Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 45 (2004) 3907–3912

polymer

www.elsevier.com/locate/polymer

Cavity size distributions in high free volume glassy polymers by molecular simulation

Xiao-Yan Wang, Kenneth M. Lee, Ying Lu, Matthew T. Stone, I.C. Sanchez*, B.D. Freeman

Department of Chemical Engineering, University of Texas at Austin, Austin, TX 78712, USA

Received 28 May 2003; accepted 8 January 2004

Abstract

Two very permeable polymers, poly(1-trimethylsilyl-1-propyne) (PTMSP) and a random copolymer of tetrafluoroethylene and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (TFE/BDD), have very similar and large fractional free volumes (FFV), but very different permeabilities. Using atomistic models, cavity size (free volume) distributions determined by a combination of molecular dynamic and Monte Carlo methods are consistent with the observation that PTMSP is more permeable than TFE/BDD. The average spherical cavity size in PTMSP is 11.2 Å whereas it is only 8.2 Å in TFE/BDD. These cavity size distributions determined by simulation are also consistent with free volume distributions determined by positron annihilation lifetime spectroscopy.

Keywords: Poly(1-trimethylsilyl-1-propyne); Fractional free volume; Cavity size distribution

1. Introduction

Polymer membranes play an important role in gas separation, and food packing applications [1] Poly(1-trimethylsilyl-1-propyne) (PTMSP) and random copolymers of tetrafluoroethylene and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (TFE/BDD) are some of the most permeable polymers known and are very useful for membrane separation technology [2].

TFE/BDD is an amorphous random copolymer with very high permeability and excellent chemical resistance [3,4]. There are two commercially available TFE/BDD copolymers containing 65 or 87 mol% BDD from Du Pont (Wilmington, DE) under the trade names Teflon AF1600 (TFE/BDD65) and AF2400 (TFE/BDD87) [3]. We chose TFE/BDD87 for this study because of its higher fractional free volume (FFV). PTMSP is known for having the largest permeability among all polymeric materials [5]. Moreover, PTMSP exhibits very unusual gas and vapor transport properties. It is more permeable to large organic vapors, such as *n*-butane, than to small, permanent gases, such as hydrogen [5,6]. Table 1 presents chemical structures and some properties of PTMSP and TFE/BDD87. PTMSP is a substituted polyacetylene that contains double bonds in the backbone and a bulky trimethylsilyl [$Si(CH_3)_3$] side group. PTMSP's density of 0.75 g/cm^3 is rather low relative to the 1.0 g/cm^3 density typical of other glassy polymers. TFE/BDD87's apparent "higher" density is because fluorine has replaced every possible hydrogen in the structure. Both PTMSP and TFE/BDD87 are loosely packed polymers with stiff chain backbones. Notice that although the FFV values are large, both polymers have relatively high glass temperatures.

The high permeability in these polymers is partially associated with the extremely high FFV. In general, larger FFV polymers are more permeable [7–9]. Group contribution and experimental methods can be used to determine free volumes [7–11].

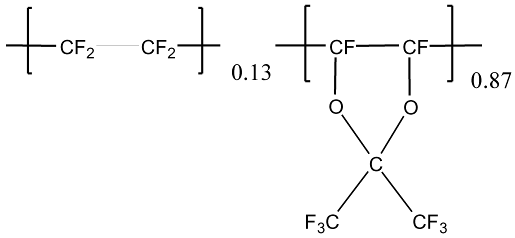
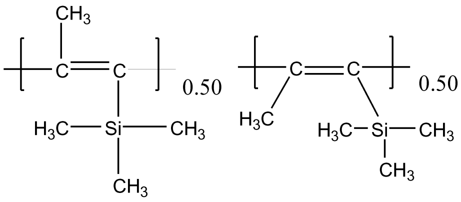
Based on density and group contribution estimates of occupied volume, the FFVs of TFE/BDD87 and PTMSP are 0.32 and 0.34, respectively [3,11]. The values were calculated using the van der Waals volumes of repeat units and group contribution increments. These values are almost twice the value for conventional, low-free-volume glassy polymers material such as polysulfone with a FFV of 0.156 [12]. Although both TFE/BDD87 and PTMSP have comparable FFV's, PTMSP is much more permeable than TFE/BDD87. This suggests that FFV is only part of the story and that the distribution of free volume is important.

