

## NEW IR-SPECTROSCOPIC METHODS FOR DETERMINING THE HYDROXYL CONTENT IN OLIGOMERS

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*Various methods were developed and compared for determining the concentration of hydroxyl groups in oligomers using azide-substituted oligooxetane diols as examples. A rapid IR spectroscopic method was the most convenient for substituted azide-substituted oligooxetane diols and had the advantages of high accuracy, good reproducibility, fast analysis, and low sensitivity to moisture. The principles underlying the developed methods were suitable for the development of other methods for determining the concentration of hydroxyl groups in various oligomers and polymers.*

**Keywords:** substituted oligooxetane diol, hydroxyl group, IR spectroscopy.

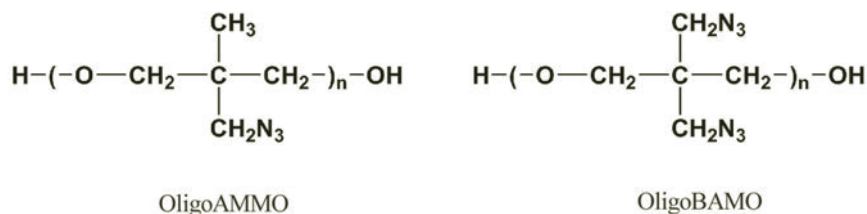
**Introduction.** Oligomers containing hydroxyl groups (OH–) at the end of polymer chains are widely used as precursors to prepare various polyurethanes [1]. Research on the formation kinetics of urethanes and the synthesis of polyurethanes with controlled physicochemical characteristics defined the requirements for the oligomers with respect to molecular-mass parameters, functionality of terminal OH groups, and their content [2–4].

Determination of the OH concentration by a chemical method is based on characterizing their chemical reactions, which should occur quantitatively. The analysis for OH content ( $C_{OH}$ , mass%) usually uses an acylation reaction, of which the most common is acetylation. Esterification of OH groups of the analyte by glacial acetic acid in the presence of  $BF_3$  or  $H_2SO_4$  can also be used [5, 6].

Let us emphasize that these methods are poorly suited to determining the content of terminal OH groups of oligomers and polymers because their concentrations in the samples are too low. Therefore, a double reverse-titration method using isocyanate (henceforth, isocyanate method) that was sensitive to a low OH content in a compound was developed to determine the OH concentration using oligobutadiene diols (OBD) as examples [7]. Furthermore, these methods are typically highly sensitive to the presence of moisture, especially that in the sample. Also, unknown side reactions occur during the analysis by the isocyanate method of the OH concentration in azido-substituted oligooxetane diols (AOOD), which are used to produce high-efficiency polyurethane materials [5, 8], so that the measurements are irreproducible. Finally, a common drawback of these methods that is related to the chemical reactions is their relatively long duration.

The goal of the present work was to develop new and as accurate and rapid as possible methods for determining small concentrations of OH groups in polymers, in particular, AOOD.

**Experimental.** Oligooxetane diols with symmetrically [oligo-3,3-bis-(azidomethyl)oxetane diol, oligoBAMO] and asymmetrically [oligo-3-azidomethyl-3-methyloxetane diol, oligoAMMO] positioned azidomethyl groups were studied:



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The oligomers were synthesized via cationic polymerization of the corresponding monomers using  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  in the presence of ethyleneglycol chain-transfer agent [9].  $\text{CH}_2\text{Cl}_2$  was purified by the standard method [10]. Added stabilizer (alcohol) was removed by treatment with 1,6-hexamethylenediisocyanate (HMDI) followed by distillation. The purity of solvents was monitored by IR spectroscopy. IR spectra were recorded on an Alpha FTIR spectrophotometer (scan step  $2 \text{ cm}^{-1}$ , range  $4000\text{--}1050 \text{ cm}^{-1}$ , 56 scans) (Bruker). Measurements were made using cuvettes with  $\text{CaF}_2$  windows.

