MOLECULAR DYNAMICS
IN PBA/PEO MIKTOARM STAR COPOLYMERS

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Molecular dynamics in PBA/PEO miktoarm star copolymers was investigated by means of Broadband Dielectric Spectroscopy (BDS) and Nuclear Magnetic Resonance (NMR) methods. The spectroscopic studies were performed for three types of copolymers which differ in the composition, namely materials containing 76%, 46% and 16% fraction of PEO arms. The materials were obtained by Gao et al. [1] by ATRP polymerization method, and have the structural characteristics, that was determined based on our previous studies [2,3].

The observation of molecular motions in the studied materials covered broad range of temperatures (from 125 K to 400 K) and of frequencies (from 1 Hz to 10 GHz). In the low temperature/high frequency regime the used spectroscopic techniques are sensitive to the different local molecular motions in PBA/PEO miktoarm star copolymers, described by the Arrhenius relation, namely: anisotropic rotation of methyl groups (revealing in the NMR data) and local motions within the PEO chain (disclosed from the BDS data). A single glass transition was observed despite the fact that PEO and PBA are known as non-miscible components. This behavior may result either from similar values of glass transition temperatures of the PBA and the PEO polymers or from partial miscibility of these polymers within the amorphous phase, which is a consequence of the unique molecular structure of the studied star copolymers.
The time-temperature superposition principle, known from mechanical and dielectric relaxation studies, was applied to obtain a NMR susceptibility master curve (Fig.1) describing the molecular mobility over a wider range of frequency (or time) compared to the range directly accessible in a single FFC NMR experiment \[4,5\]. The analysis of the NMR data included both the frequency dependence of magnetic susceptibility as well as the temperature dependence of spin-lattice relaxation times (Fig.2) determined for miktoarm star PBA/PEO copolymers. The combination of the data obtained using both NMR and BDS methods made it possible to quantitatively analyze the segmental motions of polymeric chains, associated with glass transition of the materials under study, in the broad frequency range (Fig.3). The analysis of the segmental dynamics using the VFT equation indicated that the increase in PBA content results in the increase in fragility of miktoarm star PBA/PEO copolymer.

The dielectric studies revealed also the occurrence of ionic conduction, taking place above glass transition temperature in the studied miktoarm star copolymers, being accompanied by the Maxwell-Wagner-Sillars (MWS) process (associated with the ionic conduction, which is restricted due to the structural heterogeneity of these systems).

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**Literature**