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FUNCTIONAL POLYMERS

Synthesis of Block Copolymers Based on a Macroinitiator and 2,4-Toluene Diisocyanate

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Abstract—The effect of the reaction medium and synthesis temperature on the polyaddition of 2,4-toluene diisocyanate to a macroinitiator representing a potassium-substituted block copolymer of propylene and ethylene oxides is revealed. Factors affecting the polyaddition accompanied by the opening of isocyanate groups via the carbonyl component are the use of catalytic amounts of acidic compounds, water in combination with trimethylamine, and maintenance of fairly low temperatures. The dielectric properties and static electrical conductivity of polymers obtained under different reaction conditions are studied. It is shown that the preferential formation of polyisocyanates of the acetal nature and, thus, block copolymers with their participation can be responsible for change in the electrophysical properties of the polymers.

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INTRODUCTION

Isocyanates are used in the production of a wide variety of polyurethane materials, polyurea, polyisocyanurates, and polyisocyanates [1–5]. A wide range of polymers obtained from isocyanates cannot reflect to a full extent the potential of chemical transformations related to their structural features. Formation of the final products based on isocyanates is determined by the way of monomer activation. According to the published data, at high constants of initiation and chain propagation reactions, the opening of NCO groups via the N=C bond mostly leads to formation of polyisocyanates of the amide nature [6–10]. The unusual opening of the isocyanate groups via the carbonyl component accompanied by the formation of polyisocyanates of the acetal nature (*O*-polyisocyanates), which was observed by a number of researchers, has been poorly studied. However, this effect is of true interest. For example, the isocyanate homopolymer having only the polyacetal structure of chains has not been synthesized so far. Therefore, the research of reactions leading to the formation of *O*-polyisocyanates is the mainstream in this field. A planar spatial configuration of *O*-polyisocyanate segments is an important element in designing supramolecular structures of block copolymers with their participation.

Mesoporous polymers based on anionic macroinitiators and 2,4-toluene diisocyanate, in which the opening of isocyanate groups of 2,4-toluene diisocyanate occurred via the carbonyl component, were synthesized in [11–15]. The synthesis of mesoporous polymers is based on the chemical transformations of 2,4-toluene diisocyanate initiated by macroinitiators [16, 17]. Thus, the aim of the present work is to investigate the effect of solvent nature, co-catalysts, and synthesis temperature on the polyaddition of 2,4-toluene diisocyanate and to study the properties of the resulting polymers.

EXPERIMENTAL

In the present work, macroinitiators were the block copolymer of propylene oxide with ethylene oxide with molecular mass M = 4200 (PPEG) of formula $HO[CH_2CH_2O]_n[CH_2(CH_3)CH_2O]_m[CH_2CH_2O]_nK$ ($n \sim 14$ and $m \sim 48$) containing 10.9% potassium-alcoholate groups of the total content of functional groups (Nizhnekamskneftekhim); 2,4-toluene diisocyanate (TDI) was used as a monomer; and cocatalysts were 4,4'-dihydroxy-2,2-diphenylpro-