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Surface Morphology of the Polyurethane-Based Pervaporation Membranes Studied by Atomic Force Microscopy. I. Effect of the Polyurethane Molecular Structure

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ABSTRACT

Atomic force microscopy (AFM) was employed to study the surface morphologies of the polyurethane-based pervaporation membranes and to evaluate the effect of the polyurethane (PU) molecular structure. Segmented poly(tetramethylene oxide)-based PUs varying in the length of both segments as well as in the structure of the hard segments were tested. Small spherical or extended hard domains, on the size range of tens of nm, and their large, interconnected associates for a higher hard segment volume fraction, have been observed at relatively flat surface of the diamine-based PUs. The surface of the diol-based PUs appears to be generally much coarser and shows globular or circular structures of a few micron size which are thought to be composed of the hard segment lamellae. The morphology variations observed by AFM were found to correlate well with the small-angle X-ray scattering (SAXS) data revealing the necessity of the periodic arrangement in space of the segmental level domains for the formation of a higher level of the domain morphology.

Key Words: Polyurethane; Atomic force microscopy; Morphology.

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INTRODUCTION

Segmented polyurethanes are typical condensation multiblock copolymers, which form a class of thermoplastic elastomers of great commercial importance. This is due to the unique and interesting properties displayed by this group of polymers, which are assumed to result from the microphase separation because of the thermodynamic incompatibility of the segments.^[1,2] Therefore, much attention has been focused on the elucidation of domain morphology in polyurethanes. Direct evidence of a domain structure was first suggested by Koutsky et al.^[3] using transmission electron microscopy (TEM). Since then, numerous studies of the morphological features of the segmented polyurethanes have been carried out by means of optical and electron microscopic methods and various scattering techniques, like small- and wide-angle X-ray scattering (SAXS, WAXD), or small-angle neutron and light scattering (SANS, SALS). These techniques have also been complemented by other thermal or dynamic mechanical analyses, which can give additional, however less direct information on domain structure. The wide variety of structures found for segmented polyurethanes on different levels of structural organization,^[4] including lamellar domains with the average distance between domains of $100 \div 250 \text{ \AA}$, grains or fibrillar structures in the size range of tens of nm, or spherulites with diameter up to $20 \mu\text{m}$ can be attributed to the variations in the polyurethane molecular structure, as well as to the external conditions concerning different casting solvents, thermal history or mechanical processing.

Hence, one can expect that controlling morphology of such systems provides a key to influence the performance of the final material and gives the possibility of tailoring the properties as desired. For the polyurethane-based membranes studied in this work, the correlations between structure and transport properties searched have their background in the mechanism of mass transport through dense polymeric films. It is described by a solution-diffusion model comprising the process of sorption of molecules into the membranes and then their diffusion through the membrane. Although it is assumed that in polyurethanes transport proceeds exclusively through the soft segment phase,^[5] the hard domains serving as virtual crosslinks and reinforcing filler are expected to influence that process. It can occur either by suppressing membrane swelling or by altering the path of the permeating molecules, both processes being strongly affected by the size, shape and distribution of the hard domains.

The materials presented in this work have already been a subject of extensive studies in our laboratory with respect to their transport properties^[6–8] and structure.^[9–11] In this series of papers we are presenting the studies of their morphology using the AFM method, in order to further elucidate the structural organization previously observed on the scale length of SAXS.

The AFM technique has been shown to be very useful for the characterization of the polymer surface because it can provide high resolution, three-dimensioned morphologies of non-coated untreated surfaces over a broad range of length scale. The examples of the successful application of this technique for studying polymer morphology include investigations of the polyurethanes and refer to the flexible polyurethane foams,^[12,13] and polycarbonate urethane elastomers.^[14]

The studies presented in the paper deal with correlation between molecular structure of poly(etherurethane)s and the morphology displayed by these polymers, prepared in

a form of pervaporation membranes. In the next paper of the series, we will discuss a transformation of the membrane morphology taking place when the membrane surface is subjected to the swelling behavior of a permeating liquid.

EXPERIMENTAL

Materials

Polyurethanes and poly(urethane-urea)s (PU) used in these studies were synthesized in DMF solution either by a prepolymer method, or in the reaction of equimolar amounts of 2,4-tolylene diisocyanate (TDI) and poly(oxytetramethylene)diol (PTMO, $M_w = 650, 1000, 2000$). The two-step prepolymer procedure involves the formation of a prepolymer by end-capping of PTMO with TDI, being in excess in the reaction mixture, and then the extension of a polymer chain by adding an appropriate amount of a selected low-molecular weight diol or diamine. 4,4'-Bis (2-hydroxyethoxy) biphenyl (BHBP), hydroquinone bis (2-hydroxyethyl) ether (HQE), 4,4'-diaminodiphenylmethane (PP), and ethylenediamine (EDA) were used in these studies as chain extenders (ChExt). A series of three types of samples were studied in which a molar ratio of TDI/ChExt/PTMO was 4/3/1, 2/1/1 and 1/0/1 (Table 1). The details of the synthesis are described elsewhere.^[6,8]

Preparation of PU Films for AFM Studies

AFM samples were prepared in the same way as the polyurethane-based membranes previously used in the pervaporation experiments. The 15 wt% solution of the dried PU dissolved in DMF was poured onto an aluminum plate and the solvent has been evaporated

Table 1. Characterization of PUs.