---

* Corresponding author.
E-mail address: sanchez@che.utexas.edu (I.C. Sanchez).

0032-3861/$ - see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.polymer.2004.01.080

Table 1
Structure and some physical properties of TFE/BDD87 and PTMSP at $T = 298\ K$ [3]

Polymer	Formula	Density (g/cm^3)	FFV[a]	T_g (°C)
TFE/BDD87 (AF2400)	 TFE BDD	1.74	0.32	240
PTMSP	 trans cis	0.75	0.34	>280

T_g, glass transition temperature.
[a] FFV, fractional free volume.

Positron annihilation lifetime spectroscopy (PALS) measurements support this view. They show, [2] on the time scale of the PALS experiment, that the largest accessible free volume elements in TFE/BDD87 are smaller and in much lower concentration than in PTMSP. In addition to PALS, there are several other experimental methods that can be used to characterize the cavity size distribution of a polymer, such as photochromic [20] and spin probe [21] methods.

Although tremendous progress has been made, the cavity size distribution of a material is still very difficult to measure. Molecular modeling provides an alternative method and its utility is demonstrated herein. Cavity size distributions (CSDs) for TFE/BDD and PTMSP are calculated using a combination of molecular dynamic and Monte Carlo techniques. The algorithm used to determine CSDs is based on energetic rather than geometric considerations and is described in detail in Ref. [13].

2. Simulation

The COMPASS force field (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) [14,16] was used in all the simulations. Molecular dynamics (MD) were performed using Amorphous Cell module of Materials Studio package [14].

For PTMSP, the initial polymer chain constructed consisted of 50 repeat units with a 50:50 probability for the occurrence of *cis* and *trans* monomers, mimicking the PTMSP material polymerized in the presence of a catalyst $TaCl_5$ [6,15]. Two PTMSP chains, each with 50 repeat units, were folded in the Amorphous Cell with a density of 0.75 g/cm^3 (experimental density). The resulting cell length was 29.2 Å. Sixty initial states were constructed followed by 5000 steps of energy minimization to eliminate the ‘hot spots’. Afterwards, a 10 ps NVT MD run at 298 K was performed for each of the 60 states to further equilibrate structures. The assumption is made that the resulting structures are representative of the glassy polymer.

For TFE/BDD87, the initial polymer chain was constructed with 100 repeat units with 13 mol% TFE and 87 mol% BDD at the experimental density of 1.74 g/cm^3. The resulting cell length is around 28 Å. Sixty initial states were constructed and followed by 10,000 energy minimization steps and a MD run of 10 ps in the NVT ensemble. The temperature was also set to 298 K.

A cavity-sizing algorithm [13] was then applied to each of the equilibrated configurations. The following is a quick review of cavity-sizing algorithm.

(i) A polymer structure is generated by MD (or MC) simulation.
(ii) The force field used to create the above structure is replaced with a pure repulsive force field. All atoms remain in fixed locations.
(iii) A trial repulsive particle is then randomly inserted into

Table 2
Comparison of fractional free volume (from both Bondi method [3] and zero pressure PVT data), fractional cavity volume, average cavity size and permeability (P_0) of PTMSP and TFE/BDD87

Polymer	FFV% [3]	FFV% (this work)	FCV%	Average cavity size (Å)	P_0 (O_2) [17,18] (Barrer)
TFE/BDD87	32	31.4	13.2 ± 0.9	8.2	960
PTMSP	34	NA	15.6 ± 1.8	11.2	9000

the repulsive polymer structure and a local energy minimum is located in the repulsive force field.

