Investigation of translational motion of poly(ethylene glycol) macromolecules in poly(methacrylic acid) hydrogels

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SUMMARY: The translational mobility of linear macromolecules of poly(ethylene glycol) (PEG) within a weakly cross-linked poly(methacrylic acid) (PMAA) hydrogel was investigated by means of the pulse field gradient (PFG) NMR method in order to reveal the effect of PMAA/PEG complex formation. It was found that inside the collapsed gel a fraction of the PEG molecules has self-diffusion characteristics like those of the network chains. This suggests the formation of an interpolymer complex, as a result of which some linear molecules acquired the dynamic properties of the network chains. Another fraction of the PEG macromolecules inside the collapsed gel enjoyed free diffusion, for they were not included in the complex with PMAA. In contrast, within the swollen gel (at concentrations of PEG higher than 5 wt.-%) the self-diffusion coefficient of all PEG molecules was independent of the diffusion time, which indicates an absence of the interpolymer complex (or at least that its lifetime is negligibly short).

Introduction

In recent years polymer gels have been extensively studied both experimentally and theoretically[1–3]. This is connected with their useful properties, many of which have found a practical application. One of these properties is the ability of gels to change drastically their dimensions with infinitesimal variation of external parameters such as temperature, pH and solvent composition. This phenomenon is called polymer gel collapse.

Gel collapse can also be induced by the addition of a linear polymer. For instance, the collapse of poly(methacrylic acid) (PMAA) gel can be induced by the addition of linear poly(ethylene glycol) (PEG)[4]. It was shown that in this case the collapse is caused by the formation of a hydrophobic interpolymer complex formed by hydrogen bonding between the carboxy groups of PMAA and the ether oxygens of PEG[4]. The transition of weakly cross-linked PMAA gel from a swollen to the collapsed state is observed at low concentrations of PEG solutions ($<$5 wt.-%). The detailed study of the effects of molecular weight and concentration of PEG, cross-linking density of the gel, temperature and other parameters on the gel collapse was reported in papers[4–10]. In refs.[11, 12] the processes of interpolymer complex formation were investigated by NMR methods that measured relaxation times and obtained high resolution spectra of the ^{1}H and ^{13}C nuclei.

At rather high concentrations of PEG (ca. 5–10 wt.-%) a reswelling of the collapsed gel is observed[4, 8–10]. As opposed to the collapse transition, the reswelling is poorly understood. It was suggested[8] that the reentrant transition of the gel from collapsed to swollen state is due to the fact that PEG solution of rather high concentration becomes a good solvent for hydrophobic complex PMAA gel/PEG. This statement should imply that the complex does not dissociate much into the components, although the processes, which take place on a molecular level during the gel reswelling, were not studied.

The present work is one of the first attempts to study the dynamic characteristics of molecular components in the conditions of interpolymer complex formation by pulse field gradient (PFG) NMR method. Recently PFG NMR was applied to investigate some simple systems: three-dimensional (3D) networks of radiation cross-linked poly (butadiene)[13], the hydrogels of gelatine[14] and of cellulose triacetate[15]. The translational mobility was shown to differ both qualitatively and quantitatively from that of linear molecules. The qualitative difference consists in the anomalous diffusion of chains forming 3D network, i.e., in the time dependence of the effective self-diffusion coefficient. This feature allows one to differentiate sol and gel components, which gives the possibility to use the PFG NMR method for the study of gel-formation kinetic processes[14–16]. Also it was shown[13] that a correlation exists between the value of the effective self-diffusion coefficient and the cross-link density of the network. All these results give us a hope to succeed in the application of PFG NMR method for the investigation of the processes connected with the complex formation between linear and cross-linked polymers.

