



EFFECT OF GEOMETRIC ISOMERISM OF H₁₂-MDI ON THE PROPERTIES OF POLYSILOXANE–URETHANE–UREAS BASED ON IT

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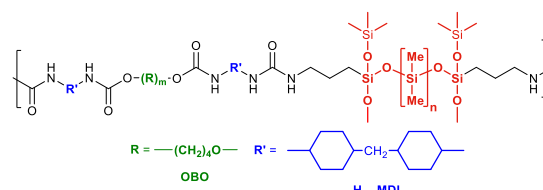
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Abstract

New polysiloxane–butylene oxide–urethane–ureas based on α,ω -bis[(3-aminopropyl)diethoxy]oligodimethylsiloxane, oligobutylene oxide, and fractions of dicyclohexylmethane 4,4'-diisocyanate (H₁₂-MDI) with different contents of a trans-trans isomer have been synthesized. The mechanical properties of the films have been tested. It is established that the strength and relative elongation at break increase with the increasing content of the trans-trans isomer.

Key words: polysiloxane–urethanes, dicyclohexylmethane 4,4'-diisocyanate, geometric isomers, mechanical properties.



Introduction

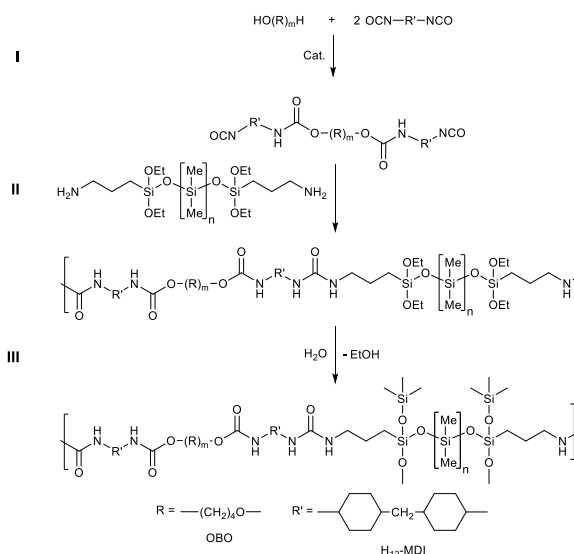
Polysiloxane–urethanes (PSUs) are unique polymers that are used in many fields and combine the properties of polysiloxanes (low glass transition temperature and surface energy, hydrophobicity, bioinertness, high gas permeability and thromboresistance) and polyurethanes (mechanical strength, abrasion resistance). A unique feature of polysiloxane–urethanes, unlike other siloxane-containing block copolymers, is the combination of high resistance to dynamic loads with good tear strength [1]. The diurethane moieties included in the PSU, owing to strong hydrogen bonds, form a rigid domain, which enhances the phase separation and thereby directly affects the mechanical properties of the resulting polymers.

In this work, H₁₂-MDI was used in the synthesis of polysiloxane–urethane–ureas. Commercial H₁₂-MDI is a liquid at room temperature and consists of a mixture of cis-cis, trans-trans, and cis-trans isomers. It is known that an increase in the content of the trans-trans isomer in polyurethanes can lead to a number of valuable properties. Saralegi *et al.* [2] showed that an increase in the content of trans-trans H₁₂-MDI leads to better phase separation owing to hydrogen bonds between the rigid segments, which, in some cases, improved the mechanical characteristics of polyurethanes. Adhikari *et al.* [3] synthesized and studied linear polysiloxane–urethanes based on α,ω -bis[(hydroxy)ethoxypropyl]polydimethylsiloxane, polyhexamethylene oxide as a soft block, and 1,4-butanediol and H₁₂-MDI with the trans-trans isomer content of 13–95% as a rigid block. The goal of this study was to obtain polysiloxane–butylene oxide–urethane–ureas based on α,ω -bis[(3-aminopropyl)diethoxy]oligodimethylsiloxane [4, 5], oligobutylene oxide, and H₁₂-MDI with different trans-trans isomer contents, as well as to study their properties depending on the composition.

Results and discussion

A peculiarity of trans-trans H₁₂-MDI is its low fusibility (~85 °C), which made it possible to isolate its enriched crystalline fraction from a mixture of the geometric isomers. The fractional crystallization afforded the fractions containing 45, 54, 62, 86, and 98% of the trans-trans isomer. The composition of the fractions was determined based on the ¹³C NMR spectra from the ratio of the integral intensities of the carbon resonances corresponding to the isocyanate group of the trans-trans isomer (122.5 ppm) and other isomers (122.4 ppm) [2].

The target polysiloxane–butylene oxide–urethane–ureas were synthesized according to Scheme 1.



Scheme 1. Synthesis of the polysiloxane–butylene oxide–urethane–ureas.

At stage I, the prepolymers based on H₁₂-MDI with different contents of the trans-trans isomer and oligobutylene oxide ($M_n = 250$ g/mol) were obtained. The synthesis was carried out in CHCl₃ using tin diethyl dicaprylate as the catalyst upon stirring at 60–61 °C for 2 h under an argon atmosphere. The reaction completion was confirmed by IR spectroscopy [6, 7].