(iv) After the minimum is determined, attractive interactions are turned on and the size of the test particle is adjusted until its potential interaction with all other atoms becomes zero. This size is taken as the diameter of a spherical cavity.

(v) A check is then made to determine whether the initial random inserting point is inside the cavity or not. The cavity is only accepted if the initial point is inside the cavity. This procedure leads to volume distribution rather than a number distribution of cavities.

(vi) Steps (iii)–(v) are repeated enough times to get a representative distribution of cavity sizes for a given structure.

3. Results and discussion

3.1. Free volume

Table 2 presents the FFV from Ref. [3] and that calculated from experimental low pressure PVT data [10]. The fractional cavity volume (FCV) and the average cavity size are from our simulations. The fractional cavity volume is the fraction of space occupied by spherical cavities defined above by our cavity size algorithm. As a point of reference, a close-packed periodic structure of spheres has a FFV of 0.26, but the FCV (from octahedral and tetrahedral spherical cavities) is only 0.069 [13]. In other words, not all of the free volume is in the form of well-defined spherical cavities. FCV is yet another measure of free volume.

Also included in Table 2 are experimental permeation coefficients for oxygen [17,18]; the average cavity size $\langle x \rangle$ is calculated as follows:

$$\langle x \rangle = \frac{\int_0^\infty x^3 P(v) \mathrm{d}x}{\int_0^\infty x^2 P(v) \mathrm{d}x} \tag{1}$$

where x is the cavity size as defined in step (v) and $P(v)$ is the volume distribution obtained from our cavity-sizing algorithm.

FFV of TFE/BDD87 and PTMSP polymers from Ref. [3] are obtained by using group contribution methods [11]. We also calculated the FFV of TFE/BDD87 based on the lower pressure PVT data from the literature [19] based on the method described in Ref. [10], which is outlined below.

FFV is usually defined as:

$$\mathrm{FFV} = \frac{v - v^*}{v} \tag{2}$$

where v is the specific volume and v^* is the specific volume at absolute zero temperature. However, it is has been suggested that $1/\rho^*$ is a better measurement of v^* [10]; ρ^* is the characteristic mass density that is obtained by extrapolating zero pressure densities to absolute zero temperature. Therefore, FFV can also be obtained by the following equation:

$$\mathrm{FFV} = 1 - \tilde{\rho} = 1 - \frac{\rho}{\rho^*} \tag{3}$$

where ρ is the mass density (reciprocal of specific volume v) at temperature T, and $\tilde{\rho}$ is the reduced mass density.

Fig. 1 shows the mass density vs. temperature at zero (atmospheric) pressure for TFE/BDD87 random copolymer. It is seen that mass density of TFE/BDD87 has a linear relationship with temperature. Polymers exhibit a linear dependence of density on temperature [10]. By extrapolating the density to zero temperature, we find that $\rho^* \approx 2.53$ g/cm^3 for the TFE/BDD87 random copolymer. The mass density of TFE/BDD87 at 298 K is about 1.74 g/cm^3 [19], so the FFV of TFE/BDD87 is 0.314 based on Eq. (3). This

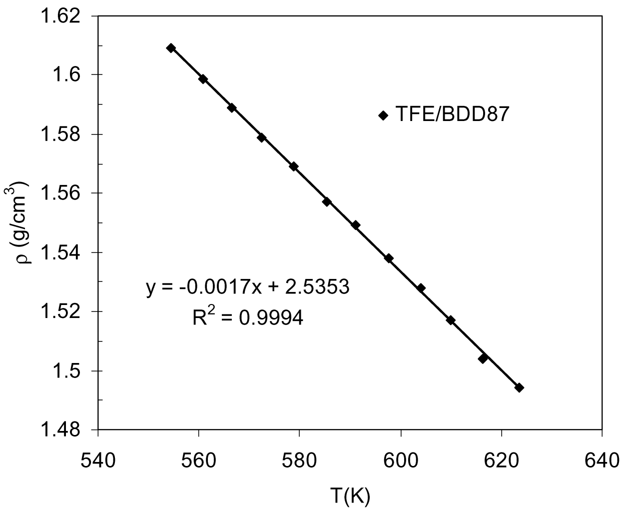


Fig. 1. Zero pressure densities for TFE/BDD87 vs. temperature. Symbols are experimental data from Ref. [19]. The straight line is a least-squares line through the data. The regress equation is also showed.