Experimental part

Samples preparation

The PMAA gel was prepared by free-radical polymerization of methacrylic acid (MAA) in 10 wt.-% aqueous solution in

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the presence of the cross-linking agent *N,N′*-methylenebis-(acrylamide) (BAA) at MAA/BAA molar ratio of 100:1. Ammonium persulfate ($4{,}4 \times 10^{-3}$ mol/L) was used as an initiator. Gelation was carried out in cylindrical glass tubes with inner diameter 8 mm at 40 °C for 24 h. The prepared gel was washed with 5×10^{-4} M HCl for one week and then with distilled water for two weeks.

PEG ("Loba Chemie", Austria) with $\bar{M}_n$ = 6000 g/mol and polydispersity $\bar{M}_w/\bar{M}_n$ = 1,1 was used as received.

For PFG NMR experiments three types of samples (A, B and C) were used. To prepare samples A and B a cylindrical piece of water-swollen PMAA hydrogel with both diameter and length of about 1 cm was immersed in water. The volume of water was about twice the volume of the gel sample. Then the calculated amount of PEG was added. When calculating the weight concentration of PEG, C_p, the overall volume of the system including the volume of the gel sample was taken into account. The gel was kept in PEG solution until the equilibrium was reached (during a week). Then the system was divided into two parts. One of them (sample A) represents the PMAA hydrogel with absorbed PEG macromolecules. The second part (sample B) represents the PEG solution, within which the PMAA hydrogel had been immersed. In order to control the change of PEG concentration in the solution surrounding the hydrogel, aqueous solutions of PEG with the concentration C_p were also prepared (samples C).

Methods of measurement

In the PFG NMR method[17, 18] the information about the self-diffusion processes is obtained from the analysis of the dependence of spin echo amplitude of a signal $A(\bar{q},t)$ on the parameters of the magnetic field gradient and the diffusion time *t*. The value of $\bar{q} = (2\pi)^{-1}\gamma\delta\bar{g}$ (where γ is the gyromagnetic ratio of the resonance nuclei) is directly connected to the amplitude $\bar{g}$ and the duration δ of the gradient pulses. The value of $\bar{q}$ is the analogue of the wave vector, for example, in neutron scattering. Thus, the diffusion decay $A(\bar{q},t)$ can be presented by the dynamic correlation function of van Hove

$$A(q,t) = \iint \rho(r) P_s(r;r',t) \exp\left(i2\pi q(r'-r)\right) dr\, dr'$$

where $\rho(r)$ is the initial spin density, P_s (r; r', t) is a "propagator", a density of the conditional probability to observe a spin in the position of radius-vector r' at moment of the time *t*, providing that the spin was at position of *r* at the initial moment of time. For the free diffusion P_s (r; r', t) has the form of a Gaussian function:

$$P_s(\bar{r},\bar{r}',t) = \frac{1}{(4\pi D_s t)^{3/2}} \exp\left\{-\frac{|\bar{r}'-\bar{r}|^2}{4D_s t}\right\} \qquad (1)$$

with a mean-square displacement $\langle[\bar{r}'(t) - \bar{r}(0)]^2\rangle = 6D_s t$, where D_s is the self-diffusion coefficient. For simplicity the mean-square displacement will be marked below as $\langle r^2(t)\rangle^{1/2}$.

For a system which is characterized by a single self-diffusion coefficient and by a single value of relaxation time, i.e., for a one-phase system from the point of view of NMR, the diffusion decay for stimulated echo sequence[19, 20] when $\delta g \gg \tau_0$ (where g_0 is the constant gradient of the magnetic field) can be written as:

$$A(g^2) = A(2\tau,\tau_1)\langle\exp(i\gamma g\delta(r'-r))\rangle$$
$$= A(2\tau,\tau_1)\exp(-\gamma^2 g^2 \delta^2 t_d D_s) \qquad (2)$$

where $\langle ... \rangle$ denotes the averaging over the all spins. In the case of an exponential relaxation we have:

$$A(2\tau,\tau_1) = \frac{A_0}{2}\exp\left(-\frac{2\tau}{T_2} - \frac{\tau_1}{T_1}\right)$$

where A_0 is the initial amplitude of the free induction decay after the first 90 ° radio-frequency pulse; T_2 is the spin-spin relaxation time, T_1 is a spin-lattice relaxation time; τ and τ_1 are correspondingly the intervals between the first and the second and the second and the third 90 ° radio-frequency pulses; Δ is the interval between gradient pulses; $t_d = (\Delta - \delta/3)$ is the diffusion time.

