Surface Morphology of the Polyurethane-Based Pervaporation Membranes Studied by Atomic Force Microscopy. II. Structure-Transport Properties Behavior

A. Wolińska-Grabczyk[a]; J. Żak[b]; A. Jankowski[a]; J. Muszyński[a]

[a] Institute of Coal Chemistry, Polish Academy of Sciences, Gliwice, Poland [b] Department of Physical Chemistry and Technology of Polymers, Silesian University of Technology, Gliwice, Poland

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A. Wolińska-Grabczyk,[1,]* J. Żak,[2] A. Jankowski,[1] and J. Muszyński[1]

[1]Institute of Coal Chemistry, Polish Academy of Sciences, Gliwice, Poland
[2]Department of Physical Chemistry and Technology of Polymers,
Silesian University of Technology, Gliwice, Poland

ABSTRACT

This second part of our research on the morphology of the polyurethane-based pervaporation membranes studied by atomic force microscopy (AFM) presents analysis of the structural characteristics, reported in the first part of the paper, with regard to transport properties of the polyurethanes determined from sorption experiments. The correlation has been found between the sorption equilibrium values, as well as the diffusivity of the permeating solvent, and morphology of the membranes studied. This can be related to the restricting role of the hard segment domains in suppressing the membrane swelling, as well as in making the movement of the permeating molecules more tortuous. AFM was also utilized to trace the morphology alteration expected to take place in the membranes exposed to solvents. The results have shown that this phenomenon can be observed for the polyurethanes with developed micron-sized structures after treating with solvent of a high swelling power. In that case, microstructural transformation from circular structures into more perfectly ordered pseudo-lamellae have been found to occur. The solvent sorption/desorption process was found not to affect the membrane initial morphology.

*Correspondence: Wolińska-Grabczyk, Institute of Coal Chemistry, Polish Academy of Sciences, Gliwice, Poland; E-mail: grabczyk@gepard.karboch.gliwice.pl.

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Key Words: AFM; Pervaporation membrane; Polyurethane; Morphology; Sorption; Diffusion; Transport behavior.

INTRODUCTION

In the first part of this publication several features of the surface of the polyurethane-based pervaporation membranes were discussed. The major interest was focused on the correlation between molecular structure of the polyurethanes and the size, shape and organization of structures observed on the surface of the cast films.

A question was raised concerning the possible role of structural elements in suppressing the membrane swelling or in changing the path of permeating molecules, and as a consequence in affecting the transport of small molecules through the investigated membranes. In addition, another question should also be given attention to regarding changes which can take place in the membrane microstructure due to the swelling action of a solvent. In this paper we report the results of investigations designed to elucidate these problems.

EXPERIMENTAL

Materials

The same series of the PTMO-based segmented polyurethanes of a molecular formula (TDI-ChExt)$_x$-TDI-PTMO was used as described in the first part of the paper. The details of the synthesis procedure have been given elsewhere.[1,2] These polymers have been previously referred to as PU-1 up to PU-10. The composition of the polymers and their basic characteristics are listed in Table 1.

Sorption Experiments

The sorption experiments were performed at 25°C by placing the PU samples in solvent. The liquid uptake was monitored gravimetrically by weighing the PU samples at regular time intervals until equilibrium weight was attained. When the samples were removed from the solvent, they were blotted to eliminate the excess of liquid from the surface. The sorption equilibrium values were determined from the mass uptake of liquid per 100 g of a dry sample at equilibrium saturation, and expressed as moles of liquid sorbed by 100 cm^3 of the theoretical polymer composed exclusively of the soft segments.

The basic Fick's diffusion equation has been used to calculate the values of diffusion coefficient (D) from the slopes of the initial linear part of the M_t/M_∞ vs. $t^{1/2}$ curves:

$$\frac{M_t}{M_\infty} = \left(\frac{16D}{l^2\Pi}\right)^{1/2} t^{1/2}$$

Table 1. Sample characteristics.

