after thermal treatment in air for 60 min at constant temperature. Molar ratio: (1) H:C; (2) O:C; (3) N:C.

temperatures up to 300°C. At higher temperatures (higher than 350°C) the isocyanuric links are rearranged, probably to cyanic links²³ which can participate in reactions leading to the formation of additional crosslinks as a result of which a more thermostable structure is obtained. At temperatures higher than 500°–600°C, a sharp decrease in the hydrogen, oxygen, and nitrogen contents and an increase in carbon content is observed, i.e., a carbonization of the cured oligomer takes place.

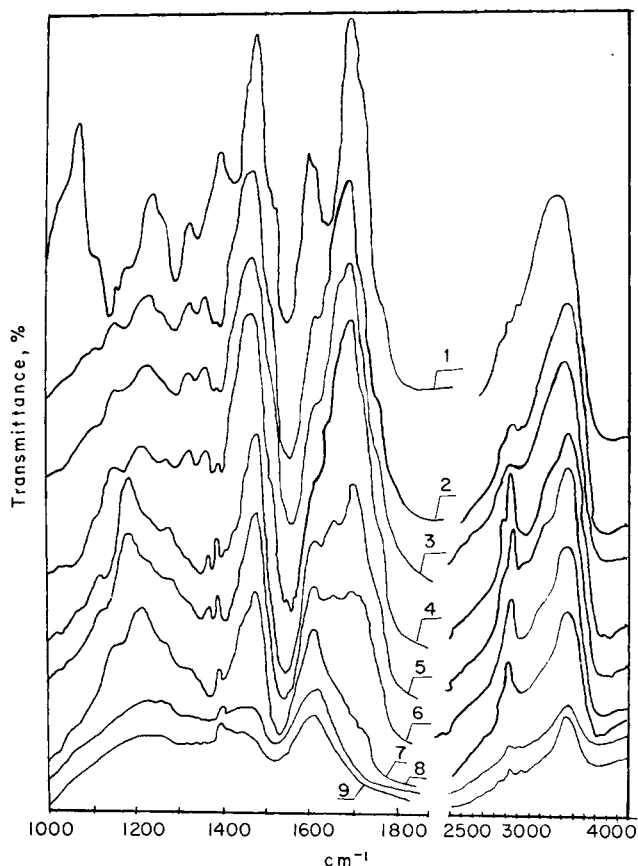


Fig. 5. Infrared spectra of resol CPFR, heated at different temperatures: (1) initial; (2) 130°C; (3) 150°C; (4) 200°C; (5) 250°C; (6) 300°C; (7) 400°C; (8) 500°C; (9) 600°C.

For a thorough understanding of the processes taking place during the thermal decomposition of CPFR, infrared spectra were prepared (Fig. 5). They can be interpreted in the following manner: the absorption frequency of 3600–3100 cm^{-1} corresponds to the valency vibrations of the OH group. The high content of hydrogen bonds masks absorption in the interval 3500–3200 cm^{-1} . The hydroxyl absorption observed at 3450 cm^{-1} and at 600°C is probably a result of partial retention of phenol hydroxyl and maybe of polycyanic hydroxyl, which are formed during

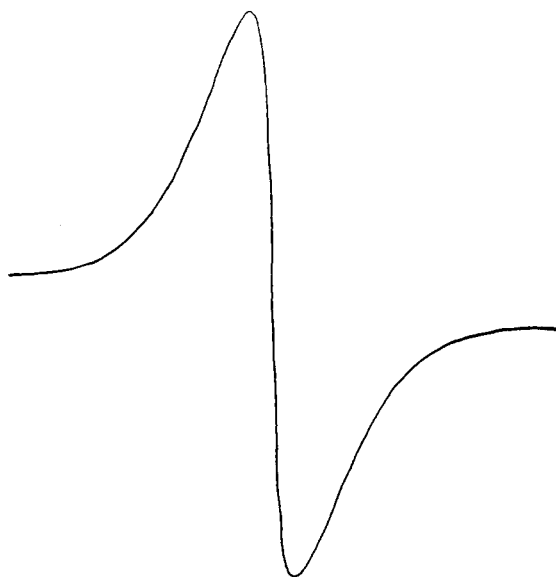


Fig. 6. EPR spectrum obtained during the thermal decomposition of CPFR.

the thermal decomposition of the isocyanuric ring²³ at temperatures higher than 350°C.

The absorption bands at 2950, 1390, 2680, and 1480 cm^{-1} are a result of the valency and deformative vibrations of the CH_3 and CH_2 groups. Strong carbonyl absorption is observed at 1700 cm^{-1} which is a result of valency vibrations of the CO group. These data indicate that cyanuric acid is bonded with formaldehyde and phenol by the nitrogen atom of the keto form. The shape of the infrared spectra shows that at temperatures higher than 350°C the carbonyl absorption sharply decreases, and at 500°C there is practically no absorption. This effect is probably a result of the rearrangement of the isocyanuric links to a secondary polymer in which nitrogen is combined as polycyanic links.²³ As a result of this, absorption appears at 1630 cm^{-1} which is characteristic for the valency vibrations of the $\text{C}=\text{N}$ bonds. The absorption band observed at 1650 cm^{-1} and at 250°C is a result of the partial oxidation of the methylene ether and methylene groups to a keto group. At higher temperatures (300°–400°C), absorption at 1680 cm^{-1} is observed corresponding to the formation of a hinoidic structure, while the absorption at 1740–1720 cm^{-1} is a result of the formation of a carboxylic group.^{24, 25} The absorption frequency (1620–1600 cm^{-1}) points to an aromatic ring in the macromolecule structure.²⁶ The absorption band 1250–1210 cm^{-1} corresponds to an aromatic ether group. The absorption frequency 1150–1120 cm^{-1} characterizes valency vibrations of the ether group $-\text{CH}_2-\text{O}-\text{CH}_2-$.²⁶ At higher temperatures, the absorption intensity of this band decreases and disappears at 400°C.