**Results and Discussion.** *Method 1* (isocyanate) was developed earlier for determining OH concentrations in OBD [7]. It was based on quantitative reaction of terminal OH groups of the polymer with *m*-chlorophenylisocyanate (CPI) in the presence of iron(III) acetylacetonate catalyst ( $C_{\text{cat}} \sim 1 \cdot 10^{-3} \text{ M}$ ) and consisted of the following steps. Urethane was produced for 1–2 h at  $40^\circ\text{C}$ . An excess of isocyanate with respect to the possible OH content of the polymer dissolved in toluene was used. Then, the amount of unreacted CPI was determined by a modified Stagg method [11]. The reaction mixture was treated with a solution ( $\sim 0.2 \text{ M}$ ) of dibutylamine (DBA) in toluene (10 mL), stored for 10 min while all isocyanate reacted with DBA, and treated with  $\text{Me}_2\text{CO}$  (30 mL) and toluene (20 mL, to homogenize the reaction mixture during titration) with bromocresol green indicator. Residual DBA was titrated with HCl solution (0.1 N) until the color changed from blue to yellow. A blank analogous to the aforementioned sample but without added isocyanate was analyzed in parallel. The OH contents (mass%) in the polymer were calculated using the formula:

$$C_{\text{OH}} = 1.7[1000m_{\text{iso}}/M_{\text{iso}} - 0.1(V_{\text{bl}} - V_{\text{work}})]/m_{\text{pol}}, \quad (1)$$

where  $m_{\text{iso}}$  and  $m_{\text{pol}}$  are the masses of isocyanate and polymer (g);  $M_{\text{iso}}$ , molecular mass of isocyanate (g/mol); and  $V_{\text{bl}}$  and  $V_{\text{work}}$ , volumes of HCl solution used to titrate the blank and working solutions (mL). The starting concentrations of the analyzed polymer and isocyanate solutions were calculated considering the estimated OH content in the sample and the DBA solution in toluene.

The studies led to the conclusion that method 1 was applicable to a variety of OH-containing oligomers and polymers provided they were soluble in toluene, which could be controlled by changing the solvent with a slight correction to the analysis conditions. The drawbacks of the method were the obvious consumption of solvents and reagents in addition to the long analysis time. The error in the OH determination was  $\leq 2\%$ . It is noteworthy that the analysis accuracy and reproducibility depended considerably on the presence or absence of side reactions, which occurred during determination of the OH content in AOOD using method 1. As it turned out, uncontrolled side reactions occurred during titration of unreacted DBA and prompted us to develop new methods for determining OH groups in AOOD.

*Method 2.* The analysis was performed analogously to the isocyanate method up to the step of determining the amount of unreacted isocyanate, which was determined not by the Stagg method but by quantitative IR spectroscopy using the absorption band for antisymmetric NCO stretching vibrations ( $\nu_{\text{NCO}} \sim 2270 \text{ cm}^{-1}$ ). HMDI was less water-sensitive and was used instead of CPI. The solvent was  $\text{CH}_2\text{Cl}_2$ , in which AOOD was more soluble. The catalyst was iron(III) acetylacetonate ( $C_{\text{cat}} \sim 1 \cdot 10^{-3} \text{ M}$ ). This method decreased significantly the consumption of reagents because the amount of solution required for the analysis was  $< 2\text{--}3 \text{ mL}$ , in contrast with the isocyanate method where 60 mL of solvent were consumed. The error in the OH determination by this method was  $\leq 2\%$ .

The OH content was calculated using the equation:

$$C_{\text{OH}} = 1700(C_{\text{NCO}_0} - \Delta D_{\text{NCO}}/\Delta l \epsilon_{\text{NCO}})/C_{\text{AOOD}}, \quad (2)$$

where  $C_{\text{OH}}$  is the OH concentration in AOOD (mass%);  $C_{\text{NCO}_0}$ , initial diisocyanate NCO concentration in solution (g-eq/L);  $\Delta D_{\text{NCO}}$ , optical density at the absorption band maximum  $\nu_{\text{NCO}} \sim 2270 \text{ cm}^{-1}$ ;  $\Delta l$ , cuvette thickness (cm);  $\epsilon_{\text{NCO}}$ , previously determined molar extinction coefficient for  $\nu_{\text{NCO}} \sim 2270 \text{ cm}^{-1}$  (L/g-eq-cm); and  $C_{\text{AOOD}}$ , solution concentration of analyzed polymer ( $\sim 20 \text{ g/L}$ ). However, the possibility of urea formation by the reaction of HMDI isocyanates with water remained even if HMDI was used. Naturally, this reduced the analytical accuracy. In this instance, the concentration of urethane groups formed by the reaction of oligomer terminal OH groups with diisocyanate NCO groups could be used for the determination. This avoided the effect of sample moisture and water in the system on the analytical accuracy (method 3).