Sample	Composition		Chain extender	Molecular weight of PTMO	Hard segment		Density ρ (g/cm ³)
	TDI/ChExt/PTMO (mol)	x^a			(wt%)	(vol%)	
PU-1	1/0/1	0	—	1000	15	5	1.093
PU-2	4/3/1	3	EDA	1000	47	34	1.142
PU-3	4/3/1	3	PP	1000	56	41	1.167
PU-4	4/3/1	3	HQE	1000	56	39	1.194
PU-5	4/3/1	3	BHBP	1000	60	43	1.197
PU-6	1/0/1	0	—	650	21	10	1.112
PU-7	2/1/1	1	PP	650	46	33	1.139
PU-8	2/1/1	1	HQE	650	46	35	1.122
PU-9	2/1/1	1	BHBP	650	49	35	1.161
PU-10	4/3/1	3	BHBP	2000	43	34	1.091

^a Number of the hard segment's repeat units (Fig. 1).

at 60°C in a dry nitrogen atmosphere for 3 days. The samples were then cut and attached to the standard AFM disc without peeling them off from the aluminum plate.

Measurements

NanoScope E (Digital Instruments (DI), 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. All roughness data reported in text were calculated for the entire surface of each AFM image presented using DI software.

A density of the polyurethane film required for the estimation of hard segment volume was determined by using a buoyancy method in water. The hard segment theoretical volume fractions listed in Table 1 were calculated from the measured mass densities of the polymers using the extrapolated soft segment mass density (PTMO-2000: $\rho = 0.985 \text{ g/cm}^3$, PTMO-1000: $\rho = 0.987 \text{ g/cm}^3$, PTMO-650: $\rho = 0.991 \text{ g/cm}^3$) and by assuming volume additivity. The hard segment weight fraction represents the relative weight of diisocyanate and chain extender incorporated into the polymer, based on the polymer stoichiometry.

The SAXS data were obtained at the Austrian SAXS beamline of the Synchrotron ELETTRA in Trieste, Italy. A part of these data has already been reported in a series of papers.^[9–11] In this work, the SAXS data were used to provide characterization of the microphase separation for comparison with the AFM results.

RESULTS AND DISCUSSION

In Table 1, the reactants that were used in the PU synthesis and their mole ratios are listed along with the weight and the volume fractions of the PU hard segments.

The modifications of the hard and soft segments, performed by changing the type of the chain extender, the stoichiometry of the TDI and ChExt components, and the molecular weight of PTMO, enabled two series of PUs to be prepared. The first series of PUs (PU-2 \div PU-5) comprises PTMO-1000 based PUs, which have the same stoichiometry of the hard segments represented by $x = 3$ (see Fig. 1, Table 1) but various chemical constitutions resulting from the chain extender chemistry. The second series of PUs (PU-7 \div PU-9) contains PTMO-650 based polymers of the same structural variations within the hard segments and the stoichiometry represented by $x = 1$. Additionally, PU-10 was synthesized to discuss the effect of the soft segment length on the morphology of PUs. The remaining two polymers, PU-1 and PU-6, which are used in this work as references, have their hard segments built exclusively from the TDI units.

Figure 2 shows a sequence of AFM images of PU-1, PU-2 and PU-3 demonstrating morphology of the polymers obtained with two different diamines as the chain extenders, and the polymer (PU-1) without chain extender units in the hard segments. Among these samples, PU-1 presents the smoothest surface with no detectable features, however with few raised regions rounded the holes, which seem to be a result of the solvent evaporation process. Morphology of the sample PU-2 is relatively uniform, formed by small spherical