For a multiphase system (that is a system in which there will be a set of relaxation times and self-diffusion coefficients), which has a "propagator" in the form of a Gaussian function (Eq. (1)), the diffusion decay can be presented as a sum of exponential terms:

$$A'(g^2) = \frac{A(g^2)}{A(0)} = \sum_i^N p_i' \exp(-\gamma^2 g^2 D_{si} t_d), \qquad (2a)$$

where each apparent population p_i' is determined by:

$$p_i' = \frac{p_i \exp\left(-\frac{2\tau}{T_{2i}} - \frac{\tau_1}{T_{1i}}\right)}{\sum_i^N p_i \exp\left(-\frac{2\tau}{T_{2i}} - \frac{\tau_1}{T_{1i}}\right)} \qquad (2b)$$

where *N* is the number of phases and p_i is the real population of resonating nuclei characterized by parameters T_{2i}, T_{1i} and D_{si}. It is easy to see that the experiment should be carried out at constant τ and τ_1. This is possible if the diffusion decay is obtained by varying the value of the magnetic field gradient *g* or, less frequently, by varying the gradient pulse duration δ. For this reason we will further consider the diffusion decay as the dependence of the amplitude of the spin echo signal on the value of the magnetic field gradient $A'(g^2)$ at constant values of all other experimental parameters.

In fact the propagator P_s (r; r', t) does not always satisfy the Eq. (1). In this case the form of the diffusion decay can differ from the simple form of Eq. (2). Especially strong deviations can be observed for porous systems[19, 21]. However, the experimental study of "anomalous" diffusion of radiation cross-linked poly(butadiene) (a chemical gel)[13, 16] swollen in deuterated benzene did not reveal any significant deviations of the shape of diffusion decay from the Eq. (2), although a strong dependence of the determined coefficients for poly(butadiene) macromolecules on the diffusion time was observed. The deviations of the propagator from Gaus-

sian form are negligible, probably because of the boundary conditions being fuzzy, if we consider the bounding of mobility of the polymer chain elements caused by their structure. In order to describe the dependence of the value of the mean-square displacements of the spins on the diffusion time formally, one can use the effective coefficient D_s^* with units m^2/s,

$$D_s^* = \frac{1}{6}\frac{\langle r^2(t)\rangle}{t} \qquad (3)$$

The effective self-diffusion coefficient D_s^*, as opposed to the usual self-diffusion coefficient D_s, is a function of time and, as a rule, may be represented by a power law $D_s^* \propto t^{-n}$, where the exponent n can take a maximum value of 1 for the so-called "completely restricted diffusion"[16]. When $n = 1$ the mean-square size of the constraints is easily obtained from Eq. (3). An additional difficulty of the study of multicomponent systems is that the propagator can be non-Gaussian for one only or for several components of the molecular system. In this case further investigations of the diffusion decay shape are necessary in order to present the propagator in a correct way for one of the simplest forms of type (Eq. (2a)), where the separate components will be characterized by the time-dependent effective coefficient $D_{si}^*(t)$[13–16].

The measurements were performed on an NMR spectrometer with a proton resonance frequency 64 MHz and a maximum value of the pulse magnetic field gradient of 200 T/m. A standard stimulated echo sequence[19] and modified sequences[20, 22] were used for the evaluation of the nuclear magnetic relaxation contributions. The self-diffusion coefficients for different molecular components of the system and their fractions connected with the populations of the diffusion decay components were determined from the analysis of the measured diffusion decays. The primary experimental results were received in the conditions of scanning of pulse gradient g at fixed values of all other parameters. The measurements were conducted at 35 °C. The values of parameters τ and $\tau_d \approx \tau_1$ were varied from 1 to 4 and from 5 to 50 ms, respectively. The duration of the magnetic field gradient pulse did not exceed 0.5 ms.

