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Visco-Elastic Dependences

Generalized Concentration Dependence of Makromolecule Selfdiffusion Coefficients in Polyethyleneoxide Solutions

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Summary

The polyethyleneoxide (PEO) macromolecule translational mobility in dioxane and benzene solutions was studied by pulsed field gradient nmr. The generalized dependence describing the macromolecule translational mobility in solutions - invariant with respect to the polymer molecular mass, solvent, as well as to temperature - was obtained.

Introduction

The universal functions describing relaxational and viscoelastic dependences (1,2) are widely used in the study of polymer viscoelasticity. These functions occurred to be useful in theory development, as well as in experimental data systematization and in predicting system properties. The aim of the present work is to obtain the generalized function describing the macromolecule translational mobility of PEO with different molecular masses in different solvents and at different temperatures.

Results and Discussion

Samples were prepared by using PEO with $M_n = 2\cdot10^3$, $M_n = 2\cdot10^4$, $M_n = 4\cdot10^4$, $M_w/M_n = 1.1 \div 1.2$, and with $M_w = 3\cdot10^6$, solvents were dioxane and benzene. The self-diffusion coefficients and the PEO transverse relaxation times T_2 in solution (0.5 - 100%) have been measured with a home-built apparatus using a pulse magnetic gradient (3). The proton resonance frequency was 60 Mc, the greatest pulsed gradient value at 5 KG/sm (4). The measurements were carried out at 60°C and 90°C. The self-diffusion coefficients were obtained from spin echo dependences on the squared pulsed gradient value. Diffusive decay of the samples (except the polymer solutions with $M_n = 2\cdot10^3$) was nonexponential, the decay shape being dependent on the diffusion time t_d. The average self-diffusion coefficients D obtained from the diffusion decay initial slope were used for plotting the concentration dependences (5).

The results of the measurements are presented in Fig.1. The dependences of D on concentration are seen to be described by smooth similar curves for all molecular masses in both solvents and for both temperatures. Consequently, in accordance with scaling concepts (6) we may expect the following relation for these curves: $D(c)/D_0 = f(c/c_n)$

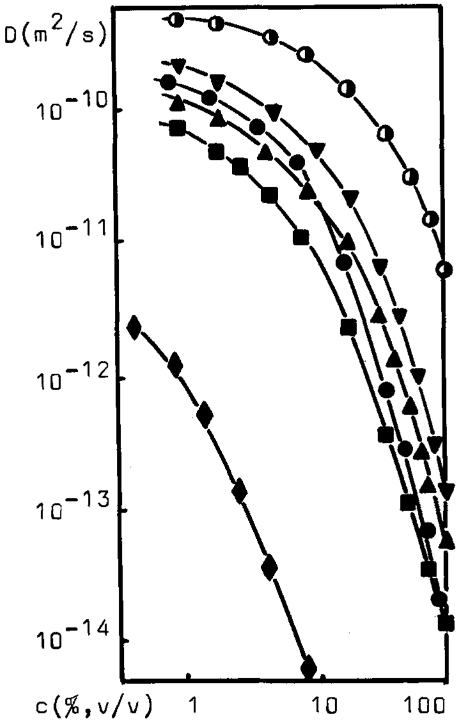

Fig.1. Concentration dependences of self-diffusion coefficients of PEO macromolecules in dioxane $M_n = 2\cdot10^3$ (◐), $M_n = 2\cdot10^4$ (▲), $M_n = 4\cdot10^4$ (■), $M_n = 3\cdot10^6$ (♦); in benzene $M_n = 4\cdot10^4$ at 60°C (●), in dioxane $M_n = 2\cdot10^4$ at 90°C (▼).

where $D_o = \lim_{c\to o} D(c)$ and $f(c/c_n)$ is a universal function with the normalizing concentration c_n. However, we failed to obtain a single function $f(c/c_n)$ for the whole concentration range for any choice of values of c_n. At high concentrations, it occurred that $f(c/c_n) \sim (c/c_n)^{-4}$, which may hardly be explained in the light of modern theories (4). We explain this by the fact that a change of local chain mobility with concentration is not taken into account in the given formula.

