

Diffusion and sorption of water in moderately hydrophilic polymers: From segmented polyetherurethanes to poly-3-hydroxybutyrate

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Abstract

In matrices of moderately hydrophilic polymers (MHP) the balance of dispersive and polar interactions determines the structure-morphological peculiarities and the mechanism of diffusion and sorption. Segmented polyetherurethanes (SPEU) were prepared from polytetramethylene oxide or copolymers of ethylene and propylene oxides with 4,4'-diphenylmethane diisocyanate with tetramethylendiol as chain extender. High-molecular weight poly-3-hydroxybutyrate (PHB) was produced by two-stage biotechnological synthesis. Isotopic accessibility and sorption-diffusion experiments were carried out using a suitable designed permeability cell for H-D exchange and vacuum balance techniques, respectively. FTIR/ATR spectroscopy and mechanical thermal analysis were used for MHP structure investigations. The main goal of the paper is to investigate the interrelation between chemical and supermolecular structure and transport processes in SPEU and PHB membranes. SPEU is characterized by a decrease of water diffusion coefficients, D_w , with increasing relative humidity and in a rise of accessibility of urethane groups in accordance with partial immobilization model of water diffusion. In the presence of water (1–2 wt.%) α -relaxation maximum is not shifted (plastification is not observed) but water molecules are immobilized in an intermediate layer between soft region and hard domain in SPEU. The latter are not penetrated by water. For PHB free and tightly immobilized forms of water were discovered by FTIR and sorption-diffusion methods. The results of this study give the basis for revealing structure-transport relationship in novel perspective polymers with a moderate hydrophilicity.

Keywords: Moderate hydrophilicity; Segmented polyetherurethanes; Poly-3-hydroxybutyrate; Diffusion; Water

1. Introduction

Theory and practice of membrane technologies are based on studies of diffusion

Presented at the 7th International Symposium on Synthetic Membranes in Science and Industry, Tübingen, Germany, August 29 – September 1, 1994.

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phenomena because these phenomena control mainly an efficiency of membrane separation [1, 2]. The intensity of interaction of a polymer matrix with water or solute molecules depends on the polarity of macromolecule fragments and determines considerably the mechanism of sorption and diffusion [3, 4]. Therefore, it would be relevant to classify all

polymers into hydrophobic ones relative to water interactions.

The analysis of solubilities in accessible noncrystalline regions for 70 polymers of different hydrophilicity shows that the plot of the Flory-Huggins equation ($\ln \varphi_w + \varphi_p$) against the product $(\delta_w - \delta_p)^2 \varphi_p^2$ is nonlinear (Fig. 1) and may be approximated by two branches in accordance with the inequalities $(\delta_w - \delta_p)^2 \varphi_p^2 < 600 \text{ J/cm}^3$ for the hydrophilic polymers (PAAM, PAA, PVA, cellulose) and $> 700 \text{ J/cm}^3$ for the hydrophobic ones (PELD, PEHD, PP, PS). The points situated in the vicinity of the intersection belong to moderately hydrophilic polymers (MHB), intermediate type, where solubilities of H_2O spread from 0.064 g/g (polyetherurethane) to 0.0125 g/g (poly-3-hydroxybutyrate).

For polymers of the intermediate type, the compensation of dispersion, nonpolar and polar, electrostatic interactions is characteristic, which makes this type of polymers different from both hydrophilic and hydrophobic ones. The balance of hydrophilicity to be partly or completely fulfilled is responsible for a variety of structural elements of matrices, their stability against corrosive

media, as well as transport mobilities of water and electrolytes.

The objectives of the present study are concerned with the transport-structure relationship for typical representatives of MHB – segmented polyetherurethanes (SPEU) and poly-3-hydroxybutyrate (PHB).

2. Experimental

The SPEU used in this study were synthesized on the base of different polyether with hydroxyl-terminated groups, 4,4'-diphenyl methane diisocyanate (MDI) supplied by Bayer Co., and 1,4-butandiol (BD) as extended with a water content not more than 0.03 w.%. In the text, the SPEU are denoted as "Hemotan-T" and "Vitur-RM" according to the manufacturer's nomenclature. For Hemotan-T synthesis copolymers of propylene and ethylene oxides have been used unlike from Vitur-RM specimens including polytetramethylene oxide. Details regarding their two-stage process and characterization are reported in earlier publications [6, 7].

