

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 ($M_n=2.4 \times 10^5$; 1.3×10^6) 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 T/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–CCl₄. 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 $M_w/M_n \lesssim 1.1$ and $M_n=3 \times 10^6$ for $M_w/M_n \sim 2$; PS – $M_n=2.4 \times 10^5$ and 1.3×10^6 for $M_w/M_n \lesssim 1.2$. The concentration of the polymer in solutions was fixed in volumetric fractions ϕ and for the solutions of PEO $2 \times 10^{-3} \lesssim \phi \lesssim 1$ and for PS $2 \times 10^{-3} \lesssim \phi \lesssim 4 \times 10^{-1}$. The measurements were made at 343 and 313 K for the PEO and PS solutions respectively.

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