independently calculated value agrees well with that obtained from the Bondi method. Unfortunately, a similar calculation for PTMSP is not possible because the requisite low pressure volume–temperature data are not available.

The FFV from Ref. [3], fractional cavity volume, and the average cavity size of PTMSP are larger than that of TFE/BDD87. However, both of them have greater free volume than conventional glassy polymers such as polysulfone (PSF), which has a FFV value of 0.156 [12] by the Bondi method [11] and 0.133 from the zero pressure PVT data [10].

3.2. Permeability

The permeability of a polymer film to a penetrant is defined as [6]:

$$P = \frac{\text{Flux}\cdot\text{Thickness}}{\text{Driving force}} = \frac{Nl}{p_2 - p_1} \tag{4}$$

where P is the permeability coefficient, N is the steady-state penetrant flux through the polymer film, l is the film thickness, p_1 and p_2 are the downstream and upstream pressure, respectively, and $\Delta p = p_2 - p_1$. When penetrant flux follows Fick' law, the permeability coefficient P could be written as:

$$P = \left(\frac{C_2 - C_1}{p_2 - p_1}\right)\bar{D} \tag{5}$$

where $\bar{D}$ is the concentration-averaged diffusivity, C_1 and C_2 are the penetrant concentrations in the polymer at the downstream and upstream faces of the membrane, respectively. For the case of negligible downstream pressure, the term in parentheses in Eq. (5) becomes C_2/p_2, which is the solubility S at the upstream pressure p_2 and Eq. (5) becomes,

$$P = S\bar{D} \tag{6}$$

The permeability is the product of solubility and diffusivity. The permeability is often expressed in units of Barrer, and 1 Barrer $= 10^{-10}\,\frac{\text{cm}^3(\text{STP})\text{cm}}{\text{cm}^2\text{ s cmHg}}$, where STP means standard temperature (0 °C) and pressure (1 atm).

Table 3 presents the permeability of PTMSP and TFE/BDD87 polymer films to some penetrants at $t = 35$ °C and $\Delta p = 0$ [17,18]. The permeation coefficients for PTMSP are much larger than those for TFE/BDD87, though both have comparable free volumes.

3.3. Cavity size distribution

Cavity size distribution provides an alternative means to examine this problem. Hofmann et al. [15] have studied the free volume distribution in ultrahigh free volume PTMSP and two lower free volume polymers by computer simulation. PTMSP shows a broader free volume distribution than the low free volume polymers.

The cavity size distributions of PTMSP and TFE/BDD87 copolymer determined in this study are presented in Figs. 2 and 3. The distribution in Fig. 2 (PTMSP) is shifted towards larger cavity sizes relative to TFE/BDD87. The largest cavity diameter found in PTMSP is about 16 Å; in contrast, the largest cavity diameter found in TFE/BDD87 is 12 Å. This is also consistent with PALS data that show larger free volume elements in PTMSP than in TFE/BDD87 [2,3]. PALS free volume distributions are bimodal [3]. The larger of the two cavities in PTMSP are 13.6 Å, while in TFE/BDD87 they are 11.9 Å.

To quantitatively compare the cavity size distribution of TFE/BDD87 and PTMSP, the cumulative distribution of cavity size distribution of two polymers is shown in Fig. 4. The cumulative distribution for PTMSP is shifted towards larger cavity sizes. In TFE/BDD, 50% of the cavities exceed 8.1 Å, whereas 50% of the cavities in PTMSP exceed 11.3 Å. Many studies have shown that the gas transport behavior of TFE/BDD87 is similar to that of conventional, low-free-volume glassy polymers, whereas PTMSP behaves more like a non-porous carbon than a conventional glassy polymer.