*Method 3* required additional determination of the molar extinction coefficient for the urethane analytical band (usually  $\nu_{\text{C=O}} \approx 1720\text{--}1740 \text{ cm}^{-1}$ ). For this, urethane formation of AOOD (oligoBAMO and oligoAMMO) with HMDI with  $C_{\text{OH}} > C_{\text{NCO}}$  was carried out under conditions as dry as possible until the isocyanates were fully consumed. This guaranteed that the concentrations of formed urethanes and starting isocyanates were equal. The molar extinction coefficient ( $\epsilon$ ) in a solvent without its own absorption bands in this region was found taking into account the optical density for the urethane analytical band (usually  $\nu_{\text{C=O}} \approx 1720\text{--}1740 \text{ cm}^{-1}$ ). The OH content in any AOOD sample was determined using the formula:

TABLE 1. Characteristics of AOOD Selected as Calibrants

$M_n$	$M_w$	$C_{OH}$ , mass%	$M_n$	$M_w$	$C_{OH}$ , mass%
OligoAMMO			OligoBAMO		
2500	3200	1.21	2800	4600	1.16
2300	2900	1.38	3600	5600	1.20
2100	2700	1.42	3500	5600	1.23
2000	2400	1.55	1200	2100	1.86
1200	1700	2.02	1300	1700	1.97
1000	1300	2.50	1200	2000	2.42
1000	1300	2.55	1000	1200	2.94
1300	2000	2.60	1100	1300	3.05
1000	1300	2.70	1100	1300	3.07
1000	1300	2.96	1000	1500	3.09
600	800	3.16	800	900	3.22

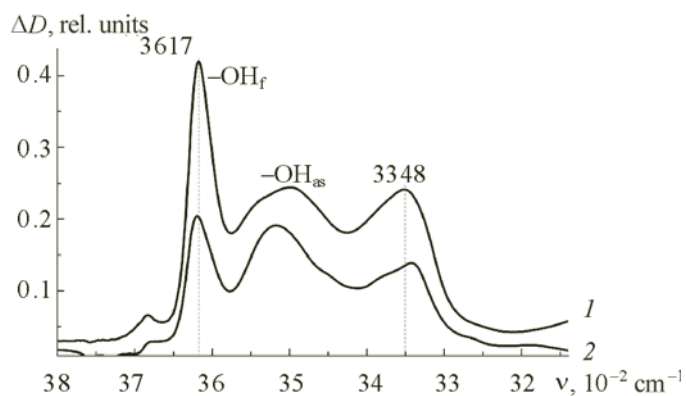


Fig. 1. Typical solution IR spectra of oligoBAMO (1) and oligoAMMO (2) in  $\text{CH}_2\text{Cl}_2$  ( $C_{AOOD} \sim 70$  g/L).

$$C_{OH} = (1700\Delta D_{C=O}/\Delta l\epsilon_{C=O})/C_{AOOD}, \quad (3)$$

where  $\Delta D_{C=O}$  is the optical density of the absorption band  $\nu_{C=O} \approx 1720\text{--}1740$   $\text{cm}^{-1}$ ;  $\Delta l$ , cuvette thickness (cm); and  $\epsilon_{C=O}$ , molar extinction coefficient of  $\nu_{C=O} \sim 1720$   $\text{cm}^{-1}$  (L/g-cm).

The error in the OH determination was  $\leq 1\text{--}2\%$ . Nevertheless, this method was encumbered by chemical reactions that lengthened significantly the analysis time and consumed additional reagents although in small quantities. Therefore, a rapid IR spectroscopic method (method 4) for determining the OH content in AOOD without performing chemical reactions was developed.

*Method 4* required the construction of calibration curves. For this, AOOD samples (calibration samples) were synthesized. Their OH contents were determined independently by method 3 (Table 1), although method 2 could have been used. Then, IR spectra of solutions of all standards in  $\text{CH}_2\text{Cl}_2$  were recorded.