Sample	Composition TDI/-ChExt/PTMO [mol]	Chain extender ChExt	Molecular weight of PTMO	Hard segment content [vol%]	Sorption data for PU/benzene systems	
					S_{eq} [a] [mol/100 cm^3]	$D \cdot 10^{-7}$ [cm^2/s]
PU-1	1/0/1	—	1000	5	2.74	2.68
PU-2	4/3/1	EDA	1000	34	1.15	—
PU-3	4/3/1	PP	1000	41	1.42	1.58
PU-4	4/3/1	HQE	1000	39	1.10	1.30
PU-5	4/3/1	BHBP	1000	43	1.04	1.08
PU-6	1/0/1	—	650	10	1.57	1.69
PU-7	2/1/1	PP	650	33	1.13	1.27
PU-8	2/1/1	HQE	650	35	1.45	1.63
PU-9	2/1/1	BHBP	650	35	0.89	1.29
PU-10	4/3/1	BHBP	2000	34	1.83	2.16

[a] S_{eq} data were calculated for a theoretical polymer composed exclusively of the soft segments.

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where M_t and M_∞ are the mole percent uptake of the liquid at time t, and at equilibrium saturation, respectively, and l is a sample thickness.

AFM Studies

Samples for AFM *in situ* swelling study were prepared as previously described.[3] After the PU film cast on aluminum foil was placed in a microscope, the solvent (benzene or cyclohexane) was injected on the surface of the film using a microsyringe. Usually two or three injections of 10 μl each caused the local saturation of the film. At this state, the AFM cantilever was immersed into a drop of the solvent. Then, the scanning was initiated and several images were taken until the surface was turned to dry. Previously,[3] NanoScope E (Digital Instruments, Santa Barbara, CA) instrument working in contact mode with the standard, D type scanning head (12 μm) and standard probe silicon nitride tips of 0.12 N/m spring constant were used in all experiments.

RESULTS AND DISCUSSION

It is believed that the kind of morphological structures may affect physical properties, especially transport properties. It has been shown, for example, that gas transport in a grainy lamellar SB diblock polymer is significantly different from that observed in samples that were specially processed to produce ordered morphology.[4,5] In order to determine the correlation between the morphology characterized by AFM technique and permeation properties of the investigated polyurethanes, benzene transport into those polymers has been studied. This solvent was found to exhibit strong affinity towards polyurethanes examined, which may lead, in the extreme, to the significant swelling of the membrane. The transport process has been investigated from sorption experiments enabling diffusion coefficient D and sorption equilibrium values S_{eq} to be established. Sorption data calculated for a hypothetical polyurethane composed exclusively of the soft segments show that the amount of benzene sorbed into a polymer depends on its structure (see Table 1). A decreasing trend for S_{eq} values which vary in the sequence PU-1 > PU-3 > PU-2 > PU-4 > PU-5 for the series of PTMO 1000-based PUs, and in the sequence PU-6 > PU-8 > PU-7 > PU-9 for the series of PTMO 650-based PUs, can be found. Both data sets exhibit the growing tendency to reduce the membrane sorption capacity as its morphology develops, starting from PU-1 and PU-6 showing no signs of microphase separation to PU-5 and PU-9 with a distinct surface morphology on a macroscopic scale, via poly(urethane-urea)s PU-2, PU-3 and PU-7 with small structures sized tens of nm.

The solvent diffusivity D into the polyurethane membranes was calculated from the sorption kinetic data using the diffusion equation based on Fick's formalism. The obtained values presented in Table 1 show a decrease of D with an increasing size of the morphological structures observed by the AFM technique according to the following sequences: PU-1 > PU-3 > PU-4 > PU-5 and PU-6 ≈ PU-8 > PU-7 ≈ PU-9. It has been shown previously[3] that the structures of macroscopic size present in the polyurethane membranes should contain an ordered morphology on the segmental level scale. Therefore, the movement restrictions imposed by the hard segment domains can

account for the differences in the diffusion coefficient values. The restricted movement can increase the length of the "path of least resistance" which brings down the diffusion coefficient even in case of small benzene molecules. This is clearly demonstrated by the D values for PUs exhibiting phase mixed morphology, like PU-1, PU-6 and PU-8, comparing to the other polymers with microphase separation.