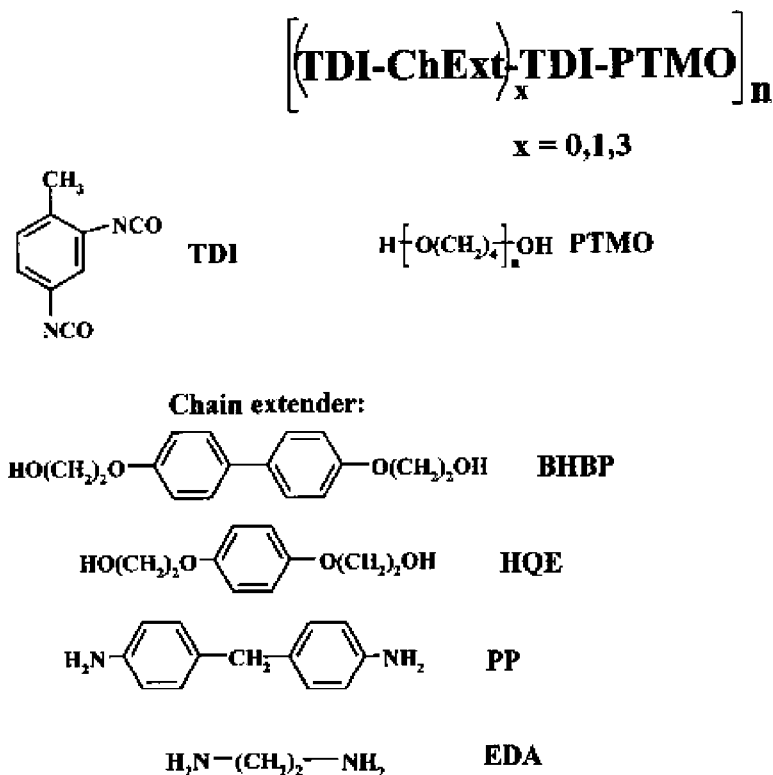


Figure 1. Schematic representation of the polyurethane chain and chemical structure of the reagents.

structures of 50 nm in size, densely packed and evenly distributed throughout the polymer surface. Clearly, a different image was obtained for PU-3 that is shown in Fig. 2 and, as a magnified inset, in Fig. 3.

As can be seen in Fig. 3, on a 500 nm scan size extended structures with dimensions of ca. 16 nm wide by 60 ÷ 100 nm long distributed in a rather organized fashion, in a short range scale, are observed. In Fig. 2, association of these structures is seen in a form of micron scale regions, which are irregular in shape and size, and highly interconnected. Although the morphologies of the samples discussed present quite different features, all those polymers surfaces appear to be relatively smooth as found from roughness measurements. RMS values are equal to 7.26 nm, 5.11 nm, and 8.99 nm for PU-1, PU-2 and PU-3, respectively. The F/F_0 parameter, which is a ratio of a real to a geometric surface area (in percents), is within the range of 100.87 to 100.22. Since the RMS roughness data, defined as the root mean square average of height deviations from the mean data plane might be the scale dependent, all roughness measurements presented here were calculated for the images of the same surface area of $10 \times 10 \mu\text{m}^2$.

Figure 4 shows AFM images of the samples from the first series of PUs synthesized using two different diols as chain extenders (PU-4 and PU-5). These samples provide

