1096 Russian Chemical Bulletin, International Edition, Vol. 60, No. 6, pp. 1096—1100, June, 2011

Structures of polymer electrolytes based on polyester diacrylate: an NMR study

A. A. Marinin,* K. G. Khatmullina, V. I. Volkov, O. V. Yarmolenko, and V. A. Zabrodin

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation.
E-mail: proshiy@mail.ru

The structure and dynamics of polymer network electrolytes for lithium batteries based on polyester diacrylate, lithium perchlorate, and ethylene carbonate were studied. The polyester diacrylate contained diacrylate units, 2-hydroxyethyl acrylate units, and product of dimerization of the initial monomer (to 10% by mass). An ^{1}H NMR study revealed three phases corresponding to ethylene carbonate in the polymer, ethylene carbonate bound to Li$^+$ ions, and cyclic dimer of 2-hydroxyethyl acrylate.

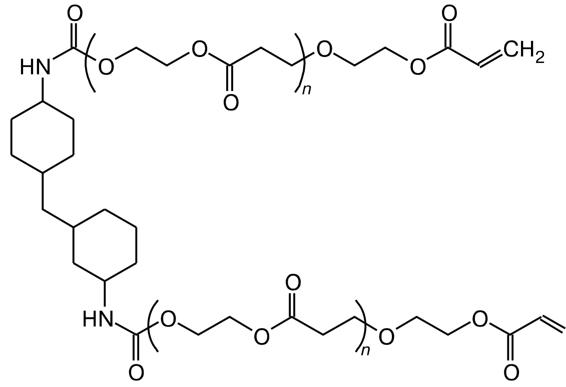
Keywords: solid polymer electrolytes, polyester diacrylate, translational mobility, self-diffusion coefficients, NMR spectroscopy.

Lithium ion batteries are widely used in portable devices, such as cell phones, cameras, tablet PCs, and notebooks. However, there is a number of severe restrictions precluding the use of lithium power cells. They include low ionic conductivity and a narrow range of operating temperatures.[1] The ionic conductivity can be increased by introducing solvents with high dielectric constants into solid polymer electrolytes.[2—5] Systems thus prepared are called gel-polymer electrolytes and can be divided into two classes, namely, heterogeneous gel-polymer electrolytes obtained by sorption of nonaqueous solutions of lithium salts into a microporous polymer matrix[2—3] and homogeneous gel-polymer electrolytes which are formed by incorporating plasticizer-solvents into polymers (or polymer blends) containing lithium salts.[4,5] Such materials are characterized by high ionic conductivity (of the order of 10^{-4}—10^{-3} S cm^{-1} at room temperature) and attract considerable attention of researchers.

The mechanisms of ionic conductivity in polymer electrolytes are most often studied by pulsed field gradient (PFG) NMR spectroscopy.[2,5—7]

In most cases, the attention is focused on self-diffusion of cations and anions[8,9] while translational mobility of solvent molecules and the dynamics of the polymer matrix are left out of consideration. However, the dependences of the ^{1}H spin echo signal intensities on the PFG amplitude (so-called diffusion decays) contain unique information on the character of inhomogeneities in the polymer matrix.[6] In particular, an analysis of the dependences of the self-diffusion coefficients on the diffusion time allows one to determine the size of the inhomogeneity regions and the lifetimes of diffusants in microphases, as well as to evaluate the cell wall permeability.[10]

In this work, we studied the self-diffusion behavior of a low-molecular-weight solvent in a gel-polymer electrolytes based on polyester diacrylate (PEDA) and lithium perchlorate by ^{1}H PFG NMR spectroscopy. Data on the conductivity and self-diffusion of lithium cations in these systems were reported earlier.[11]



PEDA

Experimental

Ethylene carbonate (EC, purity 99%, water content less than 0.005%) was purchased from Aldrich. Lithium perchlorate (95%, Aldrich) was purified by recrystallization from MeOH and then dried *in vacuo* five times at 80, 100, 150, 170, and 200 °C over a period of 12 h. Benzoyl peroxide (Aldrich) was recrystallized from chloroform and dried at room temperature in air and then *in vacuo*.

