Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

TEMPERATURE EFFECTED STRUCTURAL TRANSITIONS IN POLYURETHANES SATURATED WITH SOLVENTS STUDIED BY SAXS SYNCHROTRON METHOD

H. Grigoriew[a]; A. Wolińska-Grabczyk[b]; S. Bernstorff; A. Jankowski[b]
[a] Institute of Nuclear Chemistry and Technology, Warsaw, Poland [b] Polish Academy of Sciences, Institute of Coal Chemistry, Gliwice, Poland

To cite this Article Grigoriew, H. , Wolińska-Grabczyk, A. , Bernstorff, S. and Jankowski, A.(2002) 'TEMPERATURE EFFECTED STRUCTURAL TRANSITIONS IN POLYURETHANES SATURATED WITH SOLVENTS STUDIED BY SAXS SYNCHROTRON METHOD', Journal of Macromolecular Science, Part A, 39: 7, 629 — 642

To link to this Article: DOI: 10.1081/MA-120004508

URL: http://dx.doi.org/10.1081/MA-120004508

J. MACROMOL. SCI.—PURE APPL. CHEM., A39(7), 629–642 (2002)

TEMPERATURE EFFECTED STRUCTURAL TRANSITIONS IN POLYURETHANES SATURATED WITH SOLVENTS STUDIED BY SAXS SYNCHROTRON METHOD

H. Grigoriew,[1] A. Wolińska-Grabczyk,[2,]* S. Bernstorff,[3] and A. Jankowski[2]

[1]Institute of Nuclear Chemistry and Technology,
Warsaw, Poland
[2]Institute of Coal Chemistry, Polish Academy of Sciences,
Gliwice, Poland
[3]Sinchrotrone ELETTRA, Trieste, Italy

ABSTRACT

A set of segmented polyurethanes (PU) differing in the hard-segment structure was saturated with solvents and after the equilibrium saturation was reached, put to temperature-dependent SAXS investigations. The time-resolved mode of SAXS measurements with a linear increase of temperature from −70°C to +70°C, i.e., within the temperature range between T_g of soft and hard segments, was applied. The order-order transition leading to a greater degree of order was found at higher temperatures for almost all systems investigated. Some of the PUs exhibit two kinds of microphase separated domains. The results obtained are discussed with respect to the mean-field theory of copolymers and Koberstein and Stein model for hard microdomain structure in PUs, and correlated with temperature dependence of membrane permeability in pervaporation process.

---

*Corresponding author. E-mail: inbox@karboch.gliwice.pl

www.dekker.com

Key Words: SAXS method; Polyurethanes; Structure; Liquid permeability

INTRODUCTION

In a block copolymer a macromolecular chain consists of extended sequences of more than one type of monomer units. The component blocks are usually thermodynamically incompatible to different degrees and show the tendency for microphase separation to take place. Theoretical description of thermodynamic behavior of such systems was made by Leibler,[1] who used the mean-field theory. He calculated a phase diagram for molten diblock copolymers showing that they can undergo weak first-order transitions from the disordered phase into microphase-separated phases of ordered domain structure. The domains can be of lamellar, cylindrical or spherical type. In the SAXS technique, the structure factor of diblock copolymers is characterized by a peak at a scattering momentum q*, where $q = 4\pi \sin \Theta / \lambda$. The scattered intensity at the peak: $q = q^*$, $S(q^*)$, represents the order parameter of the system and $S(q^*)^{-1} \propto \chi$, where χ is the Flory-Huggins segmental interaction parameter, which changes linearly with T^{-1}. The Leibler theory was supplemented by Fredrickson and Helfand[2] who incorporated effects of thermal fluctuations into it. These thermal fluctuations are especially strong near the critical point of phase decomposition or at the ordering temperature. For diblock copolymers the susceptibility is related to $S(q^*)$, whose analysis yields thermodynamic parameters: the phase-transition temperatures and Flory-Huggins interaction parameters.[3,4] The schematic phase diagrams include a homogeneous part at higher temperatures and two-phase region at lower temperatures, below the binodal temperature. The experimentally observed phase transitions of block copolymers show, however, a complexity far beyond theoretical approximations.

Temperature effected structural changes of copolymers in nonselective good solvents have been described in the same way, but after a proper modification of the effective interaction parameter χ.[5,6]

The aim of this work was to elucidate structural changes observed for polyurethane/solvent systems as a function of temperature. The polyurethanes (PU), regarded as multiblock copolymers, constitute an important group of copolymers with wide applications, produced industrially on a substantial scale. Therefore, their thermal behavior and morphology have been studied intensively for many years.[7–9] The PUs seem also to be prospective membrane materials for various liquid separations, as it has appeared from the studies performed. recently[10,11] Thus, the results presented here can also be interesting from a membrane separation standpoint.