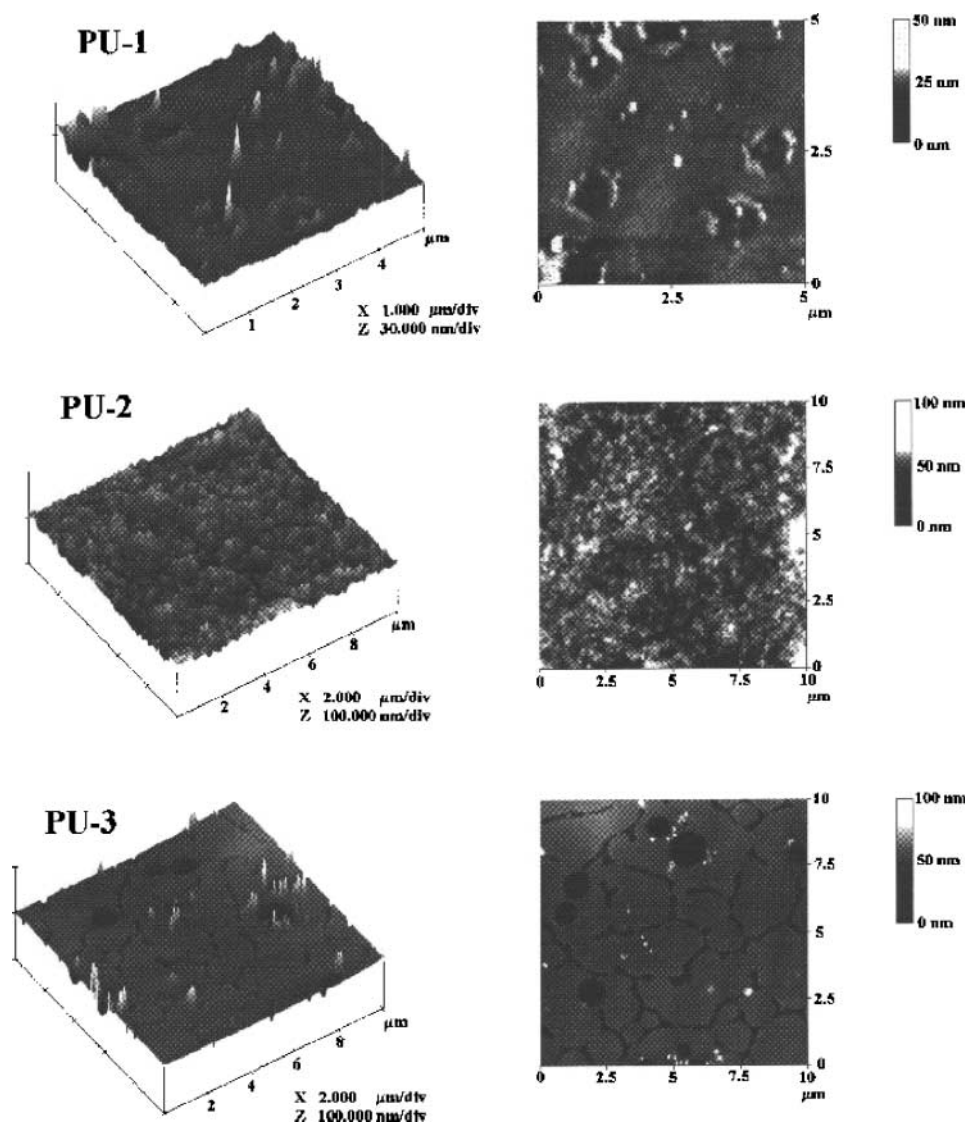


Figure 2. AFM images of the surface of the PTMO-1000 based polyurethane (PU-1) and poly(urethane-ureas) (PU-2 and PU-3).

a completely different AFM image from those obtained for PU-1, PU-2 and PU-3. Volumes filling globular structures are observed both, in PU-4 and PU-5. The globules seem to be nearly identical in appearance and relatively similar in size, typically $5.5 \mu\text{m}$ for both polymers, however, population of the smaller globules, around $3 \mu\text{m}$, can also be seen in sample PU-5. Some differences in the globules shapes observed for example in PU-4 may be explained by their different positions at the surface. The RMS roughness and