Results and discussion

The range of PEG concentrations C_p for the present study (C_p = 1–15 wt.-%) was chosen so that we could study the collapsed gel (at C_p = 1–4 wt.-%), the swollen gel (at C_p = 5–15 wt.-%) and the transition between these two states of the gel (at C_p = 4–5 wt.-%). The latter is referred to as a reentrant gel swelling[4, 10], because at high PEG concentrations the degree of swelling of the gel becomes close to that for the gel in pure water in the absence of linear polymer. The determination of the composition of PMAA gel/PEG samples reported previously[4, 10] shows that in the collapsed gel the PMAA/PEG ratio of repeat units is approximately 1 independent of C_p, while in the swollen gel the concentration of PEG is approximately the same as in the external solution.

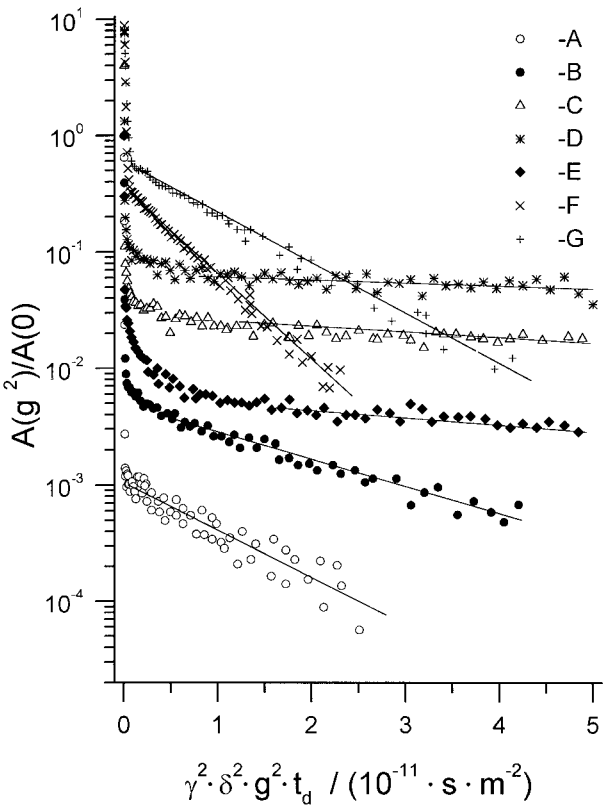

Fig. 1. The diffusion decays for PMAA hydrogel/PEG samples at diffusion time 11 ms for different concentrations of PEG: C_p = 0 wt.-% (curve A (○)), 1 wt.-% (curve B (●)), 2,5 wt.-% (curve C (△): scaled along y-axis by multiplying the values by a factor of 4), 3 wt.-% (curve D (*): scaled along y-axis by multiplying the values by a factor of 8), 4 wt.-% (curve E (◆)), 5 wt.-% (curve F (×): scaled along y-axis by multiplying the values by a factor of 8 and scaled along x-axis by multiplying the values by a factor of 10) and 10 wt.% (curve G (+): the same scaling as for the curve F)

Let us start with the simplest system, i.e., the aqueous solution of PEG. Diffusion decays for aqueous PEG solutions (samples C) as well as for the PEG solutions surrounding the PMAA hydrogel (samples B) can be fitted by the Eq. (2a) with two (N = 2) exponential terms. One of them (with the population p_p and self-diffusion coefficient D_{sp}) characterizes the PEG macromolecules, while another one (with parameters p_h and D_{sh}) characterizes the water molecules. In these samples the shape of $A'(g^2)$ did depend neither on diffusion time t_d nor on parameter τ in the whole range of their variations, which can be a consequence of sufficiently large nuclear relaxation times T_{1p}, T_{1h} and T_{2p}, T_{2h}. This fact allows us to consider the obtained values of population for these samples as reliable.