EXPERIMENTAL

Materials and Characteristics

The PUs studied in this work were composed of the soft segments derived from poly(oxytetramethylene)diol (PTMO) of a molecular weight of 1000 and the hard segments formed from 2,4-tolylene diisocyanate (TDI) and a chain extender in the molar ratio of 4:3. The structural variation introduced into the polymer chain concerned the hard segments and came from various chain extenders used in the polymer synthesis like: 4,4′-diaminodiphenylmethane (PP), ethylenediamine (EDA) or 4,4′-bis (2-hydroxyethoxy) biphenyl (BH). The investigated polymers were synthesized by a prepolymer procedure in DMF solution according to a method describe earlier.[10] The basic characteristics of the obtained polymers are given in Table 1.

Films of the thickness of about 0.3 mm were obtained by casting 15% DMF solution of the polymer onto a glass plate and by evaporating the solvent in an oven. The densities of the materials were measured by buoyancy in water. Differential scanning calorimetry was carried out using a Rheometric Scientific DSC Plus apparatus at a heating rate of 10°/min. Molecular weight determinations were performed using gel-permeation chromatography (GPC). The measurements were carried out in DMF at 80°C with Knauer apparatus, based on polystyrene standards.

The sorption experiments were performed at 25°C by placing the PU samples in solvent. The liquid uptake was monitored gravimetrically until equilibrium weight was attained. The sorption equilibrium values (Table 1) were determined as the mole uptake of liquid per 100 g of dry polymer sample.

Permeation experiments were performed using a standard pervaporation set-up. The down-stream pressure was 150 mm Hg and the permeate was

Table 1. Compositions and Physical Properties of PUs

							Sorption Equilibrium Values (mol/100 g)	
Polymer	Molar Composition 1/4/3	Calculated Hard Segment Content (wt%)	Mass Density (g/cm^3)	Molecular Weight[b] (g/mol)	M_w/M_n	T_g SS[a] (°C)	Benzene	Ethanol
PP	PTMO/TDI/PP	56	1.167	35,300	1.6	– 46	0.85	0.74
EDA	PTMO/TDI/EDA	47	1.142	–	–	– 45	0.76	1.07
BH	PTMO/TDI/BH	60	1.151	46,200	2.7	– 49	0.59	0.45

T_g HS >100°C from DMTA measurements.

[a] DSC, 10°/min.

[b] GPC, polystyrene standards.

collected in a trap cooled by liquid nitrogen. The permeation rate, expressed as normalized flux F [kgμm/m^{2}h], was determined from the variations in the condensate mass with time and recalculated for a standard (1 μm) membrane thickness.

SAXS Measurements

The SAXS measurements were carried out at the Austrian SAXS beamline of the synchrotron ELETTRA, Trieste, Italy. The beamline is mainly dedicated to time-resolved studies of fast structural transition in non-crystalline systems. A high power wiggler was used as the beamline source. A linear gas-filled detector registered the SAXS intensity simultaneously in the whole range. Due to primary beam collimation system, no desmearing correction was needed.

The samples for SAXS measurements were saturated with solvent (benzene or ethanol), and after the equilibrium saturation was reached inserted rapidly into quartz capillaries which were then sealed and put in the Oxford Cryostream System. All measurements were carried out in the transmission mode in the temperature range from −70°C to +70°C, at the heating rate of 1°/min. The measurement data were subjected to a preliminary treatment using the OTOKO program. The Lorenz correction of the all SAXS data was made by multiplying I(q) by q^2.

RESULTS AND DISCUSSION

The segmented PUs studied in this work were composed of poly(oxytetramethylene)-based soft blocks of $M_n = 1000$ and various hard blocks consisting of the three (TDI-Chain extender) repeat units. The structural variation introduced into the macromolecular chains concerned the kind of a chain extender and enabled PUs of different physical properties to be prepared (Table 1).

