# **Studying the Structure of Polysiloxane Carbonate Urethanes**

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**Abstract**—The structure of amorphous polysiloxane carbonate urethanes is studied by AFM, SEM, and TEM. It is found that the polymer structure depends on the nature of solvent used for film casting. **DOI:** 10.3103/S1062873814090329

# **INTRODUCTION**

It is known that the properties of polysiloxane organourethanes are determined by those of the blocks of which they are composed. Polysiloxane carbonate urethanes (PSCUs) in particular combine the useful properties of organosiloxanes (low free surface energy, low glass transition temperature, and high gas permeability) with the high mechanical strength of polycarbonates. The presence of urethane moieties in their chains increases their mechanical strength and contributes to additional structuring. Investigations of PSCU structure are therefore of great interest.

It follows from the literature that the morphology of polymers depends on both the conditions of their synthesis and the nature of the solvent used for film casting [1-4]. However, the authors of these works mentioned that ambiguous results were obtained in studying the structure of some polymer systems. It was shown in [2] in particular that the synthesis of amorphous polyarylates based on phenolphthalein in a polymer-dissolving medium results primarily in the formation of a fibrillar structure. Polymers with the same molecular weight, obtained by polycondensation in a medium unable to dissolve polymer, have a globular structure.

In [5], we studied the structure of crystallizing siloxane-urethane-ethylene oxide copolymers, depending on the length of their oligo(ethylene oxide) blocks and degrees of crystallinity. In this work, we study the structure of siloxane carbonate urethanes, depending on the nature of the solvent used for film casting.

X-ray diffraction showed that the obtained polymers were amorphous.

# **EXPERIMENTAL**

The studied samples were films prepared from solutions formed from two different solvents. Tetrahydrofuran (THF), a thermodynamically good solvent for the studied polymers, and chloroform, a semiselective solvent [6, 7], were used as solvents. The film thickness was 100  $\mu$ m.

The polymers studied in this work were obtained in two stages. In the first stage, a flask equipped with a magnetic stirrer and a reflux condenser was charged with solution of 4,4'-diphenyl methane diisocyanate (MDI) in chloroform under an argon atmosphere. Upon stirring, a chloroform solution of oligomeric organosilicon diol (OSD) with the formula  $HO(CH_2)_2OCH_2[Si(CH_3)_2O]_nSi(CH_3)_2CH_2O(CH_2)_2OH$ and tin diethyl dicaprylate (TDEDC) used as a catalyst was added. The reaction mixture was heated with stirring at 60°C for 2 h.

In the second stage, a solution of oligocarbonate (OLC) and triethylamine (TEA) (catalyst) in chloroform was added to the prepared adduct with stirring. The concentration of all the reagents was 0.2 mol/L. The reaction mass was heated under an argon atmosphere at a temperature of  $65^{\circ}$ C for 8 h. The completeness of the reaction was monitored via IR spectroscopy from the disappearance of the band of stretching vibrations of NCO groups at 2275 cm<sup>-1</sup>. The solution was filtered after warming, and the polymer was precipitated into hexane. A mixture of CHCl<sub>3</sub> and hexane was decanted, and the polymer was first dried in air and then under vacuum at  $T=40^{\circ}$ .

The resulting samples were studied by atomic force microscopy (AFM), scanning (SEM) and transmission (TEM) electron microscopy.

The surfaces of the samples were studied by atomic force microscopy in the semi-contact mode in air at room temperature. Scanning was done on a FemtoScan scanning probe microscope produced by the Center for Promising Technologies, Russia. Our cantilevers were manufactured by Mikromasch with an average resonance frequency of 325 kHz and a probe tip edge radius of ~10 nm. The obtained images were processed using the FemtoScan Online software.

The polymer surface was studied by SEM on a Tescan Mira LMU high-resolution scanning electron microscope (Czech Republic). The surface topogra-



Fig. 1. AFM image of PSCU film obtained from THF.

phy of the polymer fixed on current-conducting tape was studied under high vacuum using an Everhart— Thornley standard detector of secondary electrons. To prevent charging of the sample and to maintain the fine surface structure, an uncoated sample was studied in the low accelerating voltage mode and at low electron probe currents (1 kV and 20 picoampere, respectively).

The copolymers were studied by TEM on an EM-125 electron microscope (Sumy, Ukraine). The samples were prepared according to the standard procedure using an UZDN-2 ultrasonic disperser.

# **RESULTS AND DISCUSSION**

AFM microphotographs show that films cast from chloroform and THF had a globular structure (Fig. 1). Processing of the AFM images showed that samples prepared with THF had an average globule radius of 11.4 nm with an average height of 0.8 nm (Fig. 2a). The average globule radius for chloroform was 9.7 nm, and the average height was 0.9 nm (Fig. 2b). Globular particle agglomerates as large as 100–500 nm were also observed. The formation of agglomerates was probably due to the aggregation of copolymer molecules when casting films from solution in chloroform. Unlike chloroform, tetrahydrofuran, the oxygen atom of which takes an active part in the formation of agglomerates.



**Fig. 2**a, b. Globular particle size distribution for films obtained from (a) THF and (b) chloroform.

Investigations of the structure of PSCU films by SEM also revealed globular structures in preparing samples from solution in chloroform. However, the capabilities of SEM do not allow the observing of individual globules with radii of 9.7 nm and heights of 0.9 nm. Only spherical agglomerates with diameters of 50–700 nm can be observed in SEM (Fig. 3). Preliminary cleaving



Fig. 3. SEM image of PSCU film obtained from solution in chloroform.

in SEM and TEM electron microscopy allowed us to establish the existence of globular structures throughout a volume.

# CONCLUSIONS

Our results obtained by AFM, SEM, and TEM showed that films of amorphous PSCUs prepared from solutions in chloroform and THF have a globular structure. Fibrills were not observed for these polymer systems. It was shown earlier that crystallizing polymers have a fibrillar structure. According to the literature data and our results, nanospheres are structural elements of amorphous polymers, while nanofibrills are found in crystallizing polymers [8, 9]. Our experimental results are thus in agreement with the findings published in [1].

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