

Diffusion coefficient of macroradicals in polymer matrix

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Evaluation of macromolecules diffusion coefficients in polymer matrix is of a great scientific and practical interest, however, it is sufficiently complicated experimental task since many properties (in particular, the elastic ones) of polymer matrices are affected by the macromolecules conformation thermodynamics that determines their equilibrium elastic characteristics as well as by macromolecules conformation ability to react quickly or slowly upon external disturbances, that is by kinetic factors. Dynamics of macromolecules deformation and their transmission mobility are based on the general reptilian mechanism which is realized by segmental mobility of polymer chain links.

In the presented work diffusion coefficient of macroradicals in 1,6-hexanediolbiacrylate matrix was numerically evaluated by ESR-spectroscopic method of the analysis of macroradicals decay kinetics within the temperature interval of $45 \div 80^\circ\text{C}$. It was found that kinetics of macroradicals decay can not be described in the second order reaction coordinates, what is typical for quadratic chain termination. Kinetic equation, which satisfactorily describes experimental data, was obtained. On the assumption that it is connected with macroradicals propagation till their meeting and decay the kinetic equation, which satisfactorily describes experimental data, was obtained. This equation allows to obtain the numerical values of the quadratic chain termination rate constant. Using these values as well as the Smolukhovsky equation the numerical values of the macroradicals diffusion coefficients were obtained in the given temperature interval $D = (2.7 \div 31) \cdot 10^{-19} \text{m}^2/\text{s}$, the characteristic times of the polymer chain links segmental motion $\tau = (10 \div 1) \cdot 10^{-5} \text{s}$, their activation energy ($E = 76.3 \text{kJ/mol}$) and entropy ($\Delta S/R = 8.3$) were estimated. Hence, high values of τ (by 4 - 5 order more than in solutions) determine low values of the macromolecules diffusion coefficients in polymer matrices and, respectively, considerable effect of kinetic factors on their properties.