The polymer films were casted from DMSO solution. The casting was performed at room temperature for 6–8 days. The films were then dried at 60°C in vacuo until constant weight was obtained. The films were used for dynamic mechanical thermal analysis, ATR/FTIR and H-D methods, as well as the vacuum quartz microbalance technique. Sorption/diffusion measurements were carried out using a McBain by interval method. The sensitivity of the quartz spiral was 0.778 mg/mm. IR spectra were recorded on spectrometer Brucker FTIR FS40. Details of the methods are described elsewhere [7–10].

PHB films were produced by two-stage microbial synthesis by the Biochemical Society of Russia for drug release matrices and medical fibers. Additional information concerning these materials is listed in Table 1.

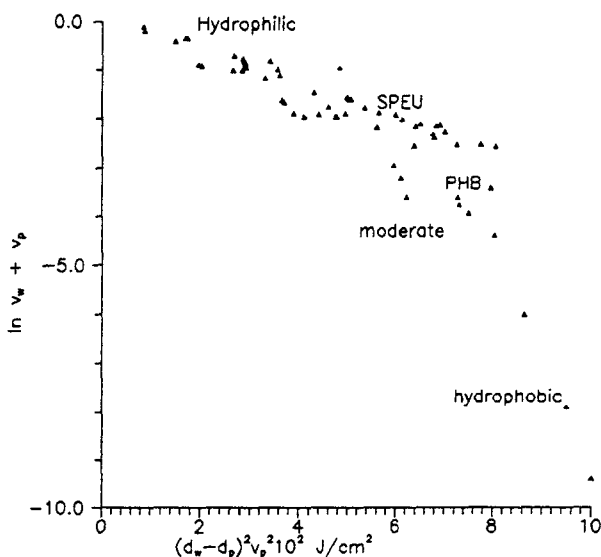


Fig. 1. Classification of polymer hydrophilicity.

Table 1
Characteristics of PHB films

Film	$M_n \cdot 10^{-3}$	σ (MPa)	ε (%)	Cluster number	Solvent
1	1,679	33.2	45.2	2.0	Acetone
2	1,609	31.1	34.2	1.5	Dioxan

3. Results and discussion

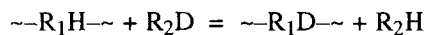
3.1. Segmented polyetherurethanes

In recent time attention has been directed toward the development of novel materials in order to satisfy simultaneously the varied constructional and biomedical demands. Among the polymers belonging to this area, the segmented copolymers of urethanes with oligoethers (or oligoesters) have been widely used due to their useful physico-chemical and transport properties as well as the acceptable biocompatibility [11, 12].

The degree of microphase separation of hard (MDI) and soft (oligoether) segments is responsible for the perfection of domain structure as well as for quite acceptable mechanical and thrombresistance properties [13]. The factors governing perfect phase separation of hard and soft segments are related to the synthetic pathway, chemical composition and the thermal history of SPEU specimens.

Despite a large number of reports on SPEU structure, studies on the relationship between morphology and transport phenomena in the copolymer matrix are scarce [14–16].

The study of domain structures for SPEU by the isotopic method of H-D exchange is founded on heavy water transport into water-accessible and noncrystalline regions of polymers and on its reaction only with mobile H atom in urethanic or uric groups of hard segments.



Ether fragments forming SPEU chains are incapable for isotopic H-D reaction as they have no mobile H atoms.

Limiting ratio for the number of reacted groups to the total functional group number of given kind in polymer determines a value of an accessibility (F). In common cases, the accessibility of urethanic groups depends on the nature, molecular weight, and activity of the deuterium agent (D_2O), as well as on the temperature of the exchange process A. As distinct from the polymer crystallinity, the accessibility determines the mutual behavior of the system "SPEU-water" but not the individual crystalline lattice of the polymer and gives an additional information on structural organization of the SPEU matrix.

The experimental increase of F with temperature is nonlinear, as it is shown in Fig. 2. In the region of room temperature, a majority of urethanic groups for SPEU are nonaccessible to heavy water, since these groups are included in compact domains. Only about a third of the total urethanic groups are affected by isotopic reaction, forming an interfacial layer of domain, where soft and hard segments are mixed.

