



SYNTHESIS OF POLYSILOXANE–(BUTYLENE OXIDE)–URETHANE–UREAS IN THE PRESENCE OF BISMUTH(III) NEODECANOATE

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Abstract

Polysiloxane–(butylene oxide)–urethane–ureas were synthesized in the presence of bismuth(III) neodecanoate. The resulting polymers were studied by differential scanning calorimetry (DSC), thermomechanical analysis (TMA), optical and atomic force microscopy (AFM); their deformation and strength characteristics were determined. It was found that the polymers obtained are characterized by two glass transition temperatures, indicating the formation of two phases.

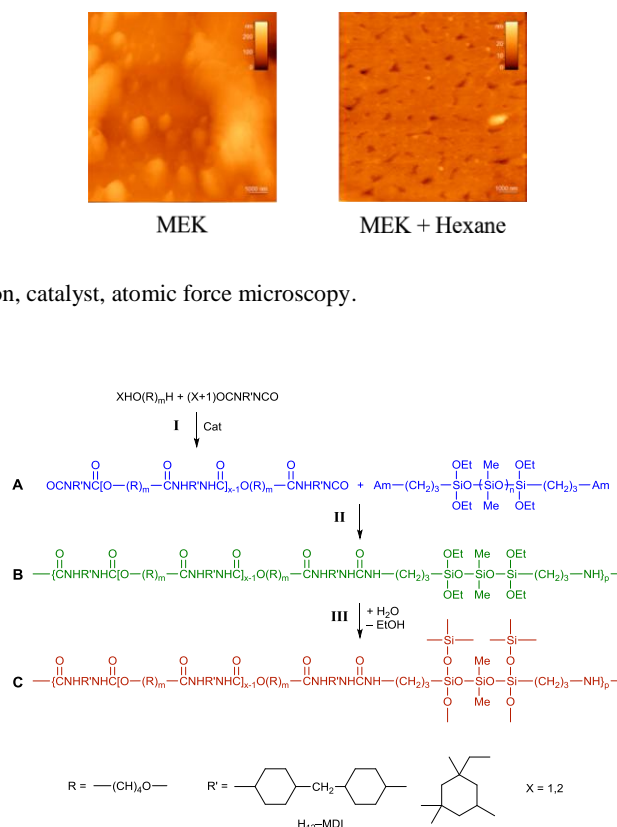
Key words: polysiloxanes, polyurethanes, microphase separation, catalyst, atomic force microscopy.

Introduction

Polysiloxane–urethanes (PSUs) are of great interest since they can combine the unique properties of polysiloxanes (low glass transition temperature, low surface energy, hydrophobicity, high gas permeability, biological inertness) and polyurethanes (high mechanical strength) [1, 2]. Toxic organotin catalysts are widely used in the synthesis of polyurethanes. Bismuth-based catalysts have lower toxicity and can also be used in the synthesis [1, 3, 4]. In this work, cross-linked polysiloxane–(butylene oxide)–urethane ureas (PSBOUUs) based on α,ω -bis[(3-aminopropyl)diethoxy]-oligodimethylsiloxanes (DASs) and oligobutylene oxides (OBOs), 4,4'-dicyclohexylmethane diisocyanate (H_{12} -MDI) or isophorone diisocyanate (IPDI) in the presence of bismuth(III) neodecanoate as a catalyst, as well as model polybutylene oxide–urethanes and polysiloxane–ureas were synthesized using the earlier published method [5], and their properties were studied.

Results and discussion

PSBOUUs were synthesized according to the general scheme (Scheme 1). At the first stage (I), prepolymer **A** was obtained from diisocyanate and oligobutylene oxide. The reaction course was monitored by back titration of free isocyanate groups and by IR spectroscopy (see Table S5 and Fig. S2 in the Electronic supplementary information (ESI)). The second stage (II) was carried out by combining solutions of the prepolymer and DAS, which resulted in the formation of soluble PSBOUUr **B**. At the third stage (III), the evaporation of the solvents resulted in the cleavage of hydrolytically unstable ethoxy groups, followed by the condensation of the resulting SiOH groups and the formation of cross-linked polymer **C**.



Scheme 1. Synthesis of polysiloxane–(butylene oxide)–urethane–ureas.

The resulting polymers were studied by DSC, TMA, AFM, and optical microscopy. The main properties of PSBOUUs, as well as those of the model polyurethanes and polysiloxane–ureas are given in Table 1 and Tables S3, S4 in the ESI.

As can be seen from Tables 1 and S4 in the ESI, the introduction of an organic block improves the mechanical properties and significantly increases a relative elongation at break of PSBOUUs compared to the model polysiloxane–ureas.