4. Conclusions

Although PTMSP and TFE/BDD polymers have large and similar FFV, PTMSP is much more permeable to gases (see Table 3). As an explanation, it has been suggested that PTMSP has larger free volume elements and more connected regions of free volume than TFE/BDD [2,6]. Our cavity size distribution results from molecular simulation support the idea that PTMSP has on average larger cavities (see Figs. 2–4). However, our algorithm does not address the issue of cavity connectivity. It is also been demonstrated that molecular simulations of glassy structures can be produced and probed with a cavity size algorithm to obtain results that are consistent with existing PALS measurements.

Table 3
Comparison of permeability of TFE/BDD87 and PTMSP to a series of gases and vapors at $t = 35$ °C and $\Delta p = 0$ [17,18]

Penetrant	P_0 (Barrer) TFE/BDD87 [17]	PTMSP [18]
H_2	2100	15,000
O_2	960	9000
N_2	480	6600
CO_2	2200	27,000
CH_4	390	15,000
C_2H_6	210	31,000
C_3H_8		38,000
CF_4	66	3100
C_2F_6	13	2400
C_3F_8		1200

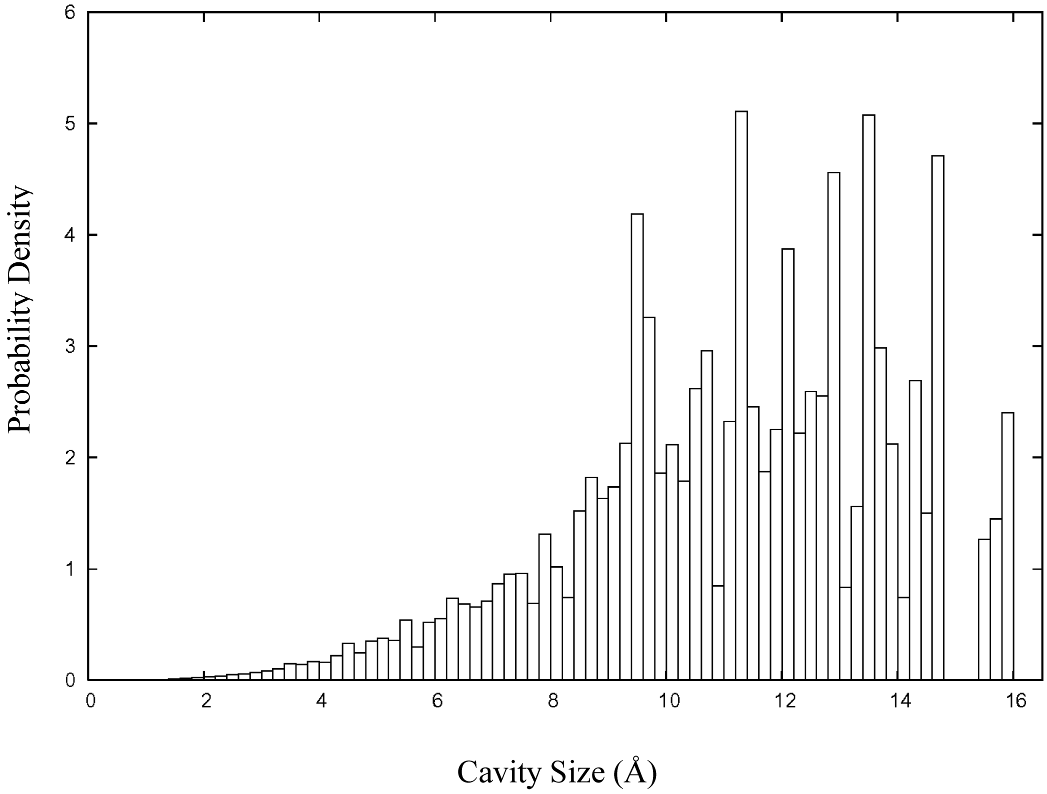


Fig. 2. Cavity size distribution in PTMSP at $T = 298$ K and $\rho = 0.75$ g/cm^3 from molecular simulation. The average cavity size is 11.2 Å, and the fractional cavity volume is 15.6%. PTMSP has higher permeability than TFE/BDD87 (see Table 3). PTMSP has a smaller fraction of smaller cavities than TFE/BDD87 (see Fig. 3).

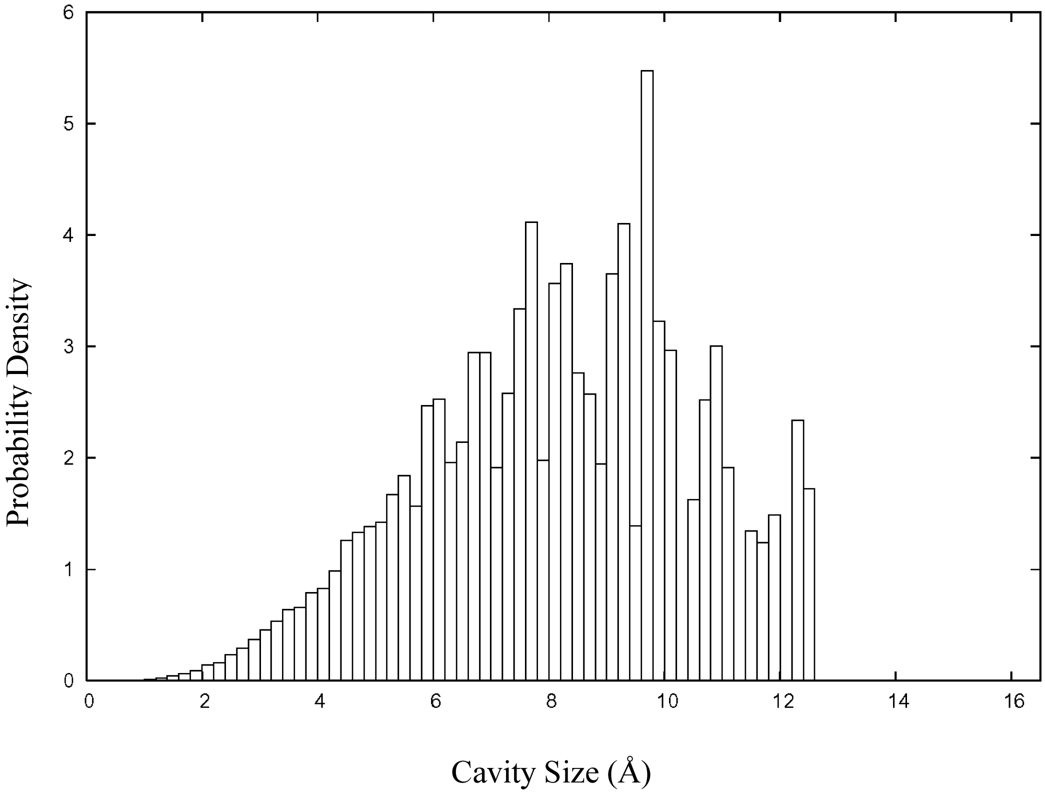


Fig. 3. Cavity size distribution in TFE/BDD87 at $T = 298$ K and $\rho = 1.74$ g/cm^3 from molecular simulation. The average cavity size is 8.2 Å, and the fractional cavity volume is 13.21% (see Table 2). TFE/BDD87 has a higher fraction of smaller cavities than PTMSP.