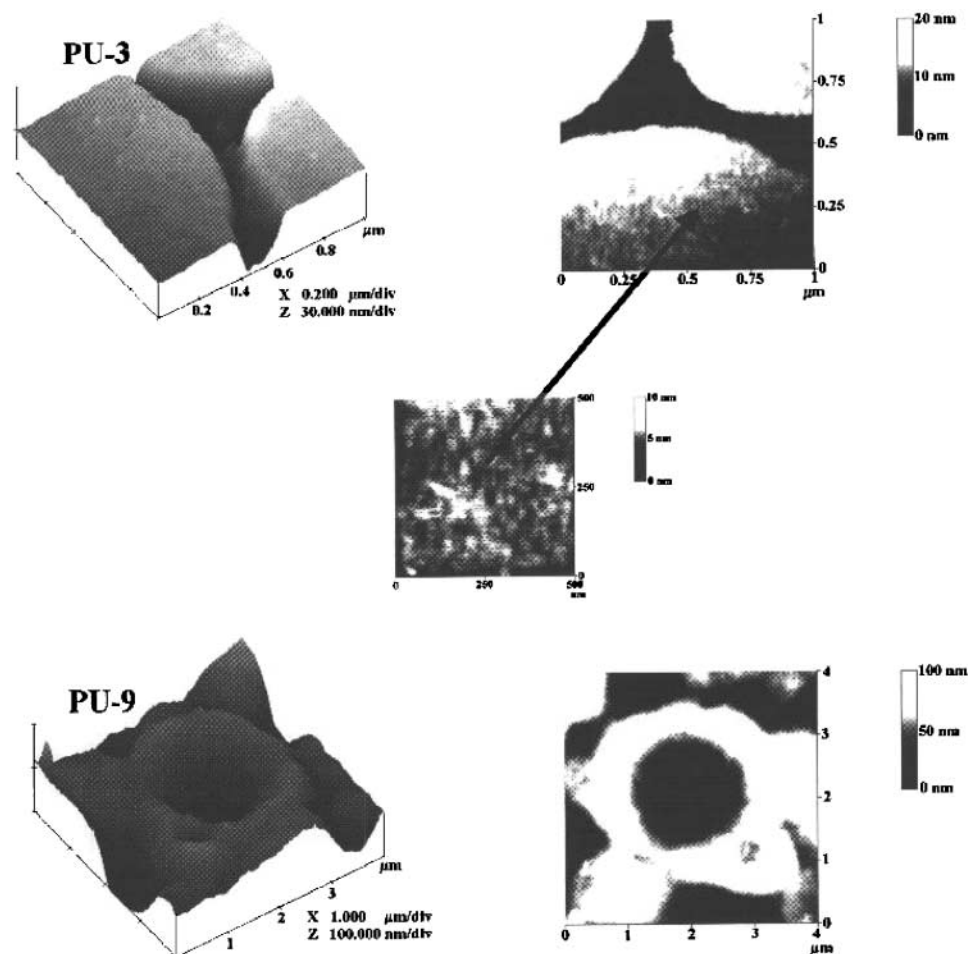


Figure 3. AFM images of the PU-3 surface, at 1 μm and 500 nm scan sizes, and of the PU-9 surface at 5 μm scan size.

F/F_0 data for PU-5, which are 188.85 and 103.49, respectively, indicate that the surface of this sample is the roughest among all the polymers studied, more, its roughness is significantly larger comparing to the PU-4 sample. The corresponding values are $\text{RMS} = 70.86 \text{ nm}$ and $F/F_0 = 100.63$.

The surface morphology changes completely, when the polyurethane soft segment length is increased while keeping the hard segment structure and the length constant (PU-10 vs. PU-5). The globules observed in sample PU-5 are not seen in PU-10, instead, a uniform distribution of distinct raised regions irregular in shape and size, and of various heights is revealed in the topographical image of PU-10. The RMS roughness and F/F_0 data, which are here equal to 89.59 nm and 109.50, respectively, prove a relatively rough surface of this polymer.

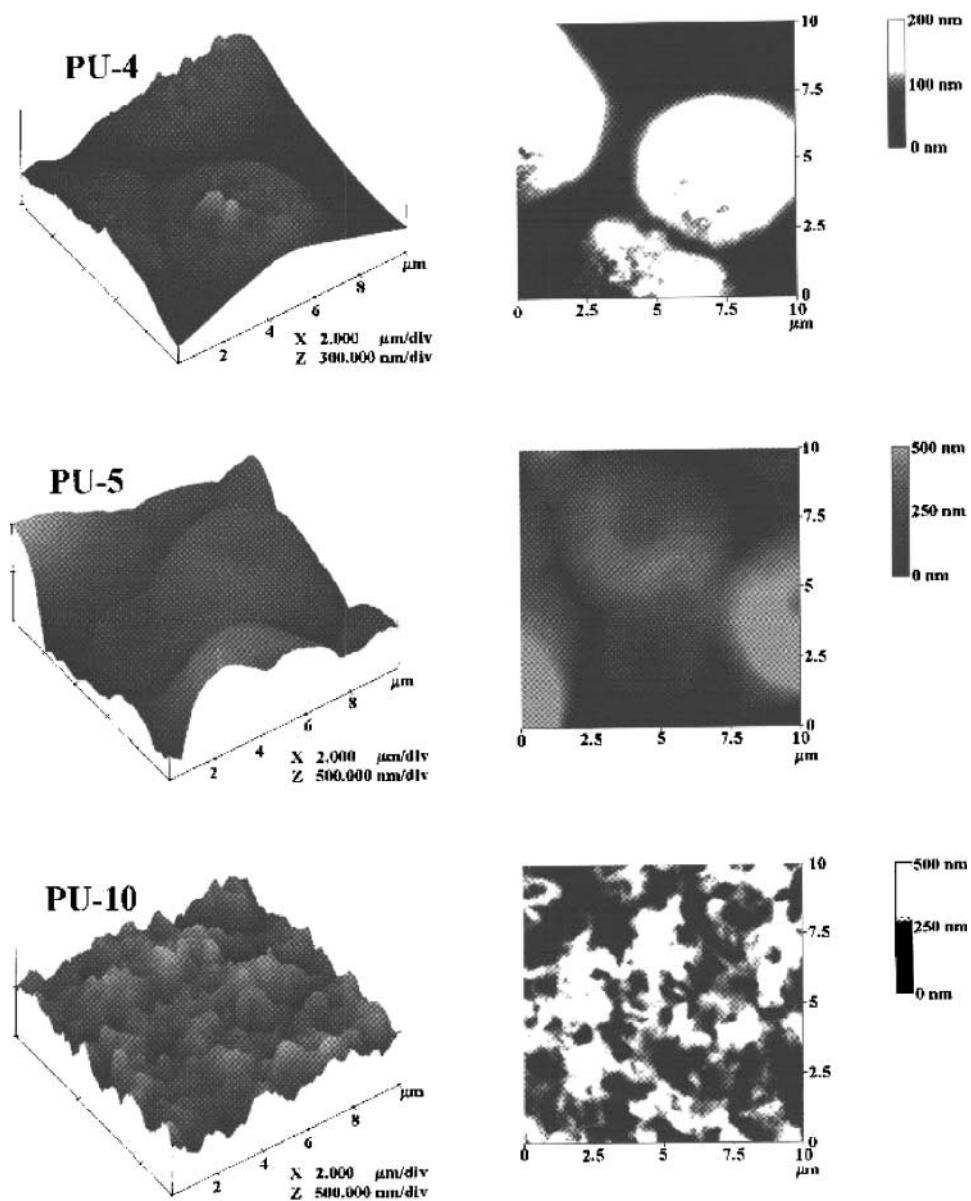


Figure 4. AFM images of the surface of the PTMO-1000 based polyurethanes (PU-4, PU-5, PU-10).