Fig. 1 depicts typical diffusion decays in the system PMAA hydrogel/PEG at different PEG concentrations C_p. All curves were found at fixed values of τ = 1,4 ms and t_d = 11 ms. These samples are more complicated than PEG solutions because they consist of three components

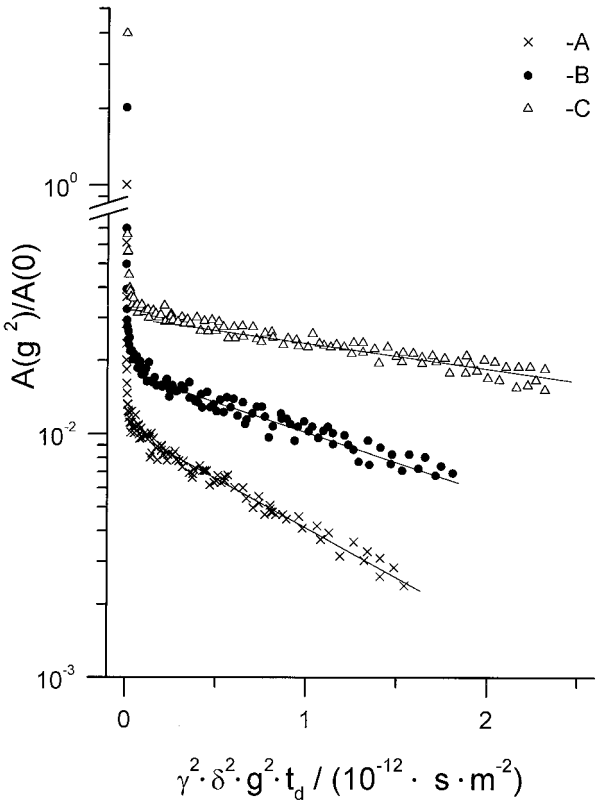

Fig. 2. Diffusion decays of the system PMAA hydrogel/PEG (C_p = 3 wt.-%) at various diffusion times: t_d = 9 ms (curve A (×)), 15 ms (curve B (●): scaled along y-axis by multiplying the values by a factor of 2) and 25 ms (curve C (Δ): scaled along y-axis by multiplying the values by a factor of 4)

(PMAA, PEG and water), each of which is able to contribute to the stimulated echo signal. Therefore the diffusion decay at zero PEG concentration is of a special interest (Fig. 1, curve A). This diffusion decay is well described by Eq. (2a) with two exponential terms. One of them corresponds to water molecules, and the other one to PMAA.

The population p'_{pm} of the PMAA component is small (less then 10^{-3}) and depends significantly on time τ and t_d, which indicates a considerable difference between spin-spin and spin-lattice relaxation of protons in water and in PMAA. So the small contribution of PMAA to the echo signal makes the analysis of the results easier. One can see (Fig. 1, curve B) that even at minimum PEG concentration (1 wt.-%) the echo amplitude at the end of the diffusion decay is ten times higher than the contribution of PMAA. This allows us to attribute this component with a good accuracy to PEG protons only. At the increase of the PEG concentration (Fig. 1, curves D, E) the signal from PEG protons becomes dominant. At PEG concentrations $C_p \geq 5$ wt.-% (Fig. 1, curves F, G) the diffusion decays are simple: they are characterized by two components with self-diffusion coefficients D_{sp} (PEG) and D_{sh} (water) and with populations p_p and p_h independent of time parameters τ and t_d.

In order to approximate the curves B–E by the Eq. (2a), it is necessary to input at least three exponential terms. It should be noted that comparative analysis of populations and self-diffusion coefficients allows one to be sure that the water molecule contribution is still one-exponential. Therefore, this is the diffusion decay for PEG macromolecules in the hydrogel which becomes more complicated in this range of concentrations (C_p = 1–4 wt.-%). Additional information can be obtained from the analysis of the data presented in Fig. 2, where the diffusion decays for the PMAA gel/PEG system (C_p = 3 wt.-%) are given at various diffusion times t_d. Fig. 2 unambiguously demonstrates the dependence of the slopes of the final part of the curves on the diffusion time, which formally indicates the t_d-dependence of the corresponding self-diffusion coefficients.