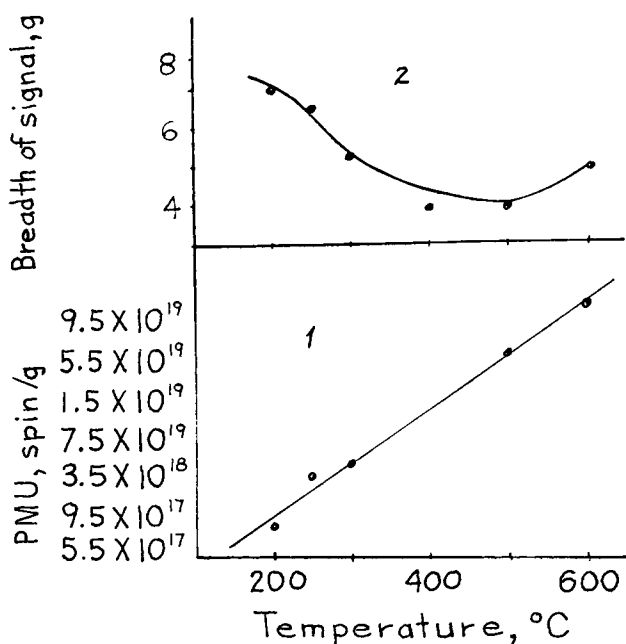


Fig. 7. Dependence of PMU concentration (1) and breadth of EPR signal (2) on the temperature of thermal treatment of CPFR.

The EPR spectra prove that the products, which have undergone a thermal treatment, contain radicals of a prolonged life. The EPR spectrum is given in Figure 6. It is a singlet with a g -factor similar to that of a free electron. The EPR spectrum is a symmetrical signal line the breadth of which varies from 8 to 4.9 gauss (Fig. 7).

The shape of the curves in Figure 7 shows that at higher temperatures the breadth of the signal decreases while the number of the PMU (paramagnetic units) increases. The concentration of PMU varies from 8.72×10^{17} to 1.21×10^{20} spin/g. In all instances the g -factor is about 20023. On the basis of the investigations carried out by us, we suppose that during the curing and decomposition of CPFR the radical processes play an important part. This supposition is confirmed by the presence of radicals in the decomposition products and also by the low activation energy of destruction, which is from 17 to 24 kcal/mole.

References

1. N. Grassi, *Himia Processov Destructsii Polymerov, Izd. Inostr. Lit. M.* (1959).
2. S. Maderskii, *Termitscheskoe Razlodzenie Organitscheskih Polymerov. Izd. Inostr. Lit. M.* (1967).
3. B. Teitelbaum and N. Anoshina, *Uspehi Himii*, **36**, 142 (1967).
4. V. V. Korshak and S. V. Vinogradova, *Uspehi Himii*, **37**, 2024 (1968).
5. U. Leikin, A. Smirnov, A. Davankov, and V. Korshak, *Vysokomol. Soedin.*, **X**, A, 157 (1968).
6. H. Anderson, *S.P.E. Trans.*, 202, July (1962).

7. H. Alaminov, Dissertation, HTI, Sofia (1964).
8. V. Kabaivanov and H. Alaminov, *C. R. Acad. Bulg. Sci.*, **17**, 625 (1964).
9. H. Alaminov and V. Kabaivanov, *Avt. Svid. No. 10494* (1963).
10. M. Michailov and H. Alaminov, *Avt. Svid. No. 10250* (1963).
11. H. Alaminov, M. Michailov, and I. Damianova, *J. Polym. Sci.*, **22**, 419 (1968).
12. H. Alaminov, M. Michailov, Z. Proynova, and N. Manyova, International Symposium on Macromolecular Chemistry, Toronto, Canada, September 3-6, 1968.
13. H. Alaminov, M. Michailov, and E. Zaharieva, *Avt. Svid.*, **No. 12061**, 1250 (1966).
14. H. Alaminov and V. Kabaivanov, *Himia i Industria*, **38**, 57 (1966).
15. H. Alaminov and V. Kabaivanov, *Godishnik HTI*, **XI**, Book 4, 45 (1964).
16. H. Alaminov and V. Kabaivanov, *Avt. Svid.*, **No. 11028** (1964).
17. F. Paulik, J. Paulik, and L. Erdey, *Z. Anal. Chem.*, **160**, 241 (1958).
18. J. S. Double, *Plast. Inst. Trans. J.*, **34**, 73 (1966).
19. H. Alaminov and N. Andonova, *European Polym. Y.*, 417(1969).
20. C. Doyle, *J. Appl. Polym. Sci.*, **5**, 285 (1961).
21. T. N. Kasterina and L. S. Kalinina, *Himitscheskie Issledovania Sinteticheskikh smol i Plasticheskikh Mass*, Goshimizdat, M.s. 111 (1963).
22. L. Brancone and H. Ferrani, *Microchem. J.*, **10**, 370 (1966).
23. Ya. M. Paushkin and A. P. Lunin, *DAN USSR*, **167**, 1346 (1966).
24. R. T. Conley and J. E. Bieron, *J. Appl. Polym. Sci.*, **7**, 103 (1963).
25. V. V. Korshak, V. A. Sergeev, L. V. Kozlov, and L. I. Komarova, *Plast. Massy*, **No. 2**, 33 (1966).
26. L. Bellami, *Infrakrasnie Spektri Molekul*, *Izd. Inostr. Lit. M.* (1957).

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