

Dependence of the Structure of Siloxane Urethane Elastomer on the Conditions of Synthesis

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Abstract—The morphology and thermal and mechanical properties of siloxane urethane block copolymers based on oligosiloxane- and oligoalkylene diols are investigated. The dependence of morphology on the conditions of synthesis is studied via atomic force microscopy and scanning electron microscopy.

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INTRODUCTION

Polyurethane (PU) elastomers find wide application in industry due to their unique combination of superior operating characteristics, e.g., hardness, elasticity, mechanical strength, and wear resistance. Introducing siloxane links into a polyurethane chain should affect both its bulk and surface properties: copolymer heat stability and resistance to light, hydrophobicity, gas permeability, biocompatibility, and mechanical and frictional characteristics. The microphase separation typical of copolymers based on such thermodynamically incompatible copolymers as polysiloxanes and polyurethanes has a substantial impact on their structure and properties, while the presence of urethane groups capable of forming hydrogen bonds should also affect structural formation.

The synthesis of this type of polyblock copolymers is based on the interaction between organic and organosiloxane oligomers with di-isocyanates [1, 2]. It was shown in [3] that the morphology of copolymers depends on the length of their blocks. In this work, we study the structure and properties of the siloxane urethane copolymers obtained in the reaction between oligomeric organosilicon diol (OSD), oligo(butylene oxide) (OBO), propylene- and ethylene oxide copolymer, glycerol (Laprol 5003, LP), and 2,4-toluene diisocyanate (TDI). We also study the dependence of the copolymer's structure on the presence of a catalyst, a chain extender (disiloxane diol or 1,4-butanediol), and the nature of the solvent. The basic properties of the studied copolymers are shown in the table: block ratios, conditions of synthesis (solvent, catalyst), glass transition temperature (T_g), maximum rel-

ative elongation (ϵ), and tensile strength (σ). Copolymers **V** and **VI** contain no linear blocks of OSD and OBO. Butyl acetate (BA) (for copolymers **I–III**, **V**, **VI**) and chloroform (CH, copolymer **IV**) were used as solvents. Synthesis was conducted either with (tin diethyl dicaprylate, **I** and **IV**) or without (**II**, **III**, **V**, **VI**) a catalyst. Disiloxane diol (DS) (**I**, **III**, **V**) and 1,4-butanediol (BD) (**III**, **IV**, **VI**) were used as polymer chain extenders (CEs). The reaction temperatures were 115°C in BA and 60°C in CH; these were chosen according to the solvents' boiling points (126 and 61.2°C, respectively). The studied samples were films skimmed from the solvents; sample thickness was ~150 μm .

The thermal properties of the polyurethanes were studied via differential scanning calorimetry (DSC) on a Mettler-Toledo DSC-822e instrument (Switzerland), in argon at a heating rate of 10°C min⁻¹.

Mechanical tests of our copolymer films were conducted on a LLOYD instruments LRSK Plus apparatus. The rate of deformation was 1000 mm min⁻¹.

Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to study the structure of the objects.

SEM investigations were performed on a Tescan Mira LMU microscope (Czech Republic). The samples were fastened on a conductive adhesive tape and studied under high vacuum using a standard Everhart–Thornley detector of secondary electrons. The study was conducted with a low accelerating voltage and a weak electron probe current.

Our AFM study was performed in the semi-contact mode in air at room temperature. A FemtoScan scan-

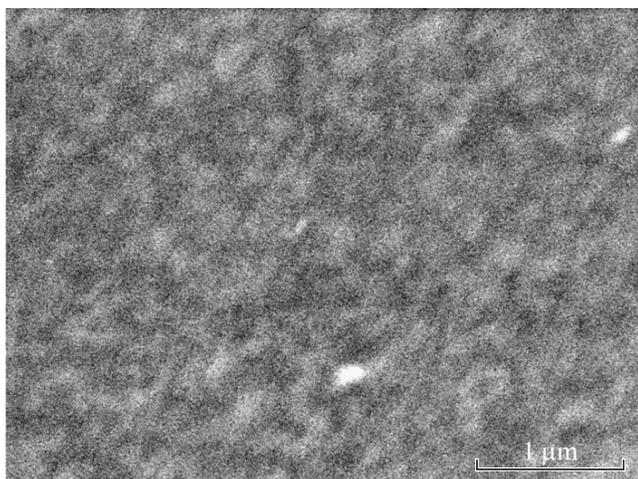


Fig. 1. SEM image of sample I.

ning probe microscope was used. MikroMasch cantilevers with a mean resonance frequency of 325 kHz and tip radius of 10 nm were employed. The obtained images were processed using the FemtoScan Online software.

RESULTS AND DISCUSSION

AFM results showed that a globule or nanosphere was the structural unit in all our samples [4–7]. According to DSC data, all of our copolymer samples were amorphous: no thermal effects were observed on the DSC curves obtained in the temperature range of -140 to $+140^\circ\text{C}$, except for a step in the heat capacity that corresponded to devitrification of the amorphous phase.

