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Diffusion Spin Echo Decay by Pulsed Magnetic Field Gradient NMR and some Structure Features in Blockcopolymer Solutions

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SUMMARY

Blockcopolymer solutions were investigated by pulsed field gradient NMR. Nonexponential diffusion decay of solvent molecules and the dependence of it's shape on time of observation were found out. These features (unusual for solvent molecules) were explained on assumption of the solution heterogeneous structure. Consideration, performed, allow us to estimate the linear dimensions of the heterogeneities, which for concentrated systems occured to be near 10000 A.

INTRODUCTION

Different submolecular structures, appearing due to segregation of the blocks are well known for blockcopolymer solutions in selective solvents (ROGOVINA, SLONIMSKY). Nevertheless, there is rather few data in literature, concerning the study of structural heterogeneity of concentrated solutions when the solvent is common one for blockcopolymer, but differs by it's thermodynamical quality with respect to different blocks. One of the methods of the solution investigation is the study of the self-diffusion by pulsed field gradient NMR. In present work the features of the shape of diffusion spin echo decay in presence of pulsed field gradient in polyblock copolymer poly-(sulfon-ethyleneoxide) are investigated and the dimensions of heterogeneities are estimated in them.

EXPERIMENTAL

The chemical structure of investigated poly-(sulfon-ethyleneoxides) and some characteristics are given in (GRINBERG). The study of spin echo was carried out by a stimulated echo method (TANNER) at proton resonance frequency equal 60 MC. The time of observation, or a diffusion time, was varied in the range (1.5 - 30) msec. The solvent used was cyclohexanone, which differs somehow by it's thermodynamical quality with respect to polysulfon and polyethyleneoxide blocks. The temperature of measurements was 303 K.

RESULTS AND DISCUSSION

Usually, in polymer - solvent systems, when both components are characterized by their own single self-diffusion coefficients (SDC) D_1 and D_2, a shape of diffusion magnetization decay $A(g^2)$ looks like following (MEERWALL):

$$A(g^2) = P_1\exp(-\gamma^2\delta^2g^2D_1t_D) + P_2\exp(-\gamma^2\delta^2g^2D_2t_D) \qquad (1)$$

where P_1, D_1 and P_2, D_2 are the relative parts and SDCs of solvent and polymer molecules, respectively; g is an amplitude and β is a duration of field gradient pulses, t_D is a diffusion time; γ is protons gyromagnetic ratio. In polymer concentrated solutions, when molecular masses are high enough ($\gtrsim$ 10000) the value of D_1 exceeds D_2 by 3-4 orders of magnitude (AZANCHEEV). Therefore, first term in (1) decreases with increase of g^2, while second term remains practically constant. That's why the part of signal caused by solvent molecules protons can be easily separated by substracting of slowly decaying exponent from the total experimental decay. Further, only the signal from the solvent protons will be discussed.

In Fig.1 the typical decays $A(g^2)$ for cyclohexanone in investigated solutions are shown. As it may be seen, the shape of diffusion decay is, generally, nonexponential, depends on the diffusion time and can be described by a following expression:

$$A(g^2)=\int_0^\infty P(D_1)\exp(-\gamma^2\beta^2g^2D_1t_D)dD_1$$

It becomes exponential when $t_D > 3$ msec and display a deviation from an exponent when $t_D \leq 3$ msec.

In the work by Kürger (KÜRGER), concerning the diffusion decay shape in system, consisting of two phases (which differ from each other by molecules SDCs), it is shown that in presence of molecular exchange between the phases caused by molecule jumps from phase to phase with correlation time τ_c, the shape of the diffusion decay can change from exponential to nonexponential in dependence on the relation between τ_c and experimental parametres. In (KÜRGER), however, the dependence of $A(t_D)$ is examined, but the influence of exchange on function $A(g^2)$, studied in our experiments, is not considered