Polyester diacrylate was obtained according to a published procedure[12] by the reaction of products of anionic polymerization of 2-hydroxyethyl acrylate (HEA) with 4,4′-dicyclohexylmethane diisocyanate (Aldrich). Depending on the method of

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1071—1075, June, 2011.

synthesis of the initial HEA, PEDA contained to 10% of cyclic dimer of 2-hydroxyethyl acrylate by mass.[12,13]

Polyester diacrylate was analyzed by size-exclusion liquid chromatography and liquid chromatography under critical conditions[13] and had $M_n = 1570$, $M_w = 2780$, a C=C bond concentration of $1.86 \cdot 10^{-3}$ mol g^{-1}, and a glass transition temperature T_g of −31.9 °C. It contained 85.3% of diacrylates and 14.7% of HEA and cyclic compounds.

All ^{1}H NMR experiments were carried out on a Bruker Avance III 400 spectrometer operating at 400 MHz. The chemical shifts are reported relative to methylene protons of ethylene carbonate (δ 4.82) used as internal reference. The structures of the electrolytes synthesized were confirmed by recording the ^{1}H magic angle spinning (MAS) NMR spectra at a $\pi/2$ radiofrequency (RF) pulse duration of 2.75 μs. Preliminarily ground gel-polymer electrolyte films were placed in a rotor 3.2 mm in diameter. The spectra were recorded at sample spinning rates to 20 kHz at room temperature.

The self-diffusion coefficients of proton-containing molecules were determined using ^{1}H PFG NMR spectroscopy and the stimulated echo pulse sequence including a $\pi/2$ RF pulse and two identical semi-sinusoidal PFGs separated by two $\pi/2$ RF pulses identical to the first RF pulse (Fig. 1).

Application of the last $\pi/2$ RF pulse is followed by the formation of the spin echo signal. The dependence of the spin echo signal intensity on the PFG amplitude (diffusion decay) was described by expression (1) derived for multicomponent systems assuming a Brownian isotropic diffusion in each phase.

$$A(g) = \sum_{i=1}^{n} p_i{}' \exp\left(-\gamma^2\delta^2 g^2 D_{si}\left(\Delta - \frac{\delta}{3}\right)\right), \qquad (1)$$

where A is the normalized spin echo amplitude upon application of the PFG; D_{si} is the self-diffusion coefficient of the ith component; n is the number of components; δ characterizes the PFG duration defined as the ratio of the area under the PFG curve to the PFG amplitude; Δ is the time interval between the PFGs; g is the PFG amplitude; and γ is the gyromagnetic ratio of the nuclei under study. The parameter $p_i{}'$ is given by

$$p_i{}' = p_i \exp\frac{\left(-\dfrac{2\tau}{T_{2i}} - \dfrac{\tau_1}{T_{1i}}\right)}{\sum\limits_{i=1}^{n} p_i \exp\left(-\dfrac{2\tau}{T_{2i}} - \dfrac{\tau_1}{T_{1i}}\right)} \qquad \sum_{i=1}^{n} p_i{}' = 1, \qquad (2)$$

where p_i is the percentage of the phase (relative number of molecules characterized by the self-diffusion coefficient D_{si}), τ is the time delay between the first and second RF pulses, τ_1 is the time delay between the second and third RF pulses, T_{2i} is the spin-spin relaxation time of the ith component, and T_{1i} is the spin-lattice relaxation time of the ith component. In the PFG NMR experiments, the PFG amplitude was varied from 0.5 T m^{-1} to the maximum value of 30 T m^{-1}, which allowed one to analyze the amplitudes of the diffusion decay signals within the limits of three orders of magnitude at fixed values of other parameters of the pulse sequence. The PFG duration was varied from 1 to 3 ms and the diffusion time $t_d = \Delta - \delta/3$ was 20 ms. In measuring the dependence of the self-diffusion coefficients on the diffusion time (t_d) the parameter t_d varied from 20 to 600 ms. The self-diffusion coefficients were measured at 30 °C.

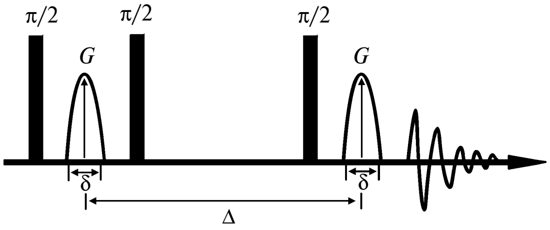


Fig. 1. The stimulated echo pulse sequence with PFG.