The sorption capacity of the synthesized polymers is one of the properties relevant to the present studies. The data listed in Table 1 show that the sorption abilities of the both poly(urea-urethane)s, aromatic PP and aliphatic EDA are higher than that of the aromatic polyurethane BH. There are also some differences in the sorption equilibrium values for the PP and EDA polymers. However, the expected slightly higher values for EDA because of its lower calculated hard segmented content, and therefore increased area available for penetrating solvent molecules, can only been observed for EDA/ethanol system. Since hard domains act as physical crosslinks and fillers for the PU matrix, the observed sorption capacity differences may be attributed to the morphology of the investigated PUs. The creation of a domain morphology and the tendency of some PUs to become organized is well known and results from the thermodynamic incompatibility between hard and soft segments. A lamellar or pseudolamellar composite of hard and soft phases is visible as a peak at the SAXS patterns. All PUs studied in this work show a peak in their SAXS data, in contrast to the PUs investigated by us previously.[12] However, this peak is broad (Fig. 1) suggesting the polydispersity in the hard segment length that is a common feature of the segmented PUs.[7–9]

In the sequence: BH, PP, EDA, the peak position shifts to higher q* (59 nm^{-1}, 77 nm^{-1}, 92 nm^{-1}, respectively), i.e., to lower segment length (9.2 nm, 7.7 nm, 5.9 nm, respectively), that was expected considering the structural differences between the chain extenders used. However, the shift is small compared to the relatively large width of FWHM of each peak, especially for EDA and BH.

The thermal behavior of the PU/solvent systems at the equilibrium saturation was studied in the temperature range from −70°C to +70°C, i.e., below Tg of the hard segments and presumably above Tg of the soft segments, expected to be located below Tg of the dry PUs listed in Table 1.

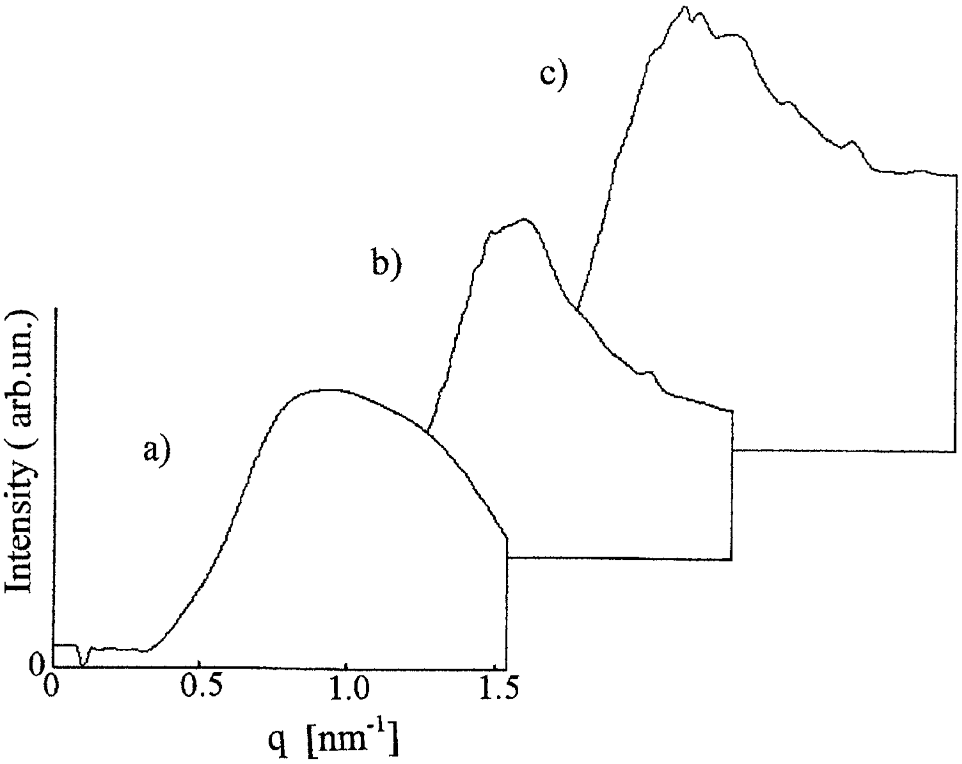

Figure 1. SAXS patterns for dry PUs: a) EDA; b) PP; c) BH.

Indeed, the DSC traces of the investigated systems showed no Tg transitions in the low temperature region down to −120°C. Plots of representative X-ray scattering intensity versus reciprocal spacing (q) as a function of temperature for various PU/benzene systems are presented in Fig. 2.

For each of the systems investigated, an increase of temperature induces a significant change in the SAXS pattern revealed as a leap in intensity, I(q), and also as a slight change in the peak position, q* (Table 2), indicating an order-order transition (OOT).