Therefore, the general analytical representation of the diffusion decay shape for the experimental data can be presented in the form:

$$\begin{aligned}\frac{A(g^2,\tau,\tau_1)}{A(0,\tau,\tau_1)} \approx\; & p_h \exp\left(-\frac{2\tau}{T_{2h}} - \frac{\tau_1}{T_{1h}}\right)\exp\left(-\gamma^2 g^2 \delta^2 t_d D_{sh}\right) \\ & + p_{p1} \exp\left(-\frac{2\tau}{T_{2p1}} - \frac{\tau_1}{T_{1p1}}\right)\exp\left(-\gamma^2 g^2 \delta^2 t_d D_{sp1}\right) \\ & + p_{p2} \exp\left(-\frac{2\tau}{T_{2p2}} - \frac{\tau_1}{T_{1p2}}\right)\exp\left(-\gamma^2 g^2 \delta^2 t_d D^*_{sp2}(t_d)\right) \\ & + p_{pm} \exp\left(-\frac{2\tau}{T_{2pm}} - \frac{\tau_1}{T_{1pm}}\right)\exp\left(-\gamma^2 g^2 \delta^2 t_d D^*_{spm}(t_d)\right)\end{aligned} \tag{4}$$

The indices “h”, “p” and “pm” refer to water, PEG and PMAA, respectively. The values of the effective self-diffusion coefficients that depend on the diffusion time (“anomalous” diffusion) are marked by asterisks. The indices “p_1” and “p_2” for PEG macromolecules are used in order to separate the contributions with “anomalous” (D^*_{sp2}) and usual (D_{sp1}) self-diffusion coefficients. The total fraction of PEG macromolecules in the system is characterized by the population $p_p = p_{p1} + p_{p2}$.

The data presented in Fig. 3 demonstrate that the values D^*_{sp2} and D^*_{spm} do depend on the diffusion time. Moreover, this dependence corresponds to completely restricted regime ($D^*_{sp2} \propto t_d^{-1}$) both for PEG (curves A–D) and PMAA chains (curve K). At the same time, the data for the system PMAA hydrogel/PEG at C_p = 5 wt.-% (curve E) show that all PEG macromolecules are characterized by a free diffusion regime: $D_{sp} \propto t_d^0$. In the same way one can attribute to the free diffusion regime the part of PEG macromolecules p_{p1} with self-diffusion coefficient D_{sp1} at C_p = 1–4 wt.-%. Strictly speaking, the uncertainty in the determination of the values of these inter-