Figure 5 shows the AFM images of two polymers from the second series containing the PTMO-650 macrodiol. PU-6 used as a reference sample represents a polymer without chain extender units within the hard segments, whereas PU-7 is parallel of PU-3 poly(urethane-urea) with shorter both, hard and soft segments. Sample PU-6 exhibits the smoothest surface

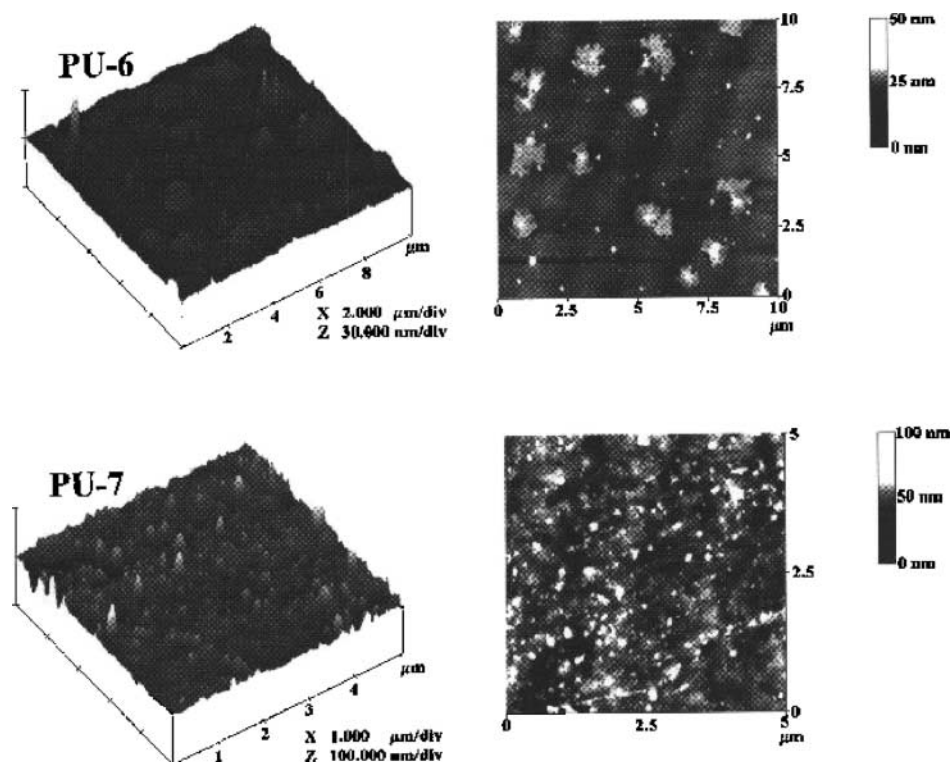


Figure 5. AFM images of the surface of the PTMO-650 based polyurethane (PU-6) and poly(urethane-urea) (PU-7).

among all the polymers studied, with a RMS roughness equal to 1.99 nm and F/F_0 equal to 100.06. Despite some slightly raised small areas, which may be assigned to impurities incorporated to the sample during a film preparation, the surface of PU-6 does not show any distinct structures similarly to its counterpart PU-1. The PU-7 sample on the other hand, presents quite different image from PU-3 being its analog to the first series. Small spherical structures of ca. 50 nm in diameter evenly distributed throughout the sample can be seen instead of the interconnected agglomerates of the extended structures observed for PU-3. The roughness of the sample surface is, however, very similar to PU-3, with RMS roughness equal to 7.51 nm and F/F_0 equal to 101.15.

Differing surface morphologies are also displayed by PU-8 and PU-9 when compared with their first series analogs, PU-4 and PU-5 (see Fig. 6). The PU-8 film exhibits relatively flat surface with RMS roughness and F/F_0 data equal to 7.15 nm and 100.42, respectively which shows an unorganized distribution of slightly raised areas irregular in shape and size. On the other hand, the large and distinct circular structures with diameters of about $1.5 \div 2.4 \mu\text{m}$ (shown in Fig. 3) are observed for PU-9 sample. The RMS roughness and F/F_0 data are equal to 37.91 nm and 101.22, respectively, indicating that the surface of this polymer is coarser than for PU-8, however, it is smoother than for the corresponding PU-5 sample.

