

Framed Aromatic Polyurethanes Based on an Anionic Macroinitiator, 4,4'-Diphenylmethane Diisocyanate, and 4,4'-Dihydroxy-2,2-diphenylpropane: Synthesis and Characterization

I. M. Davletbaeva^{a,b,*}, I. I. Zaripov^a, R. R. Karimullin^a, A. M. Gumerov^a,
R. S. Davletbaev^c, R. R. Sharifullin^d, and V. V. Parfenov^b

^a Kazan National Research Technological University, ul. Karla Marksa 68, Kazan, 420015 Russia

^b Kazan (Volga Region) Federal University, Kremlevskaya ul. 18, Kazan, 420008 Russia

^c Tupolev Kazan National Research Technical University, ul. Karla Marksa 10, Kazan, 420111 Russia

^d Laboratory of Scientific and Research Center, OAO Nizhnekamskneftekhim, Industrial zone, Nizhnekamsk, Russia

*e-mail: davletbaeva09@mail.ru

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Abstract—Polyurethanes composed of aromatic components are synthesized using the catalytic effect of potassium alcoholates on the reaction of urethane formation occurring with participation of 4,4'-dihydroxy-2,2-diphenylpropane, 4,4'-diphenylmethane diisocyanate, and polyisocyanate, which is a mixture of 4,4'-diphenylmethane diisocyanate and its branched derivatives. In the case of 4,4'-diphenylmethane diisocyanate, segmented polyurethanes with the predetermined length of the rigid block are formed, while the use of polyisocyanate gives rise to framed aromatic polyurethanes. The use of macroinitiators as carriers of potassium alcoholate groups does not cause microphase separation of flexible and rigid segments.

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Polyurethanes are known to be polymers suitable for producing materials with a wide range of performance features. Variation in the chemical nature of initial components makes it possible to obtain both impact-resistant plastics and elastomers [1–4]. Polyurethanes composed of extended flexible and aromatic rigid blocks are referred to as segmented [5–17]. In this case, the basis for controlling properties of polyurethanes is provided by their supramolecular structure specified by the microphase separation of rigid and flexible blocks.

It is important to create rigid blocks composed of aromatic units solely in urethane elastomers. Such aromatic polyurethanes possess high strength and good adhesion characteristics and resistance against acidic, alkaline, and hydrocarbon media. 4,4'-Dihydroxy-2,2-diphenylpropane is the most accessible compound for the synthesis of these polymers. In accordance with [18, 19], the reactions of 4,4'-dihydroxy-2,2-diphenylpropane with aromatic and aliphatic isocyanates proceed at low rates but may be accelerated using organotin compounds. However, their catalytic activity is not so high; therefore, the synthesis of extended rigid segments and continuous framed polyurethane structures of aromatic nature presents a challenge.

In [20], polyurethanes were synthesized using anionic macroinitiators, 4,4'-dihydroxy-2,2-diphenylpropane (BPA) and 4,4'-diphenylmethane diisocyanate (MDI). It

was shown that potassium alcoholates that replace a part of hydroxyl groups in macroinitiators exert a marked catalytic effect on the interaction of hydroxyl groups of BPA with the isocyanate groups of MDI. This interaction is accompanied by the formation of segmented polyurethanes with the desired length of aromatic blocks. Their regular structure, which is predetermined by the chemical structure of MDI and BPA, and a high fraction of urethane groups in the rigid segment create favorable conditions for effective intermacromolecular interactions.

In [21–24], macroinitiators were used to initiate the polyaddition of aromatic isocyanates via the anionic mechanism.

Because an increase in the length of the aromatic polyurethane block under the absence of chemical crosslinks is accompanied by growth of plastic deformation of polymers and reduction in their heat resistance, there was need to employ polyfunctional aromatic isocyanates (PICs). When the molar excess of PIC and BPA is high, conditions are created for formation of a continuous lattice structure involving aromatic compounds. The goals of this study are the synthesis and characterization of polyurethanes prepared using macroinitiators, polyfunctional aromatic isocyanates, and 4,4'-dihydroxy-2,2-diphenylpropane.