Above the OOT, the peak intensity is much higher than below this transition, which is a rather unusual feature because the mean-field theory of copolymers,[1−5] along with its further supplements predicts an inverse behavior. For a block copolymer solution in a nonselective solvent, the structural factor, S(q), is:

$$S(q)^{-1} = (2\phi/lN)(F(q) - 2\chi N) \tag{1}$$

where l – is the segment length, ϕ – is the copolymer concentration in solvent, F(q) is the function of radius of gyration and composition, and χ – is the effective interaction parameter, which here expresses interaction between all three pairs of components. In this formula, only χ is temperature dependent and acts on decreasing S(q) with temperature. The SAXS intensity, I(q), can be treated as being proportional to S(q). Therefore, it can be said that the SAXS peak intensity, I(q*), is generally decreasing if temperature is increasing. The observed increase in the SAXS intensity for the PU/benzene systems, can probably be elucidated as a refinement of the poorly developed initial morphology, but an open question is why it is visible as OOT.

The SAXS patterns from Fig. 2 and the data given in Table 2 show that the peak position, q*, slightly moves towards lower q if the temperature increases. After the T_{OOT} is reached, the further shift is less pronounced. According to the mean-field theory, an inverse direction of the q* changes can be expected as a function of temperature. However, polyurethanes are a class of copolymers with a large segment length polydispersity that strongly affects the SAXS peak position. The conception of the selective segregation of the blocks of a specific length has been developed by Koberstein and Stein[7] to illustrate microphase separation of the hard segments. Therefore, upon increasing χ, i.e., decreasing T since $\chi \approx a + bT^{-1}$, the peak position, q*, is anticipated to increase slightly due to the microphase separation of the successively shorter blocks (13). On the other hand, a decrease in q* and a more narrow shape of the peak can be awaited as a result of chain stretching in the block copolymers at high incompatibility, or if a poorly developed morphology is refined upon heating. Despite the SAXS patterns variations at OOT described above, no real change in the kind of ordering has been observed for the systems investigated. The similar results found for other block copolymers are interpreted as the composition fluctuations in the disordered state.