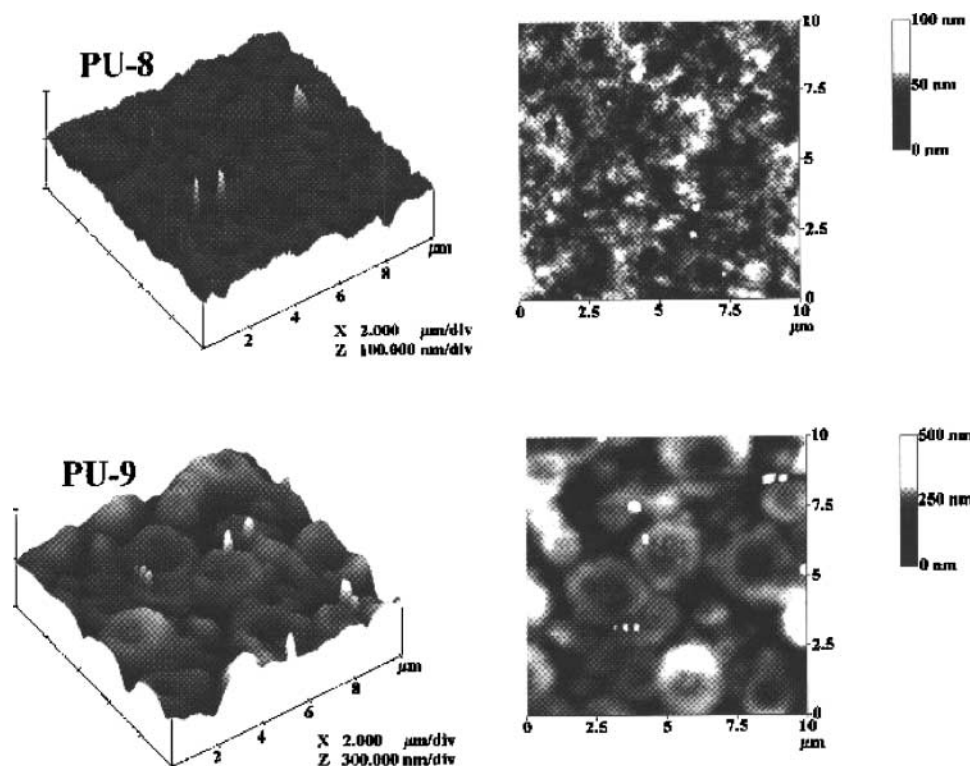


Figure 6. AFM images of the surface of the PTMO-650 based polyurethanes (PU-8, PU-9).

The results of the AFM investigations indicate the existence of various distinct types of morphological structures on the surface of the polyurethanes synthesized using different chain extenders, comparing with a featureless surface of both polyurethanes obtained without a chain extender (PU-1 and PU-6). Considering the hard segment volume fraction values given in Table 1, which are within the range of 33%–41% for all PUs with ChExt units, this suggests that the variation in the type of structure must be attributed to the molecular structure of a chain extender and the length of both segments. The surface of all PUs with the urea linkages is smoother than the surface of the other polymers by about one order of magnitude, based on the RMS roughness data, and is characterized by the RMS and F/F_0 values ranging from 5 nm to 9 nm, and from 100.22 to 101.15, respectively. The surfaces of the PTMO-650 based PU with short hard segments made up of aromatic diamine units ($x = 1$) and of the PTMO-1000 based PU with long hard segments made up of aliphatic diamine units ($x = 3$) are similar in appearance and consist of small spherical structures of 50 nm in size. When the length of the fully aromatic hard segments and the corresponding soft segments is increased, the surface of the resulting polymer is still very flat. However, its morphology is quite different and presents interconnected irregular regions, which are found to be composed of the small-extended structures of 16 nm width and $60 \div 100$ nm length.

The surface of PUs with the urethane linkages is, on the other hand, very rough, with RMS roughness data ranging from 37.9 nm to 188.9 nm and the F/F_0 data ranging from 100.6 to 109.5, except that of the PU-8 sample. The higher values in the series generally correspond to the polymers with longer segments. Structural heterogeneity is of a micron scale for these polymers and involves in most cases well-defined globular or circular structures. The exceptions, for which no regular structures have been found, refer to the PU-8 and PU-10 samples showing the extremes in terms of the roughness (RMS = 7.15 nm and $F/F_0 = 100.42$ vs. RMS = 89.59 nm and $F/F_0 = 109.50$).

