



EFFECT OF A CATALYST ON THE SYNTHESIS AND PROPERTIES OF POLYSILOXANE–(PROPYLENE OXIDE)–URETHANE–UREAS BASED ON H₁₂-MDI

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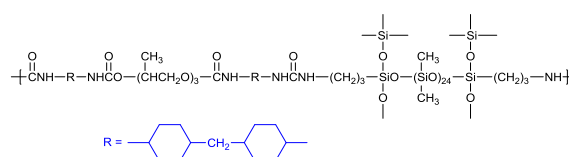
L. V. Filimonova,^a G. G. Nikiforova,^a I. O. Volkov,^a M. I. Buzin,^a
E. S. Afanasyev,^a K. L. Boldyrev,^a Z. S. Klemenkova,^a and E. A. Cherkas^b

^a Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
ul. Vavilova 28, str. 1, Moscow, 119334 Russia
^b MIREA—Russian Technological University,
pr. Vernadskogo 78, Moscow, 119454 Russia

Abstract

Network polysiloxane–(propylene oxide)–urethane–ureas based on α,ω -bis[(3-aminopropyl)diethoxy]oligodimethylsiloxanes, H₁₂-MDI and oligo(propylene oxide) were synthesized in the presence of three different catalysts: bismuth(III) neodecanoate, dibutyltin dilaurate, and diethyltin dicaprylate. The mechanical properties of the resulting polymers were studied. TMA investigations of the samples revealed the presence of two glass-transition temperatures which correspond to the glass-transition temperatures of the organic and siloxane phases.

Key words: polysiloxanes, polyurethanes, catalyst, microphase separation.



Introduction

Polysiloxane urethanes are the polymers that combine the unique properties of polysiloxanes (low glass-transition temperature, heat resistance, resistance to UV radiation and weather conditions, low surface energy, hydrophobicity, good dielectric properties, high gas permeability, biological inertness) and polyurethanes (high mechanical strength, high adhesive resistance, low cost) [1, 2].

The introduction of a urea moiety into polyurethane usually leads to improved mechanical properties, heat resistance, elasticity, tensile strength, resistance to abrasion, and flexural fatigue. Polyurethane–ureas are also distinguished by very low stress relaxation (low creep of the material) [3].

Organotin catalysts are widely used in the synthesis of polyurethanes; however, they have a negative impact on human health and the environment. According to recent studies, dibutyltin dilaurate (DBTL) has a negative effect on reproductive capacity and has mutagenic properties. Furthermore, DBTL is undesirable for use in antifouling coatings for ships due to its toxicity to marine organisms. Bismuth-based catalysts have lower toxicity and can, in many cases, replace organotin catalysts. Another important advantage of bismuth compounds over DBTL is a higher selectivity in the NCO/OH reaction compared to the NCO/H₂O reaction [4].

Results and discussion

In this work, using the previously described method [5], we synthesized cross-linked polysiloxane–(propylene oxide)–urethane–ureas (PSPOUUs) based on α,ω -bis[(3-aminopropyl)diethoxy]oligodimethylsiloxanes (DASs, $n = 24$, $M_n = 2100$ Da), oligo(propylene oxide) (OPO, $m = 3$, $M_n = 200$ Da), and 4,4'-dicyclohexylmethane diisocyanate (H₁₂-MDI) (see

Scheme S1 in the Electronic supplementary information (ESI)). The reaction was carried out in the presence of three different catalysts: diethyltin dicaprylate (DETDC), DBTL, and bismuth neodecanoate (Bi-ND). Chloroform was used as a solvent.

At the first stage (I), a prepolymer based on OPO and H₁₂-MDI was synthesized in the presence of one of three catalysts. The reaction course was monitored by IR spectroscopy (Fig. 1). The results obtained showed that all three spectra are virtually identical. In all three cases, the reaction was complete, as was evidenced by the appearance of a characteristic absorption band of the carbonyl group stretches (1699 cm^{-1}) and a band of the urethane group NH stretches (3329 cm^{-1}). The absence of a broad band in the region of $3100\text{--}3700\text{ cm}^{-1}$ indicated that all OH groups of the oligodiols also reacted.

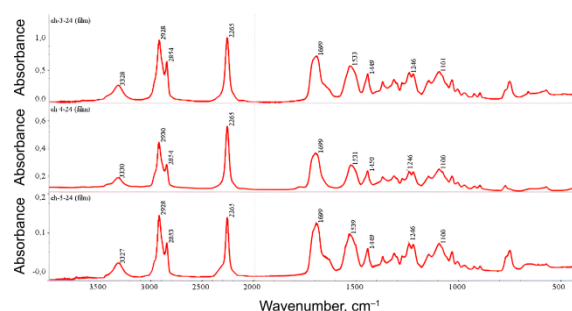


Figure 1. IR spectra of the prepolymers obtained in the presence of DBTL, Bi-ND, and DETDC (from top to bottom).

