CONCENTRATION DEPENDENCE OF THE COEFFICIENT OF SELF-DIFFUSION OF MACROMOLECULES IN POLYMER SOLUTIONS*

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The NMR method with the pulse gradient of the magnetic field has been used to study the self-diffusion of macromolecules of PEO ($M_n = 2 \times 10^3$–3×10^6) and PS ($M_n = 2 \cdot 4 \times 10^5$; $1 \cdot 3 \times 10^6$) in different solvents over a wide range of change in concentration. The concentration dependence of the self-diffusion coefficients of the macromolecules after allowing for their local dynamic properties may be described by a universal function invariant to the MM of the polymer and the quality of the solvent. Theoretical discussion of the results is based on the concept of dynamic scaling.

Self-diffusion of macromolecules in solutions has recently been closely studied both experimentally [1–5] and theoretically [6, 7]. Thus, a number of authors [4, 8–10] have obtained the concentration dependences of the self-diffusion coefficients D. However, in most cases the concentration of the polymer changed within narrow limits which did not give the full picture of the change in D in solution. Theoretical investigations based on the concepts of reptations and dynamic scaling [6, 7, 11] also still do not give sufficient clarity in the description of the concentration dependences of D.

The aim of the present work is to make an experimental study of the concentration dependences of D over a wide concentration range and generalize and attempt a theoretical explanation of the patterns obtained.

The self-diffusion coefficients were measured by the NMR method with the pulse gradient of the magnetic field using the stimulated echo technique [12] with an apparatus with a proton resonance frequency 60 MHz and a maximum value of the gradient g of the magnetic field 50 Tl/m [13]. The self-diffusion coefficients were determined from the dependence of the amplitude of the spin-echo signal A on the square of the value g. The absence of an influence on $A(g^2)$ of the non-exponentiality of nuclear relaxation was checked by special pulse techniques [14].

The test objects were the systems PEO–dioxane, PEO–benzene, PEO–chloroform, PS–benzene and PS–CCl$_4$. All the solvents were of grade chemically pure. The MWDs of the polymers studied were: PEO – $M_n = 2 \times 10^3$, 2×10^4 and 4×10^4 at $M_w/M_n \lesssim 1 \cdot 1$ and $M_n = 3 \times 10^6$ for $M_w/M_n \sim 2$; PS – $M_n = 2 \cdot 4 \times 10^5$ and $1 \cdot 3 \times 10^6$ for $M_w/M_n \lesssim 1 \cdot 2$. The concentration of the polymer in solutions was fixed in volumetric fractions φ and for the solutions of PEO $2 \times 10^3 \lesssim \varphi \leqslant 1$ and for PS $2 \times 10^{-3} \lesssim \varphi \lesssim 4 \times 10^{-1}$. The measurements were made at 343 and 313 K for the PEO and PS solutions respectively.

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