Glass transition points of the amorphous phase of the copolymers using disiloxane diol as the chain extender fell within the range of -25 to -44°C (see table). Using 1,4-butanediol as the extender lowered the T_g of the amorphous phase to -50 to -56°C , which agrees with the glass transition temperature of the OBO block [8]. The observed differences in the thermal behavior of the polymers could have been due to features of the microphase separation and require further investigation.

Studies of the morphology of different samples showed that it depended on the conditions of synthesis. SEM allowed us to observe agglomerates of globular particles in sample I (Fig. 1). AFM data show that the height of these structures was 2100 nm. The films of other samples had considerably smoother microrelief. The parameter of mean-square roughness was calculated to compare the morphologies [9]. Samples III, V, and VI had a mean-square roughness of ~ 1 nm; for sample II, this parameter was ~ 2 nm. The globular relief is not prominent in the images of

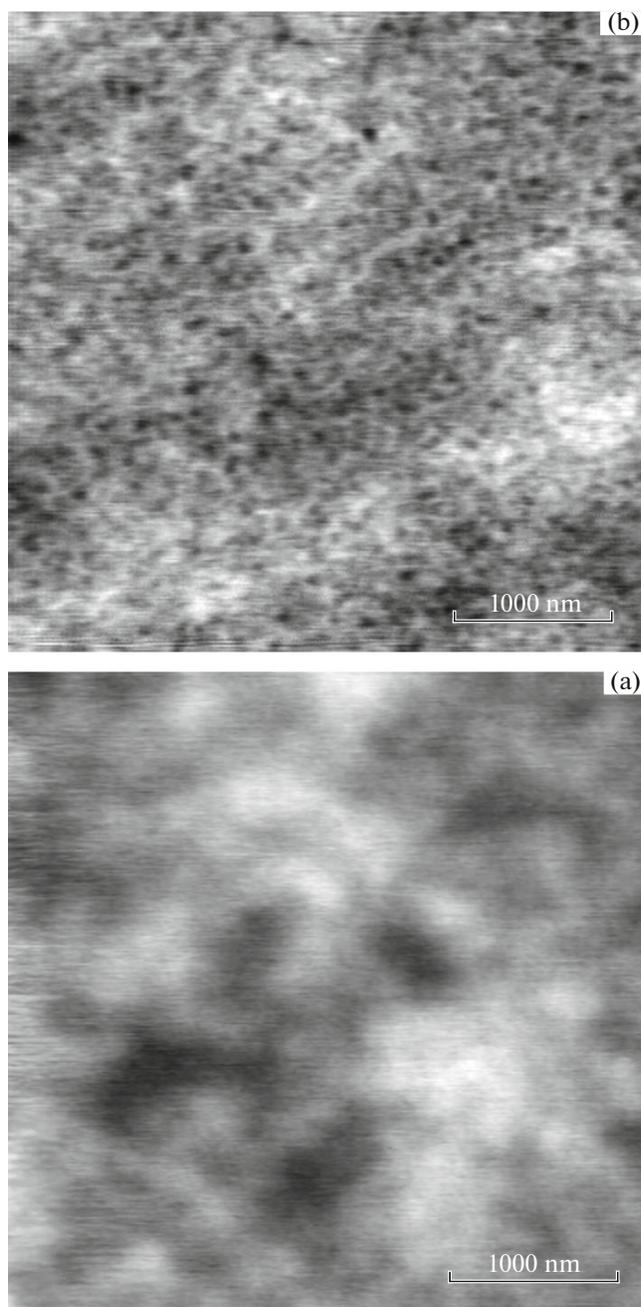


Fig. 2. AFM images of samples (a) II and (b) III.

films V and VI. The height and diameter of the globules of sample III were 0.8 ± 0.3 and 52 ± 13 nm, respectively (Fig. 2b). Film II was characterized by greater globular relief with a particle height of 3.0 ± 2.0 nm and particle diameter of 240 ± 85 nm (Fig. 2a). The size distributions of the globules for samples II and III are presented in Figs. 3 and 4. Regularly arranged pores with depths of 1.3 ± 0.4 nm and diameters of 55 ± 11 nm were observed on sample III. Such a structure formed by protrusions and hollows was

Basic characteristics of the studied copolymers

No.	CE	Catalyst	Solvent	LP : OBO : OSD : TDI : CE	T_g , °C	ϵ , %	σ , MPa
I	DS	Yes	BA	1.0 : 1.0 : 1.1 : 9.5 : 4.1	-33	110	0.88
II	DS	No	BA	1.0 : 1.0 : 1.1 : 9.5 : 4.1	-25	1190	4.10
III	BD	No	BA	1.0 : 1.0 : 1.1 : 9.5 : 4.1	-50	1060	21
IV	BD	Yes	CH	1.0 : 1.0 : 1.1 : 9.5 : 4.1	-51	540	17.5
V	DS	No	BA	3.1 : 0 : 0 : 9.5 : 4.1	-44	670	2.2
VI	BD	No	BA	3.1 : 0 : 0 : 9.5 : 4.1	-56	600	3.7

observed earlier for a series of polycyclic silicone membranes [10].