One can propose, that the nonexponentiality of diffusion decay $A(g^2)$ in Fig.1 is related with solutions being "multiphase" due to their structural heterogeneities (saying, the concentration fluctuations and, correspondingly, the SDCs fluctuations). Let SDC of molecule $D_s(t)$ change's in time, when it mooves in structure heterogeneous system. Then the transverse magnetization per unit volume $M_{tr}(\vec{R})$ in the point with radiusvector $\vec{R}$ should satisfy an equation:

$$dM_{tr}/dt = D_s(t)\,\Delta M_{tr} \qquad (2)$$

which differ from corresponding equation of work (SLICHTER) by an existence of time dependent SDC $D_s(t)$ (in (SLICHTER) - D_s is constant).

Eq.2 can be easily transposed to the form, which formally coincides with the case, examined in details in (SLICHTER):

$$dM_{tr}/\,d\tau = \Delta M_{tr} \quad \text{, where} \qquad (3)$$

$$\tau = \int_0^{t_D} D_s(t')dt'$$

If Eq.3 is solved in the same way like in (SLICHTER), then the following expression for diffusion magnetization decay can be obtained:

$$A(g^2) = M_{tr}(t_D)/M_{tr}(0) = \langle \exp(-\gamma^2\beta^2 g^2 \int_0^{t_D} D_s(t')dt')\rangle \qquad (4)$$

where $M_{tr}(0)$ is the system equilibrium magnetization. Symbol $\langle\cdots\rangle$ means averaging over all realizations of a random process of $D_s(t)$ change. Correct averaging of such a functional is a quite difficult, sometimes impracticable task. But some usefull generall conclusions in limiting cases can be made. Expanding Eq.4 in power series, one obtains:

$$A(g^2) = \sum_{n=0}^{\infty} -(\gamma^2\beta^2 g^2)^n (1/n!) \langle (\int_0^{t_D} D_s(t)dt\ )^n\rangle =$$

$$= \sum_{n=0}^{\infty} -(\gamma^2\beta^2 g^2)^n (1/n!) \int_0^{t_D}\cdots\int_0^{t_D} dt_1\cdots dt_n \langle D_s(t_1)\cdots D_s(t_n)\rangle \qquad (5)$$

Let's examine next cases.

1. Let $t_D \gg \tau_c$ (We'll call it, following (KÜRGER), a condition of fast exchange, where τ_c is a correlation time of change of $D_s(t)$, close by the order of magnitude to life time in phase τ_1. We'll understand life time as a certain time characteristic for the system during which SDCs change is insignificant ($|D_s(t+\tau_1)-D_s(t)|$) $\ll D_s(t)$. Then in Eq.(5) product average equals product of averages and

$$A(g^2) = \sum_{n=0}^{\infty} -(\gamma^2\beta^2 g^2)^n (1/n!) \langle D_s\rangle^n t_D^{\,n} =$$

$$= \exp(-\gamma^2\beta^2 g^2 \langle D_s\rangle\ t_D) \qquad (6)$$

Thus, in the case of fast exchange a simple exponent with average SDC should be observed in experiment.

2. Let $t_D \leqslant \tau_1$ (slow exchange), i.e. during the time of observation the value of $D_s(t)$ practically doesn't change, that is the molecule remains within the same phase. Then the averaging of the functional (4) is reduced to the averaging over the initial values of D_s (t=0) and

$$A(g^2) = \int_0^{t_D} P(D_s)\exp(-\gamma^2\beta^2 g^2 D_s t_D)dD_s \qquad (7)$$

where $P(D_s)$ is a distribution function ($\int_0^{\infty} P(D_s)dD_s = 1$). So, a sum of exponents should be observed in the experiment.

One can be convinced, differentiating (7) over g^2, that an initial slope of the curve $A(g^2)$ ($g^2=0$) in both cases (see also Eq.6) corresponds to average SDC (MAKLAKOV et al.)

$$\langle D_s\rangle = \int_0^{\infty} D_s P(D_s)dD_s \qquad (8)$$

Symbol $\langle\cdots\rangle$ is kept in Eq.8 because ensemble average equals time average.