Typical IR spectra (Fig. 1) showed that AOOD OH groups in a solution of this concentration existed as free ( $\text{OH}_f$ ) groups and associates formed by intramolecular H-bonds ( $\text{OH}_{as}$ ). An analysis of the IR spectra indicated that the ratio between the optical densities of the absorption bands for free and associated OH groups ( $\Delta D_{\text{OH}_f}/\Delta D_{\text{OH}_{as}}$ ) was practically constant as the polymer solution concentration decreased below certain values. This result was a consequence of the fact that the intramolecular associates were relatively unaffected by dilution whereas intermolecular ones were practically absent. It was found during method development that the solution concentrations of oligoAMMO and oligoBAMO in  $\text{CH}_2\text{Cl}_2$  should not exceed 100–120 g/L for the analysis.

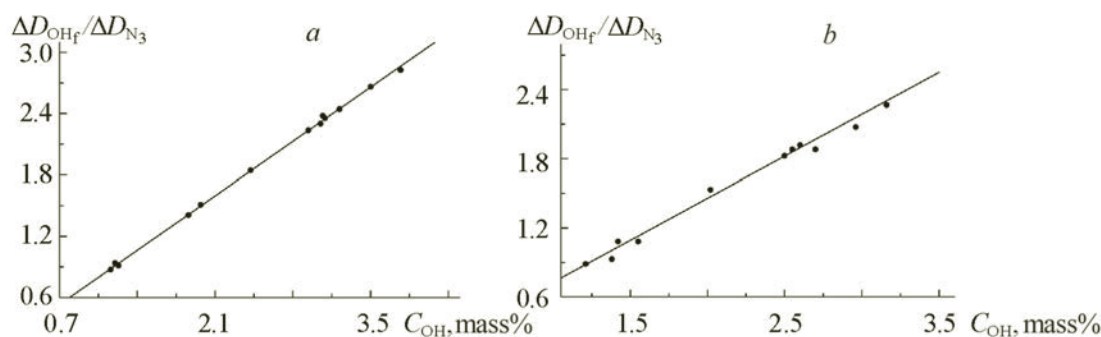


Fig. 2. Dependence of the optical-density ratio of absorption bands corresponding to stretching vibrations of free hydroxyls  $OH_f$  and combination vibrations of  $N_3$  ( $\Delta D_{OH_f}/\Delta D_{N_3}$ ) on the concentration of hydroxyl groups for oligoBAMO (a) and oligoAMMO (b).

The oligomer mass could also affect the  $\Delta D_{OH_f}/\Delta D_{OH_{as}}$  ratio [12, 13]. Thus, this ratio remained constant for oligo(ethylene oxides) in the molecular mass (MM) range  $\sim 1000$ – $20,000$  Da. However, the OBD example showed that the number ratio of associated OH groups to free ones stopped increasing at  $MM > 2000$  Da [13]. The AOOD MM values at which the  $\Delta D_{OH_f}/\Delta D_{OH_{as}}$  ratio began to change could not be established within the scope of the present work. However, it could be confidently stated that this ratio was practically constant for  $MM_{\text{oligoBAMO}} > 800$  Da and  $MM_{\text{oligoAMMO}} > 600$  Da (Table 1).

A calibration curve for determining the AOOD OH content could be constructed because the ratio between optical densities of  $OH_f$  and  $OH_{as}$  absorption bands was constant and; therefore, the optical density of the  $OH_f$  absorption band was proportional to the total oligomer OH concentration. The ratio  $\Delta D_{OH_f}/\Delta D_{N_3}$  of optical densities of absorption bands corresponding to stretching vibrations of free OH groups ( $\nu_{OH_f} = 3617$  and  $3619 \text{ cm}^{-1}$  for oligoBAMO and oligoAMMO) and bound  $N_3$  groups ( $3348 \text{ cm}^{-1}$  for oligoBAMO and  $3343 \text{ cm}^{-1}$  for oligoAMMO) should be used in order to avoid errors related to inaccuracies in calculating the oligomer solution concentration. Figure 2 shows the resulting calibration curves for the ratio of optical densities ( $\Delta D_{OH_f}/\Delta D_{N_3}$ ) as functions of OH mass fraction ( $C_{OH, \text{mass}\%}$ ) in AOOD.