At stage II, the prepolymer solution was mixed with a solution of α,ω -bis[(3-aminopropyl)diethoxy]oligodimethylsiloxane ($M_n = 1890$ g/mol) in CHCl₃. The concentration of the resulting polymer in the solution was 10 g/100 mL.

The films were obtained by casting from the solution onto a cellophane substrate. Under the effect of atmospheric moisture, the Si–O–C bonds were cleaved, followed by the condensation of the resulting Si–OH groups and the formation of the cross-linked polysiloxane–butylene oxide–urethane–ureas (stage III). The samples were dried at room temperature to constant mass. The content of the siloxane component was 65 wt %. The main characteristics of the resulting polymers are given in Table 1.

Table 1. Main characteristics of the polysiloxane–urethane–ureas obtained

Sample	$C_{\text{trans-trans}}$, %	GF, %	ε , %	σ , MPa
1	45	94	50	11
2	54	95	60	12
3	62	95	65	13
4	86	95	77	14
5	98	96	80	15

The polymers obtained were studied by reflected light optical microscopy. The micrographs show disordered rod-shaped structures (Fig. 1a), with the exception of sample 5 (Fig. 1b). The latter may be caused by the high rate of gelation and, as a consequence, non-equilibrium conditions of film formation in this case.

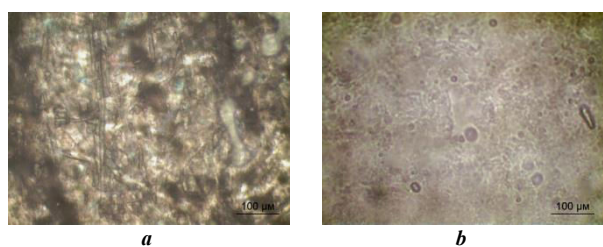


Figure 1. Optical micrographs of samples 3 (a) and 5 (b).

The dependence of the mechanical properties on the content of the trans-trans isomer is depicted in Fig. 2. It is obvious that the strength and relative elongation at break increase with the increasing content of the trans-trans isomer.

Conclusions

Thus, the polysiloxane–urethane–ureas based on α,ω -bis[(3-aminopropyl)diethoxy]oligodimethylsiloxane, oligobutylene oxide, and H₁₂-MDI with different contents of the trans-trans isomer were synthesized. The improvement of the mechanical properties with the increasing trans-trans isomer content was established.

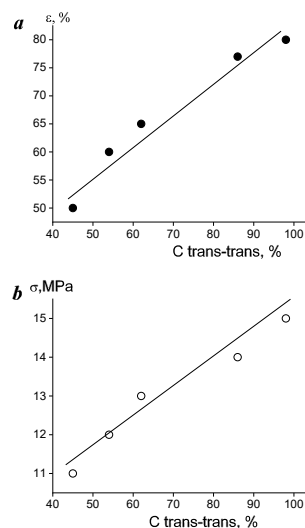


Figure 2. Dependence of the relative elongation at break (a) and tensile strength (b) on the content of the trans-trans isomer.

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References

- L. I. Makarova, G. G. Nikiforova, L. V. Filimonova, M. I. Buzin, V. G. Vasil'ev, E. S. Afanas'ev, M. N. Il'ina, O. V. Sinit'sina, E. G. Kononova, I. O. Volkov, N. N. Samsonova, S. P. Novikova, V. S. Papkov, *Polym. Sci., Ser. B*, **2019**, *61*, 20–27. DOI: 10.1134/S156009041901007X
- A. Saralegi, A. Etxeberria, B. Fernández-d'Arlas, I. Mondragon, A. Eceiza, M. A. Corcuera, *Polym. Bull.*, **2013**, *70*, 2193–2210. DOI: 10.1007/s00289-013-0930-3
- R. Adhikari, P. A. Gunatillake, G. F. Meijs, S. J. McCarthy, *J. Appl. Polym. Sci.*, **1999**, *73*, 573–582. DOI: 10.1002/(SICI)1097-4628(19990725)73:4<573::AID-APP13>3.0.CO;2-N
- A. Kalinina, N. Strizhiver, N. Vasilenko, N. Perov, N. Demchenko, A. Muzafarov, *Silicon*, **2015**, *7*, 95–106. DOI: 10.1007/s12633-014-9233-z
- I. B. Meshkov, A. A. Kalinina, V. V. Gorodov, A. V. Bakirov, S. V. Krashennnikov, S. N. Chvalun, A. M. Muzafarov, *Polymers*, **2021**, *13*, 2848. DOI: 10.3390/polym13172848
- M. F. Sonnenschein, *Polyurethanes*. Science, Technology, Markets, and Trends, Wiley, Hoboken, **2015**. DOI: 10.1002/9781118901274
- A. J. Gordon, R. A. Ford, *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*, Wiley, New York, **1972**.

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