The proton spin-lattice relaxation times were measured at 30 °C using the inversion-recovery pulse sequence including the π and $\pi/2$ RF pulses separated by the time delay τ.

Synthesis of polymer electrolytes. Solid polymer electrolytes in the form of homogeneous transparent films of thickness d = 60—130 μm were synthesized by benzoyl peroxide (BP) initiated radical polymerization of PEDA containing $LiClO_4$ in the presence of EC at 80 °C over a period of 5 h. The initial component ratios used for the preparation of the polymer electrolyte samples are listed in Table 1.

The ^{1}H NMR MAS spectrum of the polymer electrolyte containing 54.8% of EC by mass (δ): 4.82 (br.s, CH_2, EC); 4.46, 2.76 (both br.s, CH_2 and CH_2CO, 2-hydroxyethyl acrylate dimer); 3.99, 2.87 (both br.s, CH_2O and CH_2CO, polymeric units of PEDA); 1—2.50 (br.m, CH and CH_2, cyclic groups of PEDA); 7.79, 8.28, 7.93 (all br.s, NH, $H_2C=CH$, PEDA); 4.20 (br.s, OH, HEA); 3.91, 3.85, 2.50 (br.s, CH_2, HEA).

Results and Discussion

The ^{1}H, ^{7}Li, and ^{13}C NMR spectra of solid polymer electrolytes based on PEDA exhibit broad unresolved lines and are low informative. The structures of the polymer electrolytes were analyzed by ^{1}H NMR MAS spectroscopy, which allows one to obtain high-resolution NMR spectra of solids. Figure 2 presents the ^{1}H NMR MAS spectrum of the sample of the polymer electrolyte containing 54.8% of EC.

A decrease in the solvent concentration is accompanied by line broadening and weakening of the signal of

Table 1. Initial components used in the synthesis of polymer electrolytes

Sample	Component (% by mass)			
	PEDA	Ethylene carbonate	$LiClO_4$	BP
1	90.5	—	8.1	1.4
2	86.6	4.3	7.8	1.3
3	82.9	8.3	7.5	1.3
4	79.7	12.0	7.1	1.2
5	73.8	18.4	6.7	1.1
6	68.7	24.0	6.3	1.0
7	54.6	36.4	7.6	1.4
8	45.6	45.5	7.5	1.4
9	36.5	54.8	7.3	1.4

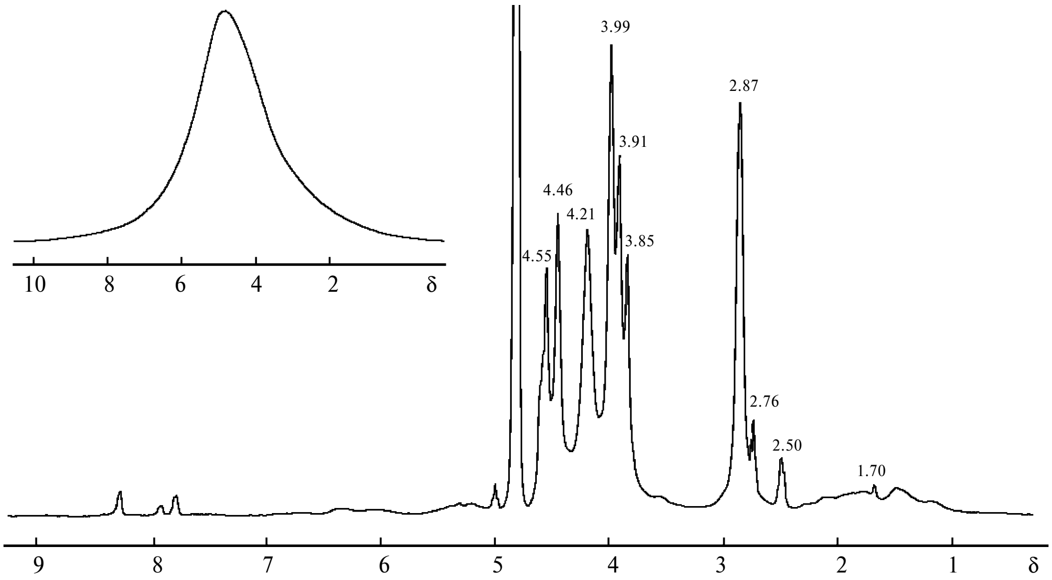


Fig. 2. The ^{1}H MAS NMR spectrum of the polymer electrolyte containing 54.8% of EC by mass. The sample spinning rate is 5 kHz. Inset: ^{1}H NMR spectrum recorded with no sample spinning.

methylene protons of EC (δ 4.82). Thus, the solid-state NMR spectra confirm the tentative chemical composition and structure of the polymer electrolyte under study.