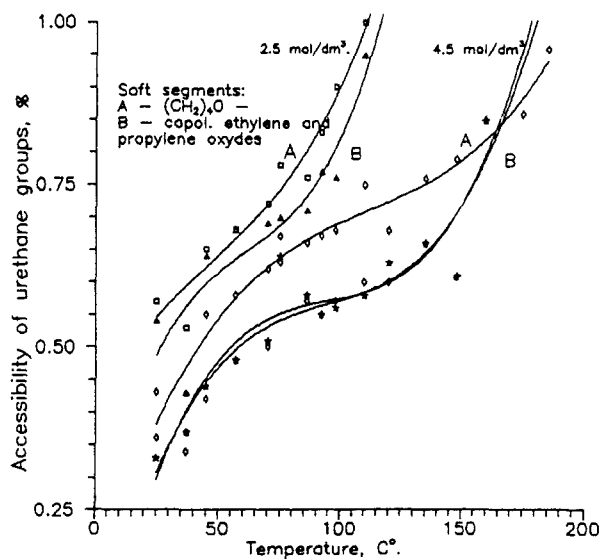


Fig. 2. Dependence of SPEU accessibility on temperature of H-D exchange reaction.

In general, accessibility-temperature curves (Fig. 2) are characterized by the three regions, which they are respectively responsible for: 1) involving of new urethane groups in reaction of H-D exchange owing to a rupture of relatively weak H-bonds between ether and urethane groups; 2) a gradual increase of the accessibility due to an increase of segmental motion and consequently an expanding of the inter-facial layer thickness; and 3) cooperative disruption of domains, when, practically, all urethane groups become accessible for an attack of heavy water.

Under isothermal conditions, the accessibility depends on the thickness of the inter-facial layer and/or domain concentration in the SPEU matrix; in other words, on the concentration of urethane groups in the oligo-ether matrix.

The dependence of the accessibility on the total urethane group concentrations is shown in Fig. 3. It is to be noted that the existence of the minimum for all types of SPEU is under investigation. Probably at this structural point the balance of dispersion and polar interactions is realized. At weight fraction of hard segments about 0.7 the most perfect structure is formed, where the accessibility is minimal.

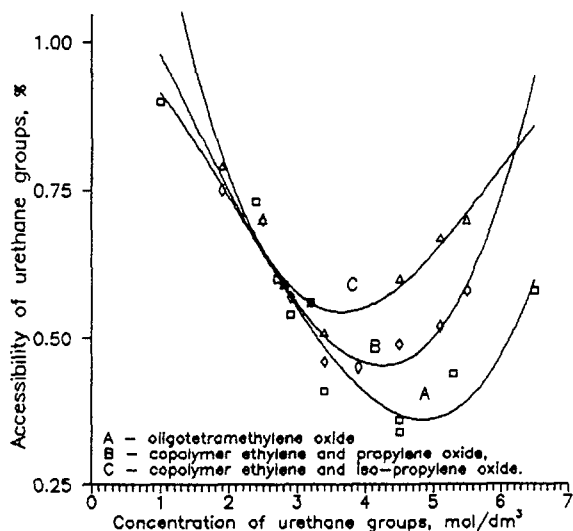


Fig. 3. Dependence of accessibility on concentration of urethane groups at different compositions of soft segments.

The shift of the minimum point is determined by nature of soft segment. For example, after inserting isopropyleneoxide fragments instead of tetramethylene oxide in macromolecule of SPEU, the experimental minimal accessibility is increased in a series tetramethylene oxide < copolymer ethylene-oxide + propyleneoxide < copolymer ethylene oxide + iso-propylenoxide. The rising branches after minimum points are likely determined by phase inversion of SPEU matrices at corresponding collapse of structure perfection.

Additional information about water behavior in moderately hydrophilic polymers can be found from experiments in mechanical relaxation spectroscopy. It is a common observation that water is a good plastisizer for hydrophilic polymers, decreasing T_g and the modulus of elasticity as compared with the glassy state. For some low-polar polymers, antiplastification is observed which means that the temperature of α -relaxation maximum and modulus of elasticity increase.

Due to 2.5 wt.% water sorption by SPEU specimens at temperatures below T_g , dynamic shear modulus is increased and two-fold growth in α -relaxation peak amplitude is observed, as it follows from Fig. 4 [17]. It should be emphasized that in contrast to phenomena plastification or anti-plastification the temperature of α -transition for SPEU do not change in the presence of water. The increase in loss factor is likely determined by hydrogen bonds' redistribution among ether and urethane groups as well as water in the interfacial layer which leads to the gain of kinetic elements number taking part in Brownian motion under α -relaxation in absence of visible plastification effect.