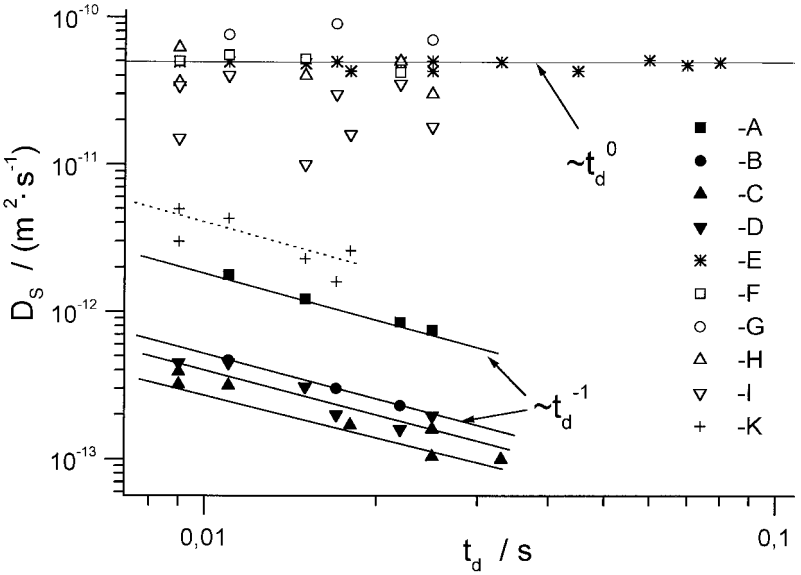

Fig. 3. Dependence of the self-diffusion coefficients of PEG on the diffusion time t_d in the system PMAA hydrogel/PEG at various PEG concentrations C_p; 1 wt.-%: D^*_{sp2} (curve A (■)), D_{sp1} (○); 2 wt.-%: D^*_{sp2} (curve B (●)), D_{sp1} (□); 3 wt.-%: D^*_{sp2} (curve C (▲)), D_{sp1} (Δ); 4 wt.-%: D^*_{sp2} (curve *D* (▼)), D_{sp1} (∇); 5 wt.-%: D^*_{sp2} (∗). The curve K (+) corresponds to the dependence of the self-diffusion coefficients of PMAA (D^*_{spm}) on the diffusion time t_d at C_p = 0 wt.-%. The dependencies $D_s \propto t_d^{-1}$ and $D_s \propto t_d^0$ are shown by solid lines

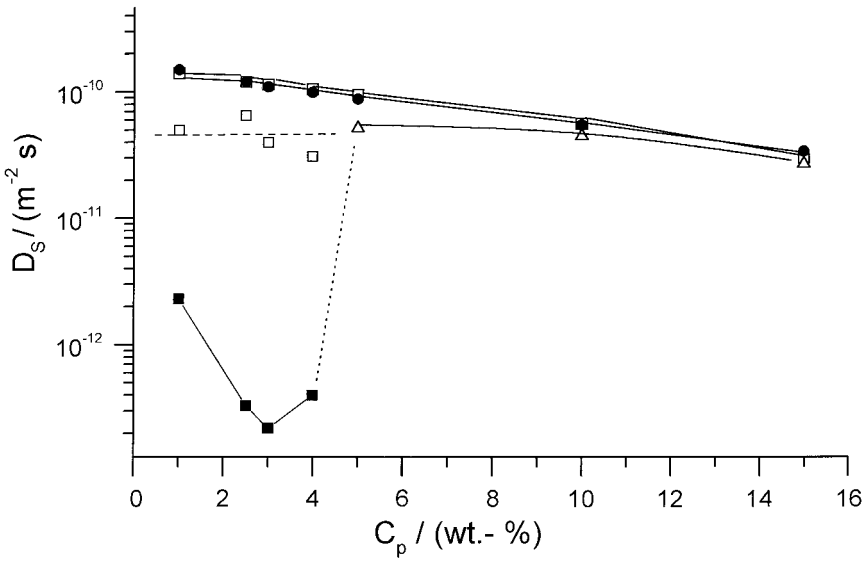

Fig. 4. The concentration dependencies of self-diffusion coefficients of PEG macromolecules: curve A (○) – in usual aqueous solutions (samples C), curve B (●) – in aqueous solution surrounding the hydrogel (samples B), curves C, D, E (□ Δ ■) – in PMAA hydrogel/PEG system (samples A). The concentration dependencies of D_{sp}, D_{sp1} and D^*_{sp2} (t_d) are shown by curves □, Δ and ■, respectively. All data are brought at diffusion time 10 ms

mediate self-diffusion coefficients does not allow us to discover the t_d-dependence.

Fig. 4 illustrates the concentration dependencies of the measured self-diffusion coefficients of PEG macromolecules both in aqueous solutions (curve A, samples C) and in PMAA hydrogel (curves C–E, samples A). For comparison the data for aqueous solution of PEG surrounding the hydrogel (curve B, samples B) are presented as well.

It is seen that the self-diffusion coefficients of the samples B and C are almost identical (curves A and B). This suggests that PMAA hydrogel does not much reduce the initial concentration of PEG by sorption.