From the results discussed so far, it appears that solvent permeation behavior is strongly dependent on the morphology of the polyurethane-based membranes estimated by the AFM method. Additional phenomenon that needs to be considered includes the effect of the solvent present within the membrane phase on its microstructure. To examine the morphology of the polyurethanes exposed to solvent action, AFM studies of the surface of the swollen PU-3 and PU-9 films with distinctly different initial topography have been performed and the results obtained have been shown in the series of the $10\,\mu m \times 10\,\mu m$ images presented in Figs. 1 and 2.

When the PU-3 film is saturated with benzene and a drop of it remains on the surface then typically an image depicted as (B) in Fig. 1 may be recorded. Since the observed corrugations are mainly situated perpendicularly to the scanning direction this may suggest that the surface is very soft, therefore the observed image is rather an effect of interactions with the cantilever, not a real topography of the film. The surface is originally very flat and stable (A), however, after swelling reveals the amplitude of the tip nearly 200 nm. The situation gradually changes when a significant portion of the solvent evaporates. The process of desorption progresses relatively quickly in an open air, therefore it is possible to record images like that shown in Fig. 1(D). An upper part of the image, similar to that in Fig. 1(B), indicates that the film is still close to saturation with the solvent, however, observations using optical microscope, which is attached to the AFM, show a benzene free surface of the film. The lower part of the image corresponds to a partially dried surface where flat domains appear with clear boundaries between them. Much smaller corrugations are observed now within the area of domains, suggesting that the surface is still not very hard. The domains are, at this state, similar to that recorded finally, when the film becomes dry, as shown in Fig. 1(E). It is worth mentioning that the full image is collected during 3 min.

The series of images shown in Fig. 2 was recorded under the same conditions when the sample was exposed to cyclohexane. As may be seen, the images are similar to those observed with benzene. However, much larger values of the corrugation amplitude may suggest significantly softer film. This can be explained by a higher amount of cyclohexane present within the membrane at the time of observations, despite its lower sorption value at equilibrium saturation ($0.24\,mol/100\,cm^3$ vs. $1.42\,mol/100\,cm^3$). Since the time of exposition of the swollen surface to air needed for AFM examinations has been approximately the same for both the PU-3/benzene and PU-3/cyclohexane systems, the lower rate of the cyclohexane desorption[6] can account for its temporarily higher content in the membrane. As a result, the softer surface of such film gives rise to its greater roughness coming from the cantilever movement. This is also demonstrated by more than 2 times higher values of the RMS and F/F_0 parameters for the PU-3 sample swollen with cyclohexane compare to that swollen with benzene (see Table 2).