Studies of samples in contact-mode AFM revealed a structure similar to fibrils. These structures were, however, made of individual globules. The formation of pores and fibrils was probably an artifact effect that can be explained by microphase separation in the copolymer film when the formed domains have different chain flexibilities. As a result, the microscope's probe deforms the softer blocks more strongly, so fibrils and pores appear in the image.

CONCLUSIONS

It was shown in [11] that the structure of a polymer depends on the solvent in which the film is obtained.

In this work, we showed that the morphology of an object depends on the presence or absence of a catalyst. It was found via AFM that the surface of the copolymer **I** film grown using a catalyst was characterized by a high degree of roughness: the relief elements were as high as 2100 nm. The copolymers synthesized without a catalyst formed smooth films with mean-square roughnesses of around 2 and 1 nm for samples **II** and **III**, respectively.

The use of 1,4-butanediol as a chain extender was shown to enhance the mechanical properties of copolymers, compared to ones of analogous composition with disiloxane diol as the extender. This could also be due to the microphase separation typical of copolymers based on thermodynamically incompatible blocks.

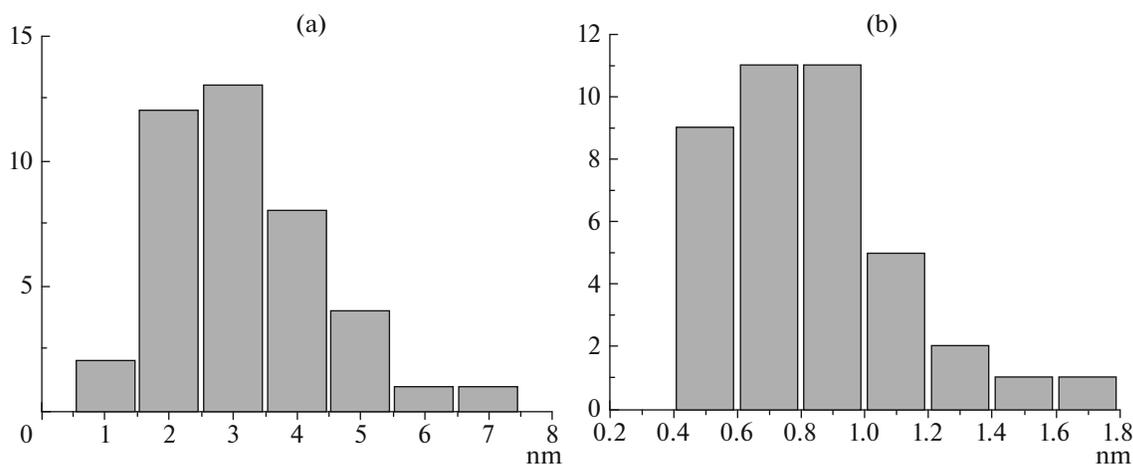


Fig. 3. Distribution of globule heights in samples (a) **II** and (b) **III**, according to the AFM data.

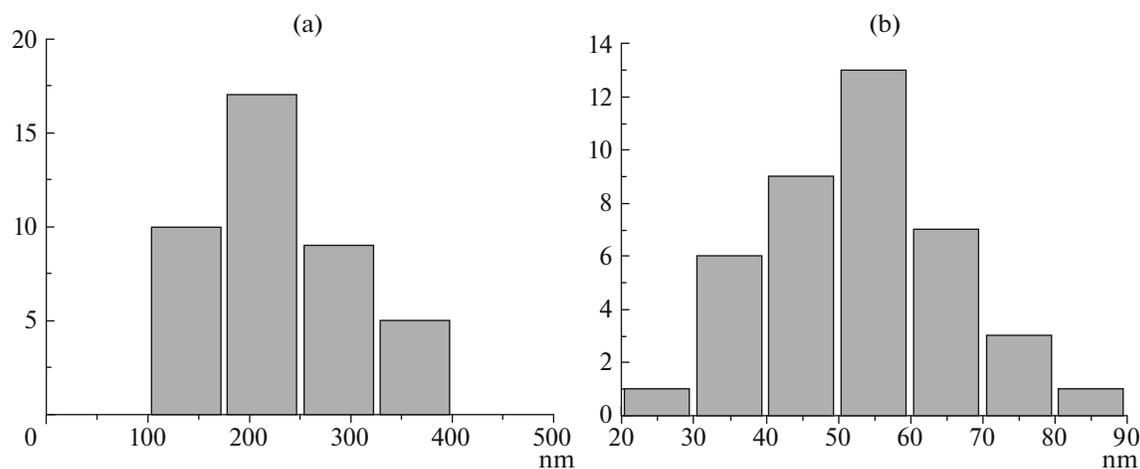


Fig. 4. Distribution of globule diameters in the samples (a) II and (b) III, according to the AFM data.

The results from this work show that the conditions of synthesis influence the morphology and mechanical properties of polymeric systems. The known data demonstrate the need for further studies of the morphology of new siloxane urethane copolymers.

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