All PSBOUUs obtained had a high content of gel fraction, which characterizes the degree of completion of the cross-linking process. The content of the siloxane component in all samples was ~50%, but PSBOUUr 1 and PSBOUUr 2 had much higher tensile strength, which is probably due to the increased concentration of urethane units and hydrogen bonds in this case. A characteristic feature of PSUs is their tendency to microphase separation caused by the thermodynamic incompatibility of the components, which can be judged, in particular, by the difference in their solubility parameters (oligobutylene oxide:

Table 1. Effect of the synthesis conditions on the thermal and mechanical properties of the resulting polysiloxane–(butylene oxide)–urethane–ureas

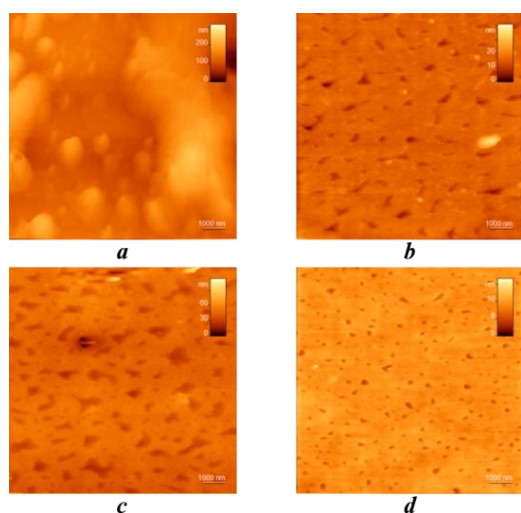
PSBOUUr	DAS, <i>n</i> / <i>Mn</i>	OBO, <i>m</i> / <i>Mn</i>	DI	<i>W</i> _{sil} , wt %	Solvent	Gel fraction, %	<i>T</i> _g	ϵ_p , %	σ_p , MPa
1^a	14/1380	3/250	H ₁₂ -MDI	47	MEK	78	–113/60	82	15
2^a	14/1380	3/250	H ₁₂ -MDI	47	MEK + hexane	79	–121/52 ^c	160	14
3^b	25/2230	18/1060	H ₁₂ -MDI	53	MEK + hexane	78	–18/–63	320	2
4^b	25/2230	18/1060	IPDI	52	MEK + hexane	88	–118/–76	230	1.5

^a X = 2; ^b X = 1; ^c the glass transition temperature was determined by TMA; *W*_{sil} is the total content of the siloxane, including terminal groups after the network formation.

$\delta = 19.2 \text{ (MPa)}^{0.5}$, oligodimethylsiloxane: $\delta = 14.6 \text{ (MPa)}^{0.5}$ [6]. For all the resulting PSBOUUs, two glass transition temperatures were observed, indicating the formation of two-phase systems. Some discrepancy between the values of *T*_g of PSBOUUs and model polymers is likely to be due to the effect of several factors, which include the phase mixing and presence of a chemical network.

From the results of AFM studies (Figs. 1 and S3 in the ESI), it is evident that PSBOUUr1 obtained from a solution in methyl ethyl ketone (MEK) exhibits a large relief and aggregates, the sizes of which can reach several microns or more.

Vshivkov *et al.* [7] found that polydimethylsiloxane forms associates in MEK. This can promote gelation in solutions and lead to the formation of heterogeneous samples. To prevent gelation, hexane, which is a good solvent for polydimethylsiloxane, was used in the synthesis [8]. The prepolymer was dissolved in MEK, and the oligodiamine was dissolved in hexane. In PSBOUUs solutions, the ratio of MEK to hexane was 1:1 (v/v). The addition of hexane afforded homogeneous films with microphase separation and led to an increase in the relative elongation at break.

**Figure 1.** AFM images of PSBOUUs: **1** (a), **2** (b), **3** (c), **4** (d).

Conclusions

Hence, polysiloxane–(butylene oxide)–urethane–ureas and model polybutylene oxide–urethanes were synthesized in the presence of Bi(III) neodecanoate used as a catalyst. It was shown that the introduction of the oligobutylene oxide block improves the mechanical characteristics compared to the model polysiloxane–urea with the same length of the siloxane moiety.

The resulting PSBOUUs were found to feature two glass transition temperatures, which indicates the formation of two phases. The effect of the solvent on the surface morphology was detected by AFM.

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Electronic supplementary information

Electronic supplementary information (ESI) available online: the experimental section, GPC data for the model polyurethanes, IR spectrum of the prepolymer, optical micrograph images. For ESI, see DOI: 10.32931/ioXXXXx.

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