The ^{1}H diffusion decay curves obtained for the samples containing at least 12% of EC by mass (Fig. 3) can be approximated by the sum of three exponents described by expression (1). The corresponding curves for the samples with lower EC content show a biexponential behavior. No spin echo signals were detected from the solvent-free polymers.

The diffusion decay curve for the polymer electrolyte containing 12% of EC by mass (sample *4*) is shown in Fig. 3. It is correctly approximated by expression (1) with the self-diffusion coefficients equal to $3.3 \cdot 10^{-13}$, $2.7 \cdot 10^{-12}$, and $2.7 \cdot 10^{-11}$ m^2 s^{-1}, which conditionally correspond to a "fast component" (phase I), "medium-rate component" (phase II), and "slow component" (phase III). The self-diffusion coefficient in phase III is almost independent of the solvent content starting with the samples containing at least 12% of EC by mass (Fig. 4, curve *3*). The percentage of phase III determined from the NMR data is close to the ratio of the number of hydrogen atoms in the cyclic dimer of 2-hydroxyethyl acrylate to that in EC. This makes it possible to attribute the slow component of the diffusion decay curve (phase III) to the molecules of 2-hydroxyethyl acrylate dimer and the "medium-rate" and "fast" components (phases I and II, respectively) to the solvent molecules. If the EC content becomes less than 12% by mass, the "slow" component of the diffusion decay is no longer observed. No spin echo signals were detected from the polymers containing no EC. This is probably due to low molecular mobility the 2-hydroxyethyl acrylate dimer and PEDA molecules at low solvent contents. As a consequence, the spin-spin relaxation time decreases and, in accordance with expression (2), the apparent percentage of phase III (p_3) becomes negligible. Figure 5 shows the ^{1}H diffusion decay curves for the polymer electrolyte sample containing 4.3% of EC by mass obtained at different diffusion times t_d. At short times t_d, the shape of the diffusion decay curve is independent of the diffusion time, thus indicating a slow molecular exchange between phases I and II. At long diffusion times, the apparent percentage of phase II decreases as t_d increases; this is characteristic of "medium-rate" exchange between phases I and II (Fig. 6). For the values

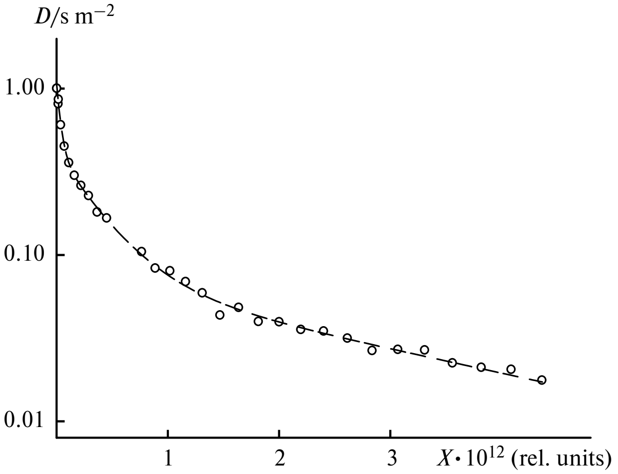


Fig. 3. The ^{1}H diffusion decay curve for the gel polymer electrolyte containing 12% of EC by mass (points) and its approximation by the least squares method (dashes). Here and in Fig. 5, $X = \gamma^2 g^2 \delta^2 (\Delta - \delta/3)$.