The problem to consider next is directly concerned with some sorption-diffusion properties of SPEU. In Fig. 5, isotherms of water sorption in films of Vitur-RM are presented for specimens containing from 1.0 to 6.5 mol/dm³ urethane groups. In order to compare solubilities of water in various specimens experimental results were corrected

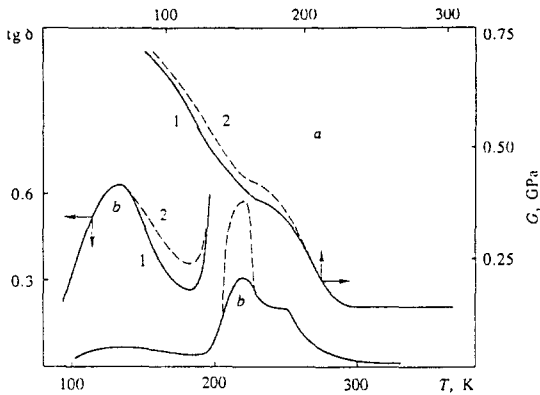


Fig. 4. Temperature dependence of G' (a) and $\tan \delta$ (b) of segmented polyetherurethane (Vitur-T) dried in vacuo (1) or saturated with water (2).

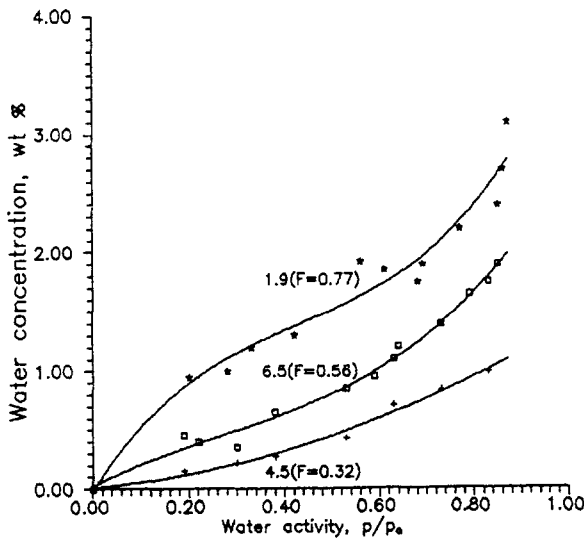


Fig. 5. Sorption isotherms in system Vitur-RM 2000, water at 25°C.

for their accessibility, that is, the water concentration was calculated in reference to the accessible volume ($v_a = F \cdot v$), but not to the total volume (v).

The quantitative analysis of sorption isotherms was made in frames of incomplete immobilization model having been put

forward earlier for hydrophobic matrices with imbedded groups, particularly for copolymer ethylene with vinylacetate [7]. In accordance with the model accessible urethanic groups situated in interface layer are the sites of water immobilization, what is confirmed by correlation between the water sorption and the values of accessibility (given in brackets on curves of Fig. 5).

It is to be noted that for Hemotan-T specimens, sorption of water occurs not only in interface layer, but in soft-segment oligoether phase, preferentially on ethylene-oxide fragments (about 10% of total sorption), as it was shown in [16].

An analysis of the concentration dependence for water diffusion coefficients in SPEU films $D_w(C_w)$ gives a valuable information about transport mechanism peculiarities for MHP. From results of SPEU-water systems (Fig. 6), it is found that coefficients extrapolated to zero concentration of water (D_w^0) tend to decrease just 100 fold with a rise in a portion of hard segments. Moreover, a negative exponent describing $D_w(C_w)$ appears the sharper, than the higher a portion of urethane groups in accessible ranges of SPEU.

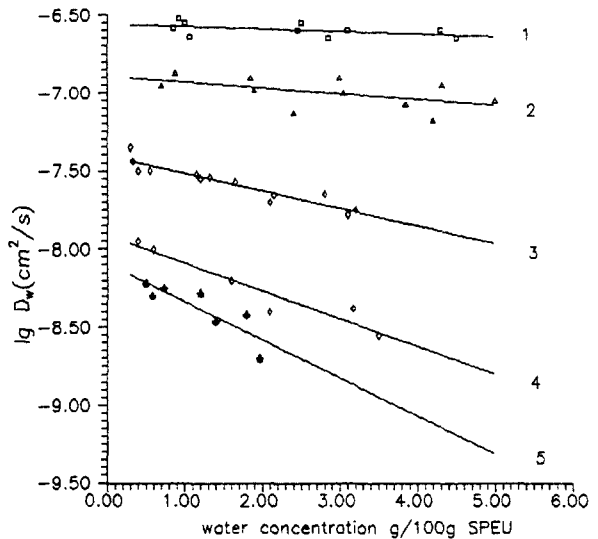


Fig. 6. Concentration dependence of D_w in SPEU. C_w : 1 (1), 2.4 (2), 2.7 (3), 4.5 (4), 6.5 (5) mol/dm^3 .