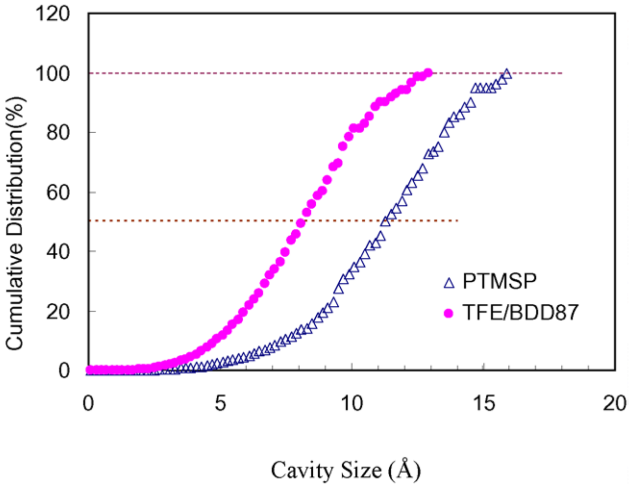


Fig. 4. Comparison of cumulative cavity size distribution in TFE/BDD87 and PTMSP.

Acknowledgements

The authors thank A. J. Hill for her stimulating seminar at UT and D.J. Walsh for providing PVT data on TFE/BDD87. This material is based upon work supported in part by the STC Program of the National Science Foundation under Agreement No. CHE-9876674.

References

[1] Nakagawa T. In: Paul DR, Yampol'skii YP, editors. Polymeric gas separation membranes, 1st ed. FL: CRC: Boca Raton; 1994. p. 155.
[2] Singh A, Bondar S, Dixon S, Freeman BD, Hill AJ. Proc Am Chem Soc Div, Polym Mater Sci Engng 1997;77:316.
[3] Shantarovich VP, Kevdina IB, Yampolskii YP, Alentiev AY. Macromolecules 2000;33:7453–66.
[4] Alentiev AY, Yampolskii YP, Shantarovich VP, Nemser SM, Plate NA. J Membr Sci 1997;126:123–32.
[5] Merkel TC, Bondar V, Nagai K, Freeman BD. Macromolecules 1999; 32:370–4.
[6] Nagai K, Masuda T, Nakagawa T, Freeman BD, Pinnau Z. Progr Polym Sci 2001;26:721–98.
[7] McHattie JS, Koros WJ, Paul DR. Polym Sci Polym Phys 1991;29: 731–46.
[8] McHattie JS, Koros WJ, Paul DR. Polymer 1992;33:1701–11.
[9] Niemelä S, Leppänen J, Sundholm F. Polymer 1996;37:4155.
[10] Sanchez IC, Cho J. Polymer 1995;36:2929–39.
[11] van Krevelen WD. Properties of polymers. Amsterdam: Elsevier; 1990. p. 71.
[12] Aitken CL, Koros WJ, Paul DR. Macromolecules 1992;25:3424.
[13] Veld PJ, Stone MT, Trunskett TM, Sanchez IC. J Phys Chem B 2000; 104:12028–34.
[14] Materials Studio is a package developed by Molecular Simulations Inc., San Diego, CA; 2002.
[15] Hofmann D, Heuchel M, Yampolskii Y, Khotimskii V, Shantarovich V. Macromolecules 2002;35:2129–40.
[16] Sun H. J Phys Chem B 1998;102:7338–64.
[17] Merkel TC, Bondar V, Nagai K, Freeman BD, Yampolskii YP. Macromolecules 1999;32:8427–40.
[18] Merkel TC, Bondar V, Nagai K, Freeman BD. J Polym Sci, Part B: Polym Phys 2000;38:273.
[19] De Angelis MG, Merkel TC, Bondar VI, Freeman BD, Doghieri F, Sarti GC. Macromolecules 2002;35:1276.
[20] Victor JG, Torkelson JM. Macromolecules 1987;20:2241–50.
[21] Wasserman AM, Kovarskii AL. Spin probes and lables in physical chemistry of polymers. Moskow: Nauka; 1986.