It is clear from above consideration that those values of t_D, at which a deviation from an exponent of the shape of $A(g^2)$ and its dependence on t_D appear, are close to τ_1.

As it is seen from Fig.1, the curves $A(g^2)$ display the behaivior, described above. At relatively high values of t_D the exponent is observed, corresponding to fast exchange $\tau_1 \ll t_D$ (curve 1). When diffusion times decrease to values $t_D \leq 3$ msec, the shape of $A(g^2)$ becomes nonexponential, corresponding to intermediate ($t_D \sim \tau_1$) or slow exchange between the phases (curves 2,3). At the same time the initial slopes of all curves, from which average $\langle D_s \rangle$ are determined, coincide, as expected from above consideration. Providing that the deviation of $A(g^2)$ from exponent occurs at $t_D \sim \tau_1$, we obtained an estimating value of $\tau_1 \sim 3$ msec for concrete case, shown in Fig.1. Proceeding from this estimation and measured value of $\langle D_s \rangle$ a rough estimation of characteristic linear size of system heterogeneities can be obtained as molecule average square displacement with average SDC during the life time in phase:

$$(\overline{r^2})^{1/2} \approx (2 \langle D_s \rangle \tau_1)^{1/2}$$

This size for the same case in Fig.1 occur to be near 10000 Å

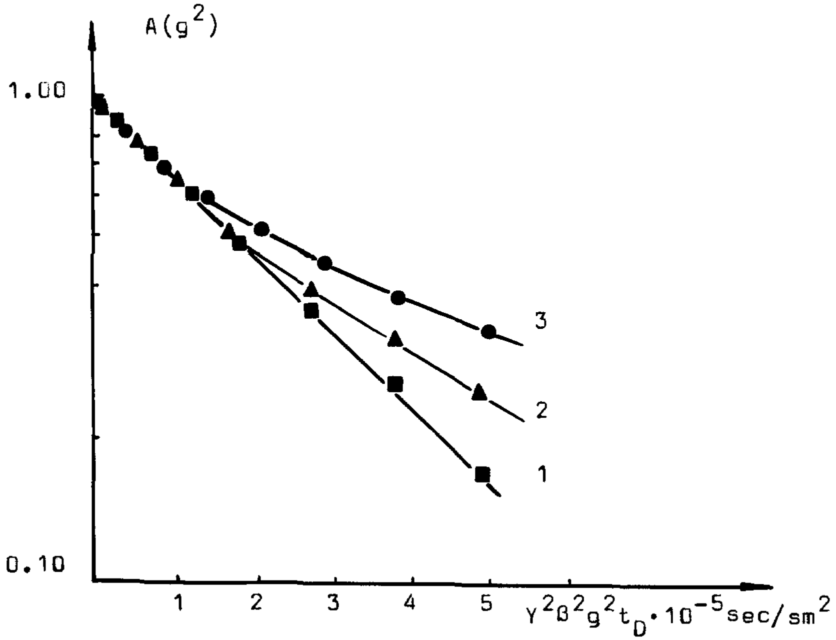

Fig.1. Typical dependence of the shape of diffusion spin echo decay on t_D for cyclohexanone molecules in poly-(sulfon-ethyleneoxide) solutions (concentration of polymer equals 50 weight %, molecular mass equals 50000) : (1) - $t_D \geq 10$ msec, (2) - $t_D = 3$ msec, (3) - $t_D = 1.5$ msec.

(the value of τ_1 = 3 msec, $\langle D_s \rangle$ = $1.67 \cdot 10^{-6}$ sm^2/sec, the concentration of solution C=50% weight of polymer). To compare, the solid microdomens, appearing in selective solvents come in radius to about 100 A (KELLER et al.; HASHIMOTO et al.). Evidently, under the heterogeneities of investigated systems the solvent concentration fluctuations should be understood, which supposily, appear in the process of microseparation of blocks of polysulfon and polyethyleneoxide.

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