Thus, the OH concentrations in the analyzed AOOD samples could be determined rapidly and accurately (relative determination error of OH content was  $\sim 1\%$ ) by performing preliminary experiments once to construct the calibration curves. For this, it was necessary:

- 1) to prepare a solution of AOOD (50–100 g/L) in  $CH_2Cl_2$ ;
- 2) to record the IR spectrum of this sample solution in the same cuvette that was used to record IR spectra of the standards ( $\Delta l \approx 0.06 \text{ cm}$ );
- 3) to calculate from the obtained IR spectrum the optical densities of the absorption bands corresponding to free OH stretching vibrations ( $\nu_{OH_f} = 3617$  and  $3619 \text{ cm}^{-1}$  for oligoBAMO and oligoAMMO) and absorption bands of  $N_3$  ( $\nu_{N_3} = 3348$  and  $3343 \text{ cm}^{-1}$  for oligoBAMO and oligoAMMO);
- 4) to determine the OH contents ( $C_{OH, \text{mass}\%}$ ) in oligoBAMO and oligoAMMO from the calibration curves (Fig. 2) or using the formulas:

$$C_{OH(\text{oligoBAMO})} = (\Delta D_{OH_f}/\Delta D_{N_3})/0.760, \quad C_{OH(\text{oligoAMMO})} = (\Delta D_{OH_f}/\Delta D_{N_3})/0.721, \quad (4)$$

where 0.760 and 0.721 are coefficients calculated using the slopes of the calibration curves (Fig. 2).

*Method 5.* This rapid IR spectroscopic method for determining the OH content in AOOD differed from the previous ones by the use of polar solvents, which was required for samples that were insoluble in chloroalkanes. The polar aprotic solvents (THF, MeCN, ethyl- or butylacetate, *N*-methylpyrrolidone, etc.) contained a strong proton-acceptor group that interacted with the OH group of the analyzed polymer. Thus, the AOOD IR spectrum in the OH absorption region showed only one band corresponding to stretching vibrations of OH groups interacting with a polar group of the used solvent (Fig. 3).

The molar extinction coefficient ( $\epsilon_{OH}$ ) determining the optical density of the analytical OH band ( $\nu_{OH} \approx 3430$  and  $3450 \text{ cm}^{-1}$  for oligoBAMO and oligoAMMO) and the sample OH concentration that was determined independently (e.g., by method 3) were found beforehand in order to determine the OH content.

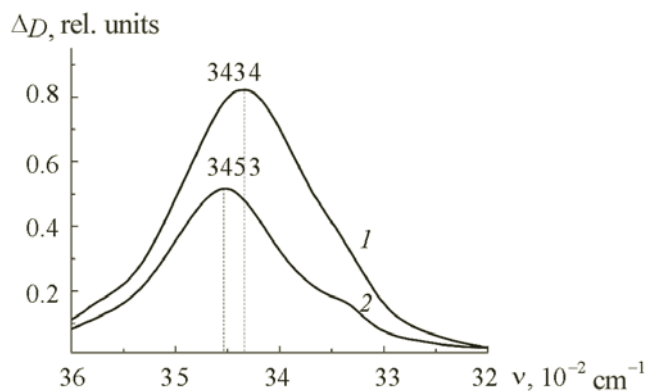


Fig. 3. Solution IR spectra of oligoBAMO (1) and oligoAMMO (2) in THF that were typical for polymers during OH determination using rapid method 5.

The analysis was performed as follows. A sample solution of known concentration (50–60 g/L) was prepared. The IR spectrum of this solution was recorded in the same cuvette (thickness  $\leq 0.06$  cm) that was used to determine  $\epsilon_{\text{OH}}$ . The OH concentration in AOOD was calculated using the formula:

$$C_{\text{OH}} = (1700\Delta D_{\text{OH}}/\Delta l\epsilon_{\text{OH}})/C_{\text{AOOD}}, \quad (5)$$

where  $\Delta D_{\text{OH}}$  is the optical density of the absorption band  $\nu_{\text{OH}} \approx 3400\text{--}3500$   $\text{cm}^{-1}$ ;  $\Delta l$ , cuvette thickness (cm);  $\epsilon_{\text{OH}}$ , previously determined molar extinction coefficient  $\nu_{\text{OH}} \sim 3400\text{--}3500$   $\text{cm}^{-1}$  (L/g·eq·cm);  $C_{\text{AOOD}}$ , solution concentration of analyzed AOOD (g/L). The determination error of OH groups was  $\leq 3\%$ .