Figure 3 shows the data obtained for the PU-9 membrane exposed to cyclohexane. The images of the surface recorded for this sample in its swollen state present the similar features as for the PU-3/benzene and PU-3/cyclohexane systems. On the other hand,
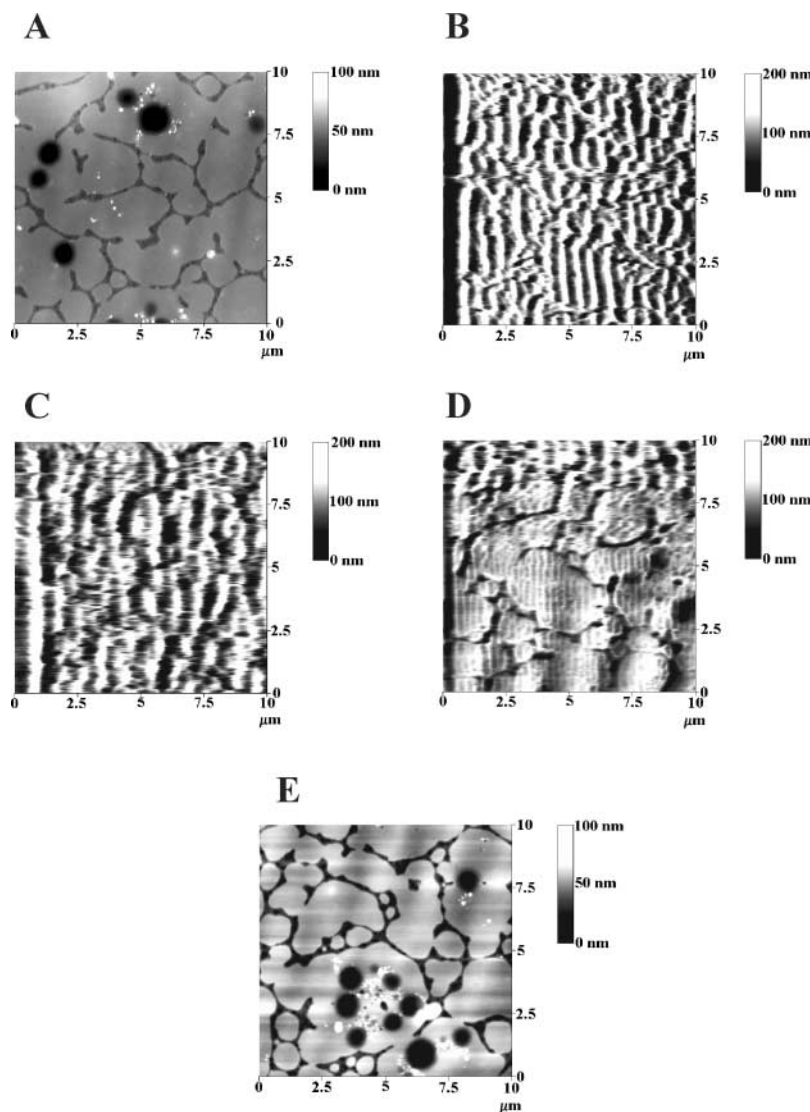
Figure 1. AFM images of the surface of a dry (A) and benzene swollen (B–E) PU-3 membrane. Figure B–E presented in order of desorption process.

the morphology of the PU-9 membrane is completely different from that found for the PU-3 sample.[3] It is illustrated by the coarser surface of PU-9 with circular structures of a few micron size (see Fig. 4(A)) vs. flat surface of PU-3 in a form of large, interconnected associates, composed of small extended domains on the size range of tens of nm. (see Fig. 1(A)). Therefore, the similarity of the AFM images of the swollen films support the former interpretation of false topography of those films. Also here, like in all other cases, drying leads to the fully recovered topography of the initial film. The process of solvent
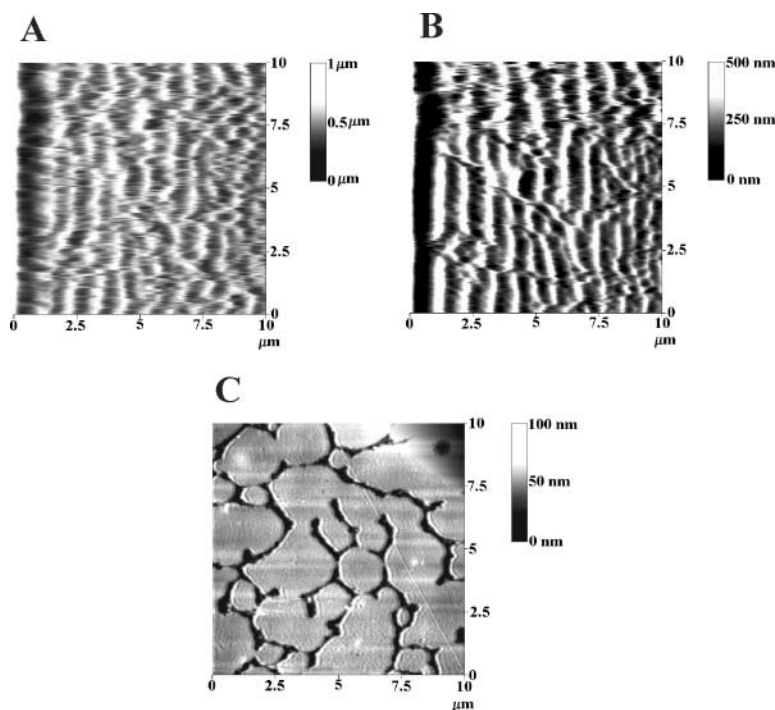
Figure 2. AFM images of the surface of PU-3 membrane swollen with cyclohexane. Figures A–C presented in order of desorption process.