In (7) the transverse relaxation time T_2 in PEO with M_n $3\cdot10^3$ was noted to characterize the polymer chain short-range or local motion. In Fig.2 the dependences of T_2 are given for PEO with $M_n = 2\cdot10^3$. With increasing polymer concentration, the time T_2 decreases and the changes are most notable at high c . For the system PEO-benzene, more strong dependence of $T_2(c)$ is observed in comparizon with the system PEO-dioxane, which correlates with corresponding dependences D(c). This indicates a relation between macromolecule translational mobility and its local mobility. Taking into account the change of polymer chain local mobility due to the change of concentration:

$$D(c)/D_o \cdot T_{2o}/T_2(c) = f(c/c_n)$$

where $T_2(c)$ are taken from corresponding dependences (Fig.2), and $T_{2o} = \lim_{c\to o} T_2(c)$. Experimental data given in the coordinate

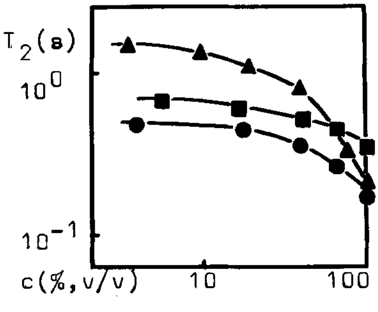

Fig.2. Concentration dependence of the transverse relaxation time T_2 of PEO macromolecules ($M_n = 2\cdot10^3$) in dioxane at 60°C (●), at 90°C (■), in benzene at 60°C (▲).

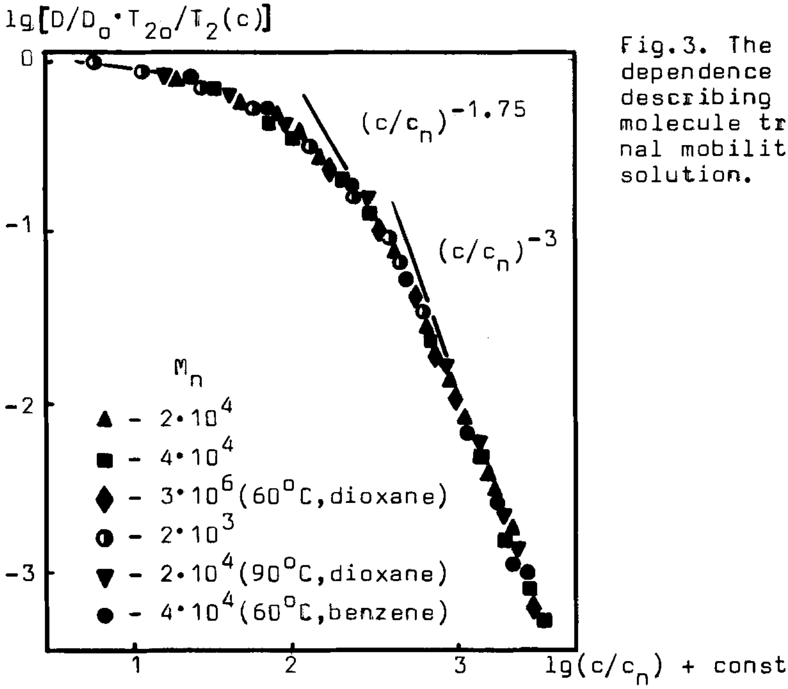

Fig.3. The universal dependence for describing PEO macromolecule translational mobility in solution.

axes $\lg[D/D_o \cdot T_{2o}/T_2(c)]$ - $\lg(c/c_n)$ in Fig.3, confirm the validity of the above formula for describing PEO macromolecule self-diffusion in the whole concentration range. Thus, there does exist the single function $f(c/c_n)$ which is invariant with respect to PEO molecular mass, temperature and solvent type. When $c \to 0$ then $f(c/c_n) \to 1$, and when concentration are high $f(c/c_n) \sim (c/c_n)^{-3}$ which is consistent with modern theoretical representations (8). The dependence $f(c/c_n) \sim (c/c_n)^{-1.75}$, which is expected from scaling concepts, is observed only in a quite small range of medial concentrations.

Table 1 - The values of normalizing constants used in the construction of the generalized curve for the PEO-dioxane solution at 60°C.

M_n	$D_o \cdot 10^{10}$, m^2/s	$c_n \cdot$const
$2 \cdot 10^3$	5.2	15
$2 \cdot 10^4$	1.6	4.3
$4 \cdot 10^4$	1.1	3.3
$3 \cdot 10^6$	0.12	0.27

The reduction parameters D_o and c_n depend on polymer molecular weight, solvent and temperature. The values of D_o and c_n in dioxane solution at 60°C are given in Table 1.

The values obey to the relation $D_o \sim M^{-0.55}$. The latter dependence enables us to interpret c_n as c^* which is the concentration of a transition from the dilute regime to the semidilute one (6).

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