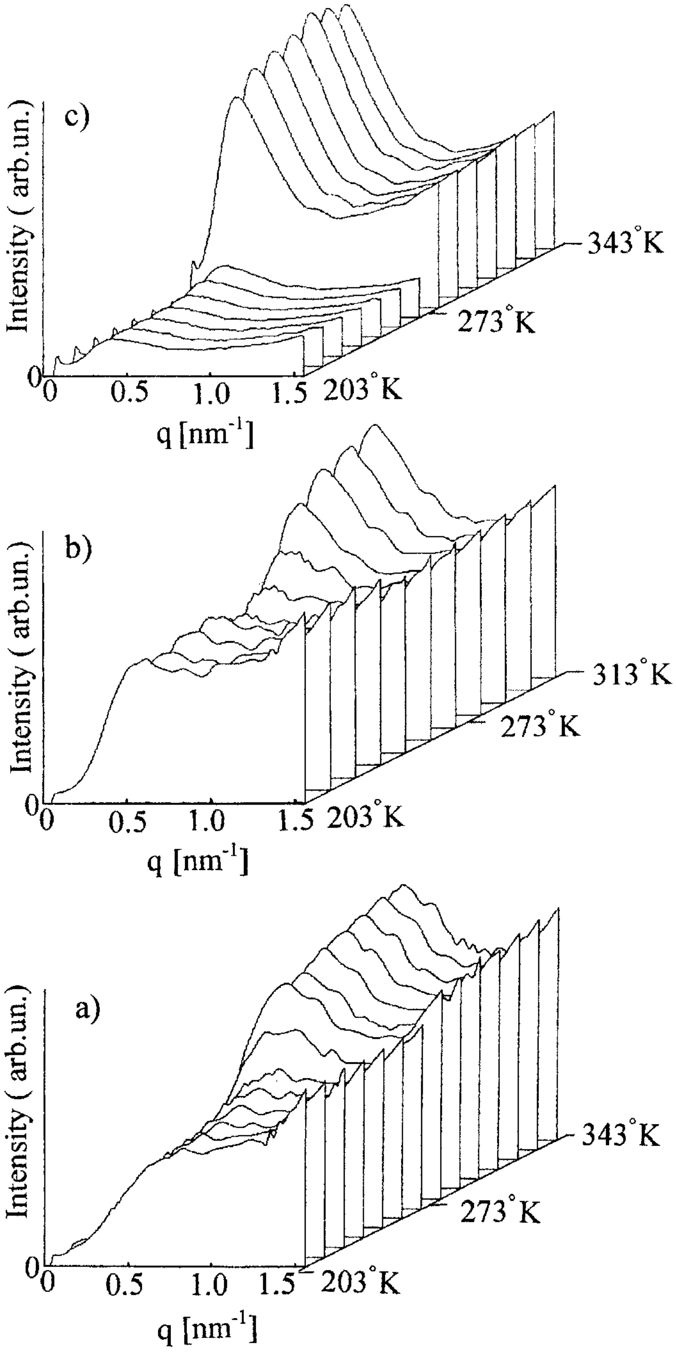

Figure 2. SAXS patterns as a function of temperature for PU/benzene systems a) EDA, b) PP, c) BH.

Table 2. Parameters of the SAXS Curves

	Benzene								Ethanol					
	q* (nm^{-1})			FWHM (nm^{-1})			q*$_2$ (nm^{-1})		q* (nm^{-1})			FWHM (nm^{-1})		
PU	First Curve	at$_{OOT}$	Last Curve	First Curve	Last Curve	T_{OOT} (K°)	First Curve	Last Curve	First Curve	at$_{OOT}$	Last Curve	First Curve	Last Curve	T_{OOT} (K°)
EDA	–	0.74	0.66	–	0.31	268	0.82	0.79	0.74	0.86	0.90	–	–	288
PP	0.60	0.52	0.52	–	0.38	268	0.81	0.81	–	–	–	–	–	–
BH	0.46	0.41	0.38	0.29	0.33	273	–	–	0.46	0.44	0.39	0.22	0.31	293

For the two systems, PP/benzene and EDA/benzene, a small second peak is visible on the right side of the main one (Fig. 2 and Table 2). Contrary to the transformations at OOT concerning the main peak, the position and intensity of the second peak are almost unchanged during the temperature treatment. In the case of the PP system, the position of the second peak is comparable to the position of the main peak of the dry sample. A similar effect has been observed by us previously for one of the PUs saturated with benzene,[14] the chemical constitution of which was analogous to PP but of other proportion of the hard and soft segments. This result can suggest that a domain structure already existing in the dry material is to some extent preserved during saturation, and then during heating, i.e., this structure is impenetrable for solvent. A comparable two-type domain microstructure can also be assumed for the EDA system; however, the position of the second peak is not equal to the average position of the very broad oval of the SAXS curve of the dry sample (Fig. 1), but is involved in this oval shape very well. On the other hand, a one-type domain microstructure can be suggested for the BH system due to the lack of any additional peak in its SAXS patterns (Fig. 2). Thus, an existence of the two types of domain structures in PUs in the presence of solvent depends on the hard segments molecular structure and may be a specific feature of the polyurethanes with urea bonds (PP, EDA vs. BH). Similar, though somewhat less pronounced, SAXS changes as a function of temperature and PU structure have been found for the PU/ethanol systems (Fig. 3).

Precise values of the OOT temperatures given in Table 2 were determined from the discontinuity at the OOT transition of the $I(q^*)^{-1}$ vs. T^{-1} and q^* vs. T^{-1} graphs (Fig. 4).

The character of these correlations, i.e., the inverse direction of the curves and their non-linearity demonstrates the departure from the mean-field theory.

It can be seen from Table 2 that the OOT temperature values are influenced by both the type of solvent and the structure of PU. The OOT temperatures for the PU/benzene systems, which are close to the melting temperature of benzene, increase by 20°C for the corresponding PU/ethanol systems. The OOT temperature difference with respect to the kind of PU is much lower, 5°C, and shows again the differentiation between the poly(urea-urethane), PP or EDA, and the polyurethane, BH. It should be noted that there is no appreciable change in the SAXS scattering intensity as a function of temperature for the dry PUs.