desorption and restoration of the initial surface morphology is outlined also by the changes in the RMS and F/F_0 values. The data listed in Table 2 show that the RMS roughness and F/F_0 parameter values decrease as desorption proceeds with time, reaching finally the values characteristic for the initial dry films.

Table 2. AFM roughness parameters for dry and swollen PU membranes.

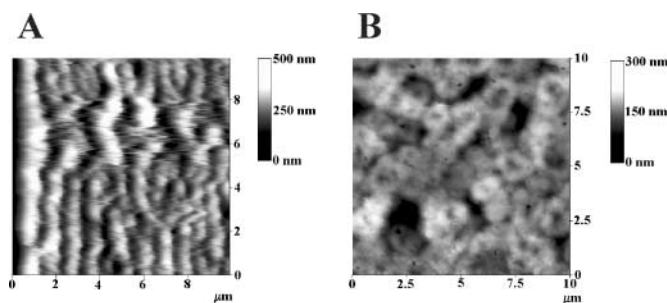| Sample	Swelling agent	RMS [nm]	F/F_0 [%]
	A—dry	9.0	100.38
	B—benzene	43.16	116.14
	C—benzene	35.38	119.82
	D—benzene	27.50	108.46
PU-3	E—benzene	12.72	100.95
	A—cyclohexane	102.35	218.51
	B—cyclohexane	95.04	155.28
	C—cyclohexane	10.29	101.29
	A—dry	37.90	101.22
PU-9	B—benzene	213.03	208.50
	C—benzene	170.90	179.34
	D—benzene	56.62	101.28

Figure 3. AFM images of the surface of PU-9 membrane swollen with cyclohexane. Figures A–B presented in order of desorption process.

A completely different image was obtained for the film of PU-9 when exposed to benzene. Figure 4 shows the presence of uniformly distributed distinct raised regions in a spaghetti-like form. This system presents the roughest surface, with RMS roughness as high as 213 nm. Since there are no effects of scan direction similar to that observed previously for the PU-3 and PU-9 samples, it may suggest that the sample is relatively hard at this stage of swelling. From the images given in Fig. 4, it can also be noted that
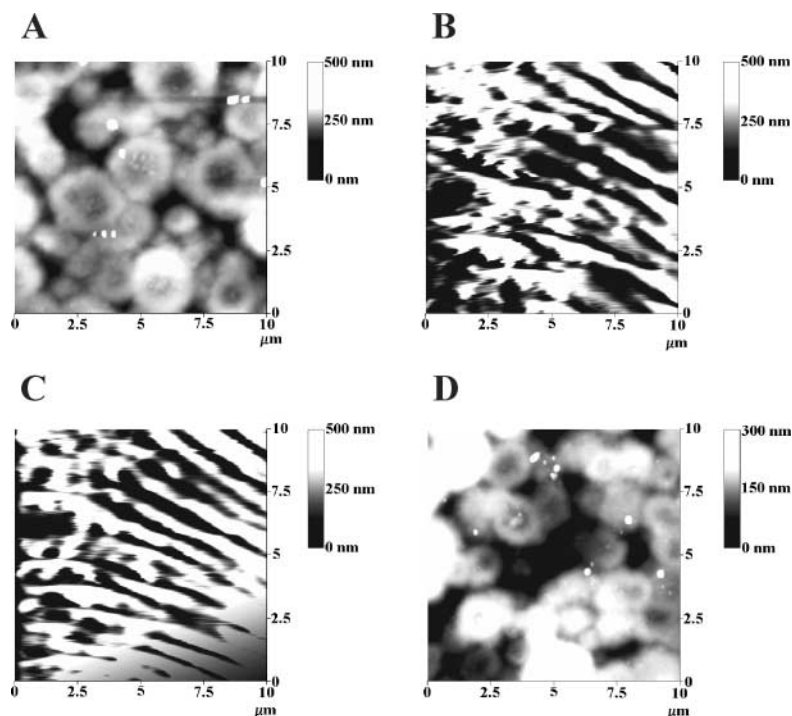

