Characterization of Topological Structure and Self-Diffusion of Elastomers by NMR Method

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For carrying out operated synthesis and application of elastomers (El) and composites on their basis, data on their structure, molecular mobility and diffusion are necessary. The data are defined by different methods NMR. The success in quantitative definition of these characteristics in many respects depends on the accuracy of a choice of a technique of NMR and well developed theory, allowing to connect structural and dynamic parameters with observed signals of NMR [1-4].

Topological structure of ready El characterizes functionality, connectivity and concentration of chemical or physical knots, function of the molecular-weight distribution (MWD). In this work the theory of free induction decay (FID) in linear, cross-linked and branched flexible polymers with a various average length of a polymeric chain in a wide temperature is represented. The theory is based on the concept of residual dipole - dipole interactions (DDI) connected with anisotropy of internodes chains, a polymer chain consists of N statistically independent segments, and the motion of the polymer chain in a wide temperature range at $T > T_g$ is envisioned as consisting of several types of motion on disparate time scales. In the low-temperature range, only small-scale molecular motion inside segments is manifested. In the middle-temperature range, large-scale (segmental) motion is manifested. The high-temperature range is characterized by the motion of the chain as a whole associated with all possible conformational positions of the chain segments.

The general approach to calculation of signals of diffusion attenuation spin echo and its application to determination of coefficient of self-diffusion in elastomers with various topological structures is offered. It allowed to explaining observed experimentally anomalous diffusion. The theory of stimulated echoes for sequence of three RF pulses is represented. The methods of determination of correlation function of molecular mobility of polymer chains from NMR experiments directly (FID and stimulated echo) are developed on the base of the theory.

The theory and comparison with the experiments, show the influence of average molecular weight on topological structure and self-diffusion in elastomers. Emergence of pronounced breaks in high-temperature area on the dependence of time spin-spin relaxation on the average chain length is explained by change of topological structure of linear polymers at average molecular weight $M_w > 10^5$. The same structural changes influence on the dependence of self-diffusion coefficient on M_w. The theory of NMR relaxation spectra of El is offered to analyze the molecular mobility and topology of linear, cross-linked and branched El.

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