Thus, the SAXS data presented here reveals the ability of the investigated PU/solvent systems to change their microphase separation and the ordering degrees with temperature, though not to change the kind of ordering. The temperature effected structural transformations depend on both the polymer molecular structure determining the amount of hydrogen bonding, and the kind of solvent. Since the microstructure of the

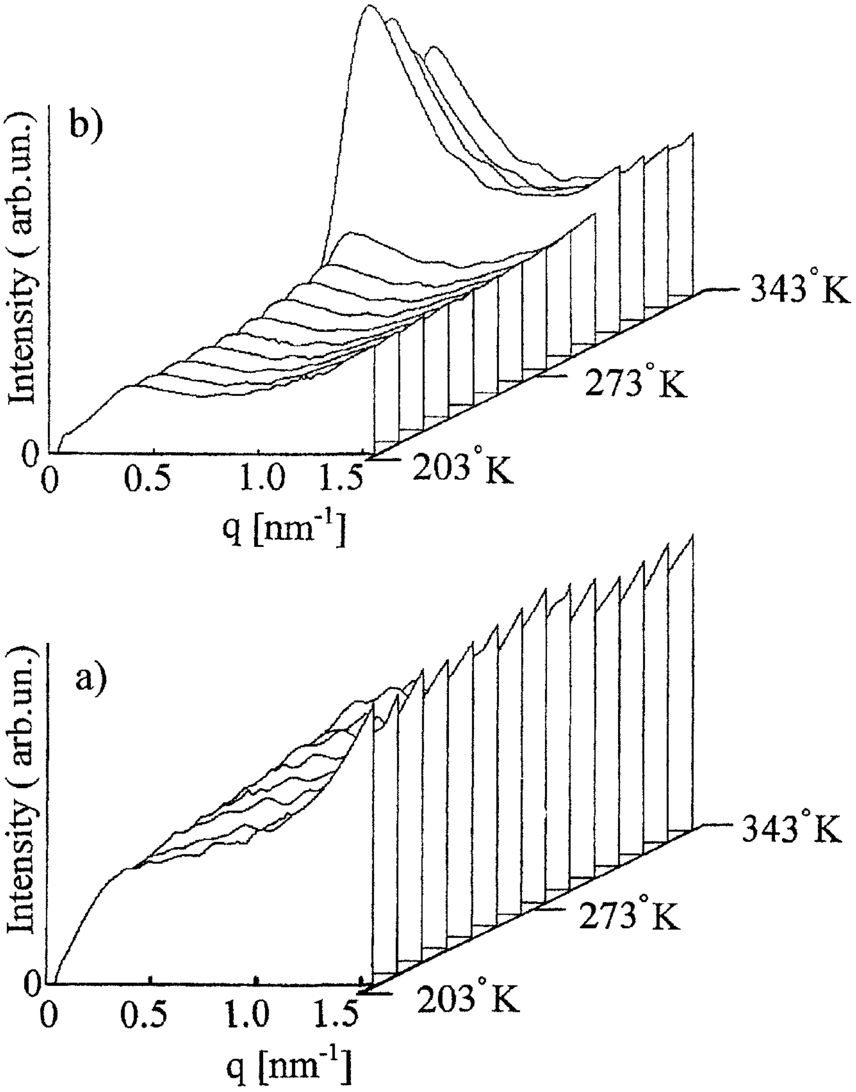

Figure 3. SAXS patterns as a function of temperature for PU/ethanol systems; a) EDA; b) BH.

system acting as a semipermeable barrier for the permeating molecules is one of the most important factors governing the transport behavior, the structural changes observed should also be accompanied by the appropriate changes in the permeation data. The effect of temperature on the permeation flux for one of the PU/solvent systems investigated is shown in Fig. 5.

The permeation flux generally increases with increasing temperature. However, when plotted as Arrhenius relation, the experimental data can be