**Conclusions.** The positive and negative aspects of the five methods for determining the OH concentration in polymers were compared. Method 1 was suitable for a large class of OH-containing oligomers and polymers of various types, with the exception of AOOD. However, the method had a lengthy analysis time, relatively large consumption of reagents, and sensitivity to moisture. Methods 2–5 that were developed to determine the OH concentration in AOOD were to one extent or another devoid of these drawbacks. Thus, methods 2 and 3 decreased the analysis time and reduced the consumption of reagents. The accuracy of method 3 was practically independent of the presence of moisture. The method was very convenient for determining the OH content in polymers acting as calibration standards for rapid methods 4 and 5. The advantages of the last methods were the high accuracy, short analysis times, and small solvent and analyzed polymer consumption with the ability to use the solutions for further analyses by other methods. The principles underlying the developed methods were suitable for determining the OH content in not only AOOD but also oligomers and polymers of various chemical types.

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## REFERENCES

1. J. H. Saunders and K. C. Frish, *Polyurethanes. Chemistry and Technology. I. Chemistry*, J. Wiley and Sons, New York, London (1962), pp. 41–58.
2. E. V. Stovbun, V. P. Lodygina, E. R. Badamshina, V. A. Grigor'eva, I. V. Doronova, and S. M. Baturin, *Heterophase Network Polymers. Synthesis, Characterization and Properties*, B. A. Rozenberg and G. M. Sigalov (Eds.), Taylor & Francis, London and New York (2002), pp. 129–138.
3. M. A. Zaverkina, V. P. Lodygina, E. V. Stovbun, E. R. Badamshina, and Yu. M. Mikhailov, *Vysokomol. Soedin., Ser. B*, **53**, No. 9, 1642–1647 (2011) [M. A. Zaverkina, V. P. Lodygina, E. V. Stovbun, E. R. Badamshina, and Yu. M. Mikhailov, *Polym. Sci., Ser. B*, **53**, No. 9–10, 505–510 (2011)].
4. M. A. Zaverkina, V. P. Lodygina, and E. R. Badamshina, *Zh. Prikl. Spektrosk.*, **81**, No. 1, 11–18 (2014) [M. A. Zaverkina, V. P. Lodygina, and E. R. Badamshina, *J. Appl. Spectrosc.*, **81**, No. 1, 7–14 (2014)].
5. S. Siggia and J. G. Hanna, *Quantitative Organic Analysis Via Functional Groups*, J. Wiley and Sons, New York (1979), pp. 17–79.

6. L. S. Kalinina, M. A. Motorina, N. I. Nikitina, and N. A. Khachapuridze, *Analysis of Condensation Polymers* [in Russian], Khimiya, Moscow (1984), p. 91.
7. M. P. Gafurova, V. A. Grigor'eva, V. P. Lodygina, G. I. Chernyi, V. V. Komratova, and S. M. Baturin, *Vysokomol. Soedin., Ser. A*, **24**, No. 4, 858–864 (1982).
8. Yu. M. Mikhailov and E. R. Badamshina, in: *Energy-Saturated Polymers: Synthesis, Structure, Properties* [in Russian], GosNIP Raschet, Chernogolovka (2008), pp. 32–43.
9. A. E. Tarasov, Ya. I. Estrin, O. M. Ol'khova, V. P. Lodygina, and E. R. Badamshina, *Vysokomol. Soedin., Ser. B*, **52**, No. 3, 515–521 (2010) [A. E. Tarasov, Ya. I. Estrin, O. M. Ol'khova, V. P. Lodygina, and E. R. Badamshina, *Polym. Sci., Ser. B*, **52**, No. 3, 144–150 (2010)].
10. A. Weissbergerf, E. Proskauer, J. Riddick, and E. Toops, *Organic Solvents. Technique of Organic Chemistry*, Vol. VIII, Interscience Publishers, New York and London (1955).
11. P. Stagg, *Analyst*, **71**, No. 844, 557 (1946).
12. G. Langbein, *Kolloid Z. Z. Polym., B*, **203**, No. 1, 1–7 (1965).
13. E. G. Atovmyan, V. P. Lodygina, and T. N. Fedotova, *Vysokomol. Soedin., Ser. A*, **25**, No. 8, 1649–1654 (1983).