On the basis of these data, it can be concluded that NHCOO groups are responsible for an immobilization of diffusing H₂O. As supported with H-D exchange and sorption methods, water molecules do not penetrate into domains. Thus, it should be suggested that the water transport occurs not only in the soft-segment phase but also in the interphase layers, where the urethane groups are the traps for the diffusant.

The effect of impenetrable domains may be evaluated, in the first approximation, by the introduction of a tortuosity factor F^n , where n is an empirical constant ($= 2$). In general, a decline of water diffusion coefficients (D_w) depending both on the urethane group concentration (C_u) and on the water concentration (C_w) is described by equation

$$D_w = D_w^0 (F^n) \exp(-aFC_w) \exp(-bC_u) \quad (1)$$

where a and b are empirical constants, and D_w^0 is a constant limiting value for $D_w(C_w)$ function.

The exponential decrease of D_w with a rise in a portion of accessible hydrophilic groups (F) was observed not only for SPEU series, but for other classes of MHP, such as aliphatic polyamides [18] and graft copolymers Nylon-6 with poly-N,N-dimethyl aminoethyl-methacrylates (PDMAM) [19]. It is worthwhile to note that D_w^0 for polyamides, copolymers Nylon-6 + PDMAM and SPEU correspond to D_w in PELD, in PDMAM, and in PTMO, respectively.

3.2. Poly-3-hydroxybutyrate

Poly(β -hydroxyalkanoate)s have found a wide range of biomedical and ecological applications because of the combination of physico-chemical and membrane transport properties coupled with their biodegradation [20, 21].

Fig. 7 shows the water sorption isotherms for PHB. An upward curvature which became more pronounced at higher humidity in-

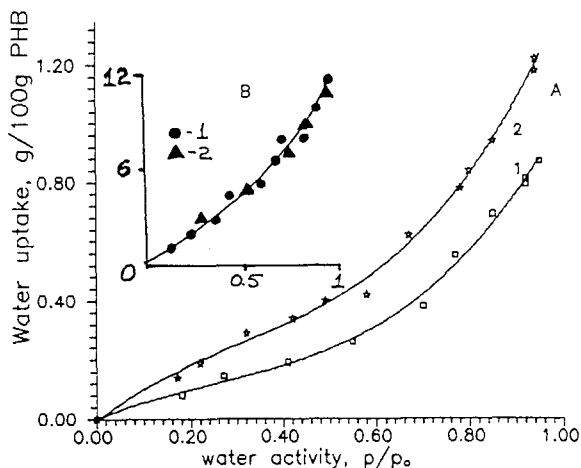


Fig. 7. Sorption isotherms of water (A) and acetone (B) by PHB films.

dicates that water-water interactions (cluster formation) are strongly preferred than water-polymer ones. The size of the water clusters is judged from the Zimm-Lundberg's model [22], which enables to estimate the excess of mean number of sorbate molecules around a given molecule. The start of cluster formation of water lies in the range of $p/p_0 = 0.3-0.35$. The cluster numbers ($\phi_w G_{ww}/V_w$) are 2.0 and 1.5 molecules for specimens #1 and #2, respectively (see Table 1).

In contrast to water sorption experiments, isotherms of acetone resembled each other for N1 and N2 specimens. Probably, the small molecule of water acts as structure probe, which is sensitive to morphology of PHB. The molecules of acetone having greater size do not "feel" the difference of structures for N1 and N2 specimens. It is confirmed by concentration dependence of diffusion coefficients in PHB

$$-\lg D = 9.97 C^{-0.0975} \quad (2)$$

There is no difference between diffusion coefficients (D) of acetone for N1 and N2 specimens.