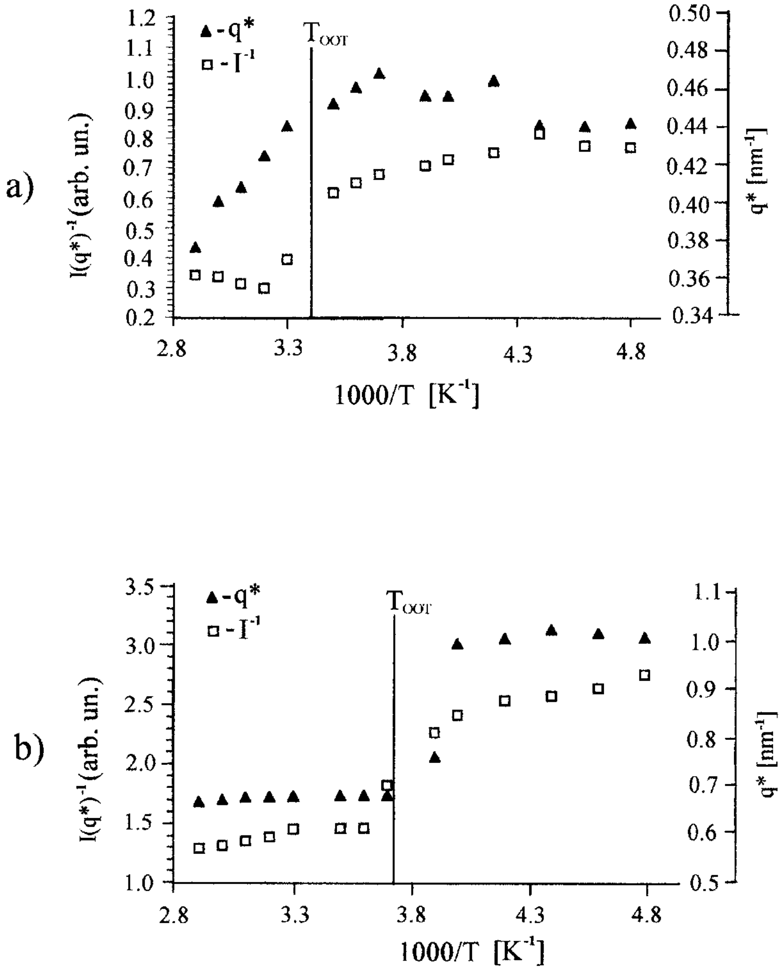

Figure 4. Inverse peak intensity I(q*) and peak position q* vs. 1/T; a) BH/ethanol; b) EDA/benzene.

fitted by the two different regression curves. The activation energy values, E_F, evaluated from the slopes of the both plots are found to be 20.7 kcal/mol for the lower temperature interval and 6.9 kcal/mol for the temperatures above 22°C. The smaller activation energy of the permeation process at higher temperatures suggests that there is a significant change in the membrane microstructure which makes the mass transport through the membrane easier. It coincides very well with the results of the SAXS measurements, demonstrating the structural transition (OOT) to occur at the similar temperature. Moreover, both the SAXS and permeation data allow the conclusion to be made that the ordered structure developed upon heating enables the transport of small molecules to proceed more freely. The obtained results correspond also to our previous observations concerning the

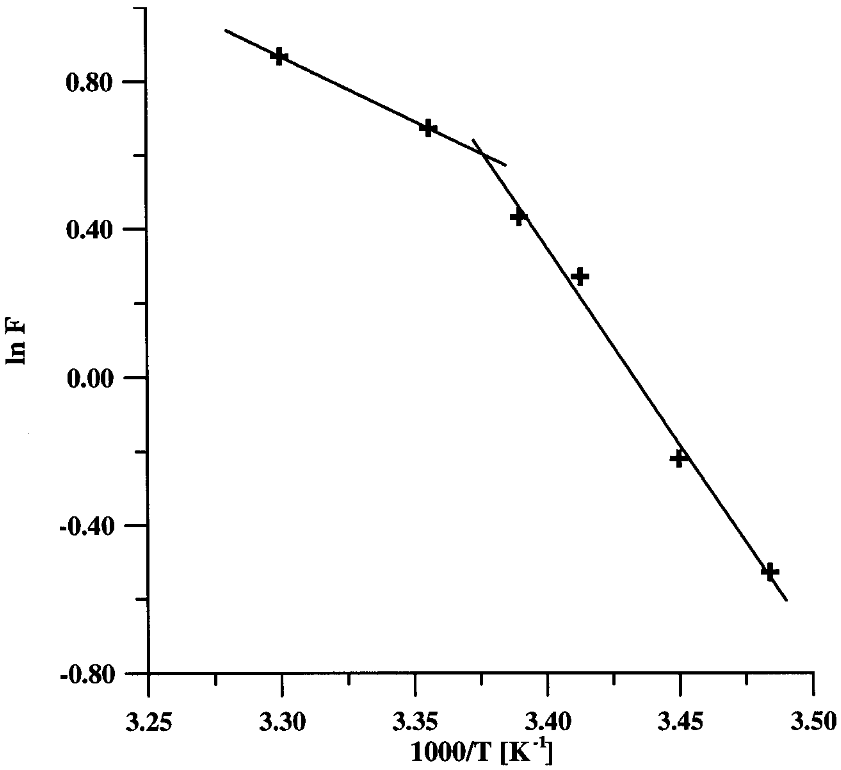

Figure 5. Effect of temperature on the permeation flux of ethanol through the BH-based membrane.

correlation between the structure and the degree of ordering of the PU/solvent systems with PUs of various molecular structure and the permeation rate through these polymers.[15]

CONCLUSION

Structural transformations (OOT) into more ordered structures upon heating observed for PU/solvent systems are unusual and inconsistent with the mean-field theory. These transformations depend on the polymer molecular structure and the kind of solvent, and have not been found for the dry PUs.