The AFM images for both samples correspond very well with the SAXS data, which provide the information about the segmental level segregation. The lack of an intensity maximum for these polymers suggests that either the hard and soft segments are not sufficiently segregated, that can be the case of PU-8 with short both segments, or the domains resulting from the segments segregation are randomly distributed in space, as it is supposed to be the case of PU-10 sample with the longest hard and soft segments.^[12] On the other hand, a periodicity in changing electron density has been observed as an intensity maximum in SAXS for all the remaining polymers studied in this work. The SAXS interdomain spacing values, calculated from the peak position assuming a lamellar model, show two groupings, below 10 nm for the poly(urethane-urea)s (7.7 nm, 10.1 nm, and 8.8 nm for PU-2, PU-3 and PU-7, respectively), and above 10 nm for the polyurethanes (11.2 nm, 17.5 nm, and 12.2 nm for PU-4, PU-5, and PU-9, respectively). The microphase separation, as shown by these data, can be related to the macrophase separation observed by AFM through the formation of lamellae-like hard domains, which have a potential to aggregate to the form of larger structures. From Fig. 3, it appears that the hard domains of PU-3 are in a form of the extended structures, 16 nm wide and 60–100 nm long, the association of which gives large interconnected regions seen in Fig. 2. For other two poly(urethane-urea)s with lower SAXS spacing values (PU-2 and PU-7) hard segment domains are observed as grains of 50 nm dimension.

This lower level of structures corresponding to the hard domains was not detected on the AFM micrographs of the polyurethanes, probably due to the resolution limitation concerning very rough surfaces. However, it seems reasonable to propose that the globular or circular superstructures observed via AFM for those polymers, are composed of the lamellar hard segment microdomains, as suggested by the SAXS results.

The presence of superstructure organization observed in this study is not associated with the crystallization either of the hard or the soft segments. The hard segment domains are unable to crystallize because of the asymmetry of the two NCO groups in 2,4-TDI molecules. In the case of the PTMO-based soft segments, if they are able to crystallize, e.g. in case of longer segments ($M_w \geq 2000$), their T_m is well below the room temperature. The biphenyl units, on the other hand, which are responsible for the mesomorphic properties of the resulting BHBP-based polyurethanes, and which were found to introduce some degree of order into the hard domains, strongly influence the ability for microphase separations (PU-9 vs. PU-8) but do not affect the final morphology of the well phase-segregated samples (PU-4 and PU-5).

Considering the both levels of structural organizations studied by AFM and SAXS methods, some correlation can be found between

the polyurethane molecular structure and the AFM and SAXS results. Analysis of the SAXS spacing for the PTMO-1000 based poly(urethane-urea)s of the same number of the hard segment repeat units ($x = 3$) but various chemistry of the chain extender units (PU-2 or PU-3) shows a significant difference between both polymers. This is also reflected in the size and shape of their hard domains. The smaller both, distance between like domains and the domain size for PU-2 can be explained by the smaller size and the greater flexibility of the aliphatic EDA units. This, in turn, should result in a smaller persistence length of the hard segment sequence. The rigid and appreciably large aromatic PP units (see Fig. 1) can also account for the extended shape of the resulting hard domains, comparing to the spherical one observed for the EDA-based PU. Application of the biphenyl-based chain extender (BHBP) instead of the smaller and less aromatic HQE significantly increases the interdomain spacing (PU-5 vs. PU-4) and the degree of microphase separation (PU-9 vs. PU-8). However, it shows no effect on a higher level of structural organization. Considering the molecular structure of the chain extended polyurethanes displaying no distinct surface morphology (PU-8, and PU-10), it can be noted that the sample with high degree of phase mixing (PU-8), resulting either from the less aromatic character of the hard segments (PU-8 vs. PU-9), or from the smaller degree of hydrogen bonding (PU-8 vs. PU-7), or the relatively shorter length of both segments, has its surface very smooth. On the other hand, the sample with high degree of microphase separation (PU-10) due to a high both, the length of the segments, and the aromatic character of the hard segment, shows an opposite effect of a very rough surface.

CONCLUSION

Polyurethanes synthesized using low molecular weight diamines and diols as chain extenders have been shown to exhibit quite different surface morphologies. The surface of polyurethanes with urea linkages, able to form strong hydrogen bonding, is very flat and consists of small spherical or extended hard domains on the size range of tens of nm. For a higher hard segment volume fraction, these domains have been found to associate themselves to give large, micron scale, interconnected regions. The common feature of the surface of diol-based polyurethanes with a high degree of microphase separation is its high roughness and the existence of large globular or circular structures of a few micron size. It is also suggested that these superstructures are clusters of the hard segment lamellae. Segmental level of phase segregation, which depends on the segment nature and length, along with the periodic arrangement in space of the resulting microdomains have been found to be necessary for the formation of a higher level of the domain morphology.

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