In PHB membranes differential diffusion coefficients (D_w) of water are presented in Fig. 8. The dependence of D_w 's on water sorption has linear character. The weak concentration dependence of D_w agrees with our representation of mechanism of water transport in moderately hydrophobic type of polymers, where both cluster formation and plastification of PHB matrix occur under action of solvent. The predominance of the plastification effect leads to linear dependence of D_w 's on concentration of water.

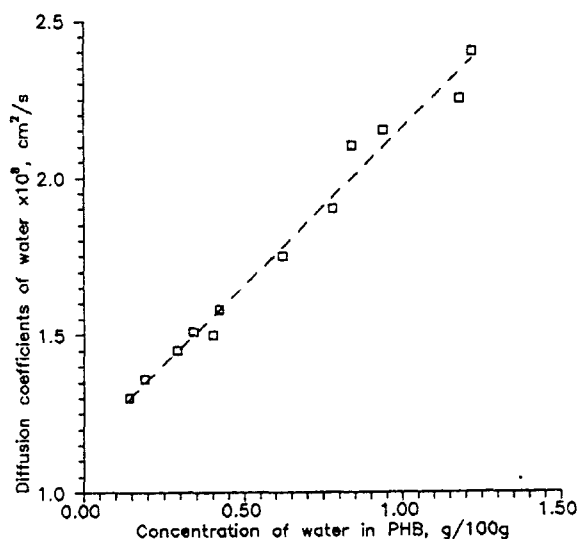


Fig. 8. Concentration dependence of water diffusion coefficients in PHB, 25°C. Quartz spring microbalance method.

A previous analysis of FTIR spectra for PHB membranes [23] has shown the participation of C=O groups in forming of the immobilized water structures, where water molecules were included in cyclic structures. The fragment O...H...O exists in the cyclic structures, where vibration band of the proton is near by $1,690\text{ cm}^{-1}$ on condition that the distance between two oxygen atoms is less than 2.6 \AA . The availability of bonded water allows to produce interchain network of H-bonds which is probably formed at the boundary of PHB crystallites. The formation

of H-bond network will enable more perfect orientation in the matrix. The closer packing of crystallites and the formation of interchain H-bonds lead to an increase of thermostability of films [24].

Besides, the perfect packing of crystallites due to formation and saturation of interchain H-bonds leads to a decrease of inhomogeneity for electron density of the polymer and hence to the decline of an intensity of SAXS. Therefore, the higher the concentration of cyclic structures, the lower the relative intensity of small angle X-ray pattern for PHB membranes (Table 2).

Table 2
Comparison of relative concentration for cyclic ester structure and intensity of SAXS

Sample	N1 ^a	N1 ^b	N2 ^a	N2 ^b
D ₁₆₉₀ /D ₂₉₃₄	0.25	0.23	0.19	0.15
I/I ₀	0.33	0.37	0.77	0.81

a = chloroform, b = dioxan-cast films, I₀ = SAXS phone intensity.

4. Conclusions

Summing up the results of the paper, the following main features should be emphasized for moderately hydrophobic polymer-water diffusion systems:

Solubilities of water in MHP do not exceed 8–10 wt.%, in contrast, solubilities of hydrophilic gels (PVA, PHEMA, PAAm, etc) approach tens or even hundreds wt.% [25].

Most polymers (PVAc, Nylon-6, Nylon-66, epoxy resins, PHB, etc.) are characterized by the compensative effect, when immobilization of a diffusant by functional groups and plastification compete and affect water mobility in opposite ways, due to compensative effect the functions $D_w(C_w)$ either vanish or slowly change in contrast to

hydrophilic polymers characterized positive exponent function [25].

When exposed to water (electrolyte media), structural transformation can occur at different structural levels: 1) at primary chemical level: H-D-isotope reaction, re-distribution of H-bonds in noncrystalline area of matrix, formation of cyclic structure in PHB; 2) at crystal level: lattice transformation from non-perfect to more perfect modification (γ - α crystal transition in polyamides); and 3) at supermolecular level: collapse of domains, change of porosity, transformation in interface layer of SPEU.

The results of this study give the basis for understanding structure-transport relationships in novel perspective polymers with moderate hydrophilicity, where the balance of the dispersion and polar interactions controls the structure and the morphology of polymer matrix as well as sorption capacity and diffusivity of water and electrolytes.

Acknowledgments

The authors gratefully acknowledge support for this work from The Fond of Fundamental Investigation of the Russian Academy of Sciences.

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