There is no real change in the kind of ordering at OOT, so the structural transformations are probably caused by composition fluctuations.

The change of q* position for the PU/solvent systems vs. temperature strongly confirms the Koberstein and Stein conception of selective segregation of the blocks of a specific length.

The second microphase is observed for the poly(urea-urethane)/solvent systems. This microphase also exists in a dry material and is unchangeable upon heating.

There is a drop in the activation energy value of the permeation process through the PU membrane when passing the OOT temperature.

The ordered structure of the PU/solvent systems developed upon heating enable the transport of small molecules to proceed more freely.

ACKNOWLEDGMENTS

The financial support of this work by the State Committee for Scientific Research under Contract No. 1297/T09/99/16 is gratefully acknowledged. Authors also thank M.Sc. M.Płusa for technical assistance.

REFERENCES

1. Leibler, L. Theory of Microphase Separation in Block Copolymers. Macromolecules **1980**, *13*, 1602–1617.
2. Fredrickson, G.H.; Helfand, E. Fluctuation Effects in the Theory of Microphase Separation in Block Copolymers. J. Chem. Phys. **1987**, *87*, 697–705.
3. Fredrickson, G.H.; Helfand, E. Rheology of Homogeneous Block Copolymers Near the Microphase Separation Transition. J. Chem. Phys. **1988**, *89*, 5890–5897.
4. Schwahn, D.; Mortensen, K.; Yee-Madeira, H. Mean-Field and Ising Critical Behavior of a Polymer Blend. Phys. Rev. Lett. **1987**, *58*, 1544–1546.
5. Fredrickson, G.H.; Leibler, L. Theory of Block Copolymer Solutions: Nonselective Good Solvents. Macromolecules **1989**, *22*, 1238–1250.
6. Olvera de la Cruz, M. Theory of Microphase Separation in Block Copolymer Solutions. J. Chem. Phys. **1989**, *90*, 1995–2002.
7. Koberstein, J.T.; Stein, R.S. Small-angle X-Ray Scattering Studies of Microdomain Structure in Segmented Polyurethane Elastomers. J. Polym. Sci., Polym. Phys. **1983**, *21*, 1439–1472.
8. Velanker, S.; Cooper, S.L. Microphase Separation and Rheological Properties of Polyurethane Melts. 2. Effect of Block Incompatibility on the Microstructure. Macromolecules **2000**, *33*, 382–394.
9. Koberstein, J.T.; Galambos, A.F.; Leung, L.M. Compression-Molded Polyurethane Block Copolymers. 1. Microdomain Morphology and Thermomechanical Properties. Macromolecules **1992** *25*, 6195–6204.
10. Muszyński, J.; Wolińska-Grabczyk, A.; Penczek, P. Synthesis, Characterization and Pervaporation Properties of Segmented Poly(urethane-urea)s. J. Appl. Polym. Sci. **1999**, *71*, 1615–1625.
11. Wolińska-Grabczyk, A.; Muszyński, J.; Jankowski, A. Applications of Polyurethane-Based Membranes in Pervaporation Separations. Chem. Papers **2000**, *54*, 389–392.

12. Grigoriew, H.; Wolińska-Grabczyk, A.; Chmielewski, A.G.; Amenitsch, H.; Bernstorff, S. SAXS Study of the Influence of Ethanol on the Microstructure of Polyurethane-Based Membrane. J. Membr. Sci. **2000**, *170*, 275–279.
13. Fredrickson, G.H.; Milner, S.T.; Leibler, L. Multicritical Phenomena and Microphase Ordering in Random Block Copolymer Melts. Macromolecules **1992**, *25*, 6341–6354.
14. Grigoriew, H.; Bernstorff, S.; Wolińska-Grabczyk, A.; Domagała, J.; Chmielewski, A.G. Depth-influenced Structure Through Permeating Polymer Membrane using SAXS Synchrotron Method. J. Membr. Sci. **2001**, *186*, 1–8.
15. Grigoriew, H.; Wolińska-Grabczyk, A.; Bernstorff, S. Solvent Influenced Mesostructures in Polyurethane-based Membranes of Different Transport Parameters using SAXS Synchrotron Method. Journal of Materials Science Letters, *in press*.

Received January 5, 2002