The second stage (II) of the synthesis was carried out at room temperature, mixing the solutions of the prepolymer and oligodiamine. The resulting mixtures were poured onto cellophane substrates.

The formation of a cross-linked polymer occurred upon evaporation of CHCl₃ (stage III) due to the condensation of OH groups, which were formed during the elimination of

Table 1. Main characteristics of polysiloxane (propylene oxide) urethane ureas.

PSPOUUr	Catalyst	Gel fraction, %	ε , %	σ , MPa	Gel fraction, % ^a	ε , % ^a	σ , MPa ^a	T_g , °C ^a
1	DBTL	90	58	10.0	93	34	11.0	-120/81
2	Bi-NDE	85	300	6.5	91	160	7.0	-116/59
3	DETC	90	53	10.5	92	44	10.0	-127/94

^a in 1 month of aging under normal conditions.

hydrolytically unstable OEt units, affording colorless transparent films (Table 1). The mass fraction of the siloxane component, including the terminal groups after the network formation, was 68 wt %.

It is known that all three catalysts promote both the urethane formation and cross-linking reaction, and in the second case, the catalyst activity decreases in the series DBTL > DETDC > Bi-ND [6].

To study the effect of the catalysts on this process, the model polysiloxane–ureas (PSUr, Scheme S2 in the ESI) were synthesized. The content of the siloxane component in all samples was 83 wt %.

The reaction of the oligodiamine with H₁₂-MDI does not require the addition of a catalyst and proceeds at room temperature. In this case, the catalysts can only affect the formation of a cross-linked polymer. The synthesis was carried out at room temperature by mixing the solutions of the diisocyanate and DAS. The solution was cast onto a cellophane substrate. The polymer was formed by evaporation of the solvent under the effect of atmospheric moisture. The model PSUr (Table 2) were also colorless and transparent.

Table 2. Main characteristics of the model polysiloxane–ureas

PSUr	Catalyst	Gel fraction, %	ε , %	σ , MPa
1	DBTL	91	45	3.5
2	Bi-NDE	88	120	3.0
3	DETC	91	31	3.8

Figure S1 in the ESI shows the stress–strain curves of the PSPOUUr explored. It is obvious that the use of different catalysts affects the stress–strain characteristics of the polymers (curves 1–3). It should be noted that the use of Bi-ND (sample PSPOUUr 2) leads to a decrease in the elastic modulus and tensile strength, as well as an increase in the relative elongation at break (Table 1, Fig. S1 in the ESI). Furthermore, in the case of PSPOUUr 2, the deformation of the material leads to its strengthening. The samples synthesized using DBTL and DETDC have similar stress–strain characteristics and the degree of cross-linking. Similar dependences were also observed for PSUr. PSUr 2 synthesized in the presence of Bi-ND showed a much higher relative elongation value and slightly lower gel fraction and tensile strength (Table 2). This is probably due to the lower efficiency of this catalyst in the network structure formation.

The comparison of Tables 1 and 2 shows that the introduction of PPO into the polymer chain enhances the tensile strength in PSPOUUr compared to the corresponding PSUr.

The definition of the stress–strain characteristics and gel fraction in 1 month showed that the cross-linking process continues in the films and leads to a decrease in the relative elongation and a slight increase in the gel fraction content and tensile strength.

For all three samples, two different glass-transition temperatures were observed, indicating the occurrence of microphase separation and the formation of mixed phases. The values of T_g were determined by the phase composition and, in general, depended on the sample preparation conditions.

In the presence of three different catalysts, the rates of sample formation differed, which can lead to the formation of different structures (Fig. S3 in the ESI) [2].

Conclusions

Hence, the polysiloxane–(propylene oxide)–urethane–ureas and model polysiloxane–ureas featuring a high content of the siloxane component (68 and 83 wt %, respectively) were synthesized in the presence of three different catalysts (DBTL, Bi-ND, and DETDC); their mechanical and thermal characteristics were determined.

The TMA studies of PSPOUUr revealed the presence of two glass-transition temperatures which correspond to the glass-transition temperatures of the organic and siloxane phases.

It was shown that the polymers obtained in the presence of different catalysts differ in the mechanical and thermal characteristics.

The investigations on the application of alternative catalysts in the synthesis of polysiloxane–urethanes are of particular interest for further development.

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Corresponding author

* E-mail: lufilia@inbox.ru (L. V. Filimonova).

Electronic supplementary information

Electronic supplementary information (ESI) available online: the stress–strain curves, AFM and optical micrographs, experimental section. For ESI, see DOI: 10.32931/ioXXXXx.

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