Figure 4. AFM images of the surface of a dry (A) and benzene swollen (B–D) PU-9 membrane. Figures B–D presented in order of desorption process.

the macroscopic dimensions of specimen detected in the swollen film of PU-9 are generally of the same order as for the dry sample. The structural changes from the circular structure (A) to the spaghetti-like pseudo-lamellae (B) or (C), observed after the addition of benzene, can be explained based on the idea that the presence of a preferential solvent with affinity toward soft segments will increase their size. Consequently, in a particular swelling degree regime, characteristic for a given swelling agent, the morphology can change in a manner that leads to the expected more regular lamellar textures. It is also worth noting that rather sharp boundaries are observed between the phases suggesting that the improvement of the phase separation has occurred in these systems upon the solvent action. Observation that domain structure changes from the lamellar to the ill defined spherical structures as the block length decreases has been made for PMDS-PS diblock polymers.[7] However, there are also other observations for triblock polymers which provide that the morphological features were not as predicted based on composition ratio.

The AFM results presented above are consistent with the SAXS data recently obtained by us.[8] In that case, a clear and systematic decrease of the lamellar repeat distance was noted as the amount of benzene in the swollen samples of polyurethanes was reduced during the desorption process. It appears therefore that both length scales are changing in the same fashion during the sorption process that leads essentially to the more perfectly ordered morphology on the macroscopic level.

CONCLUSION

The results presented here show that relationships between morphology of the polyurethane-based pervaporation membranes, as described by AFM technique, and their solvent permeation ability characterized using sorption method, do exist. It has been clearly demonstrated that the more developed morphology is accompanied by the lower sorption capacity of the membrane. This confirms the expectations of the restricting role of the hard segment domains in suppressing membrane swelling. In addition, the movement restrictions imposed on solvent molecules by the hard domains have been demonstrated by the differences in the diffusion coefficient values for polymers with phase-mixed and phase-separated morphology.

The AFM examination of the microstructure of the polyurethane films exposed to solvent action showed the morphology dependent effect of solvent. The polyurethanes with micro-scale domain morphology exhibit no changes in domain structure originating from the increasing or decreasing content of the solvent in the membrane. However, based on the previous SAXS data, the systematic decrease in the lamellar repeat distance during solvent desorption was noted for these PUs. For polyurethanes with macro-scale morphology, it has been found that solvent induced morphological changes depend on the kind of solvent, i.e., its affinity towards PU soft segments. The microstructural transformation from circular structures into the spaghetti-like pseudo-lamellae have been observed as a result of the interaction between polyurethane soft segments and solvent molecules with a high swelling power. Since these observations coincide with the SAXS data, it appears that both length scales are changing in the same fashion during the sorption process, leading to the more perfectly ordered morphology. The solvent sorption/desorption process was found not to affect the membrane initial morphology.

Thus, the use of AFM method enabled information on morphological features of various length scale to be collected which can be of great assistance in formulating more general morphology-transport properties relationships.

ACKNOWLEDGMENTS

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