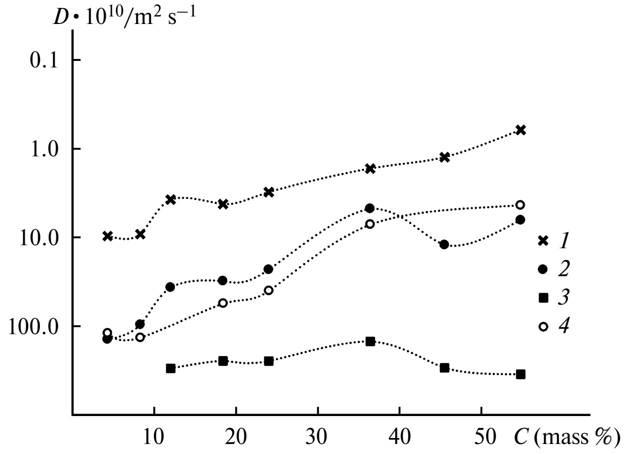


Fig. 4. The ^{1}H self-diffusion coefficients for the "fast" (*1*), "medium-rate" (*2*), and "slow" (*3*) components, and the self-diffusion coefficients of lithium ions**[11]** (*4*) plotted *vs*. solvent concentration (*C*).

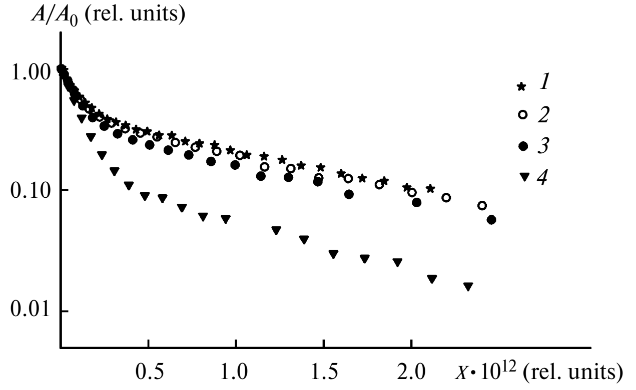


Fig. 5. The diffusion decay curve for the polymer electrolyte sample containing 4.3% of EC by mass at diffusion times of 10 (*1*), 20 (*2*), 35 (*3*), and 120 ms (*4*).

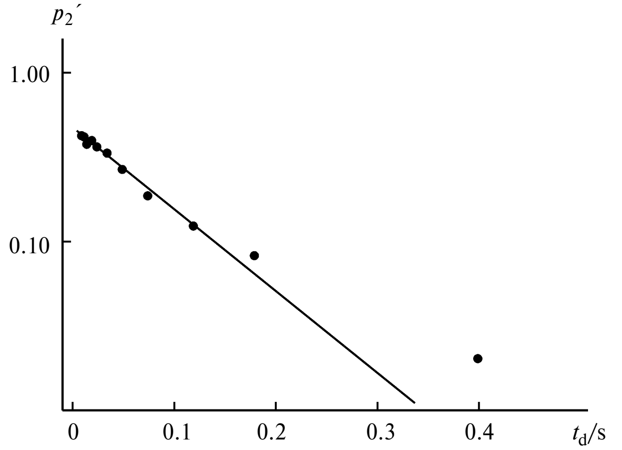


Fig. 6. Dependence of the apparent percentage of phase II ("medium-rate component") on the diffusion time for the polymer electrolyte sample containing 4.3% of EC by mass.

lying within an order of magnitude, this dependence can be approximated by expression (3) (see Ref. 14)

$$p_2'(t_d) = p_2'(0)\exp(-t_d/\tau), \qquad (3)$$

where $t_d = \Delta - \delta/3$ is the diffusion time, $p_2'(0)$ is the apparent percentage of phase II at $t_d = 0$, and τ is the lifetime of the diffusant molecules in phase II. For the sample with the minimum solvent content (4.3% by mass) the lifetime of the EC molecules in phase II was 90 ms. The dependence of the percentages of the phases on the spin-lattice relaxation time T_1 was ignored because the relaxation times were at least 600 ms, being an order of magnitude longer than the lifetime τ.

The self-diffusion coefficients of the EC molecules in phase II showed a slight dependence on the diffusion time, because the self-diffusion coefficients only halved as the diffusion times changed from 20 to 600 ms. This also indicates a relatively free exchange of the solvent between different phases.

The dependence of the self-diffusion coefficients on the solvent concentration is shown in Fig. 4. As can be seen, the self-diffusion coefficient of the "medium-rate" component is close to that of lithium ions. One can assume that the "medium-rate" component is due to motions of the EC molecules solvating lithium ions, while the "fast" component corresponds to the EC molecules bound to PEDA. A rather fast exchange of the solvent molecules between phases I and II is also indicated by the fact that the decrease in the longitudinal magnetization was characterized by one spin-lattice relaxation time which varied from 600 ms to 1 s depending on the solvent concentration.

Solid-state ^{1}H NMR spectroscopy was used to study PEDA/lithium perchlorate based gel-polymer electrolytes for lithium cells, containing EC as solvent (from 0 to 55% by mass). The chemical compositions and structures of the polyelectrolytes were confirmed by the ^{1}H MAS NMR spectra. Translational mobility of the low-molecular-weight solvent in the gel-polymer electrolytes was studied by ^{1}H PFG NMR spectroscopy. Three different phases with the molecular self-diffusion coefficients differing by an order of magnitude were revealed. They correspond to the EC molecules bound to the polymer (phase I), EC molecules solvating lithium ions (phase II), and cyclic dimer of 2-hydroxyethyl acrylate molecules (phase III). The dependences of the self-diffusion coefficients on the EC content and on the diffusion time (in the range from 20 to 600 ms) were obtained and the exchange time of the EC molecules between phases I and II was estimated. It was found that lithium cations and the EC molecules solvating them move together in phase II.

The authors express their gratitude to Prof. V. D. Skirda for useful discussions.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 10-03-00862).

References

1. S. Suarez, J. Jayakody, S. Abbrent, S. G. Greenbaum, T. J. H. Shin, S. Passerini, *Solid State Ionics*, 2005, **176**, 1113.
2. Yu. Saito, H. Kataoka, T. Sakai, S. Deki, *Electrochim. Acta*, 2001, **46**, 1747.
3. W. Pu, X. He, L. Wang, Ch. Jiang, Ch. Wan, *J. Membr. Sci.*, 2006, **272**, 11.
4. J. Adebahr, M. Forsyth, D. R. MacFarlane, P. Gavelin, P. Jacobsson, *Solid State Ionics*, 2002, **147**, 303.
5. M. J. Williamson, H. V. St. A. Hubbard, I. M. Ward, *Polymer*, 1999, **40**, 7177.
6. H. Walderhaug, O. Soderman, D. Topgaard, *Prog. Nucl. Magn. Reson. Spectrosc.*, 2010, **56**, 406.
7. K. Hayamizu, Y. Aihara, S. Arai, W. S. Price, *Electrochim. Acta*, 2000, **45**, 1313.
8. C. Capiglia, Y. Saito, H. Yamamoto, H. Kageyama, P. Mustarelli, *Electrochim. Acta*, 2000, **45**, 1341.
9. S. Suarez, S. Abbrent, S. G. Greenbaum, J. H. Shin, S. Passerini, *Solid State Ionics*, 2004, **166**, 407.
10. Ch.-H. Cho, Y.-Sh. Hong, K. Kang, V. I. Volkov, V. Skirda, Ch.-Y. J. Lee, Ch.-H. Lee, *Magn. Reson. Imaging*, 2003, **21**, 1009.
11. A. A. Marinin, K. G. Khatmullina, V. I. Volkov, O. V. Yarmolenko, *Elektrokhimiya*, 2011, **47**, 766 [*Russ. J. Electrochem.* (*Engl. Transl.*), 2011, **47**, 717].
12. B. A. Rozenberg, L. M. Bogdanova, G. N. Boiko, L. L. Gur´eva, E. A. Dzhavadyan, N. F. Surkov, G. A. Estrina, Ya. I. Estrin, *Vysokomolekulyar. Soedineniya. Ser. A*, 2005, **47**, 952 [*Polym. Sci., Ser A* (*Engl. Transl.*), 2005, **47**, 582].
13. G. A. Estrina, B. A. Komarov, Ya. I. Estrin, B. A. Rozenberg, *Vysokomolekulyar. Soedineniya. Ser. A*, 2004, **46**, 207 [*Polym. Sci., Ser. A* (*Engl. Transl.*), 2004, **46**].
14. A. I. Maklakov, V. D. Skirda, N. F. Fatkullin, *Samodiffuziya v rastvorakh i rasplavakh polimerov* [*Self-Diffusion in Polymer Solutions and Melts*], Kiev, Izd-vo Kievskogo Univ., 1987, 227 pp. (in Russian).

Received March 4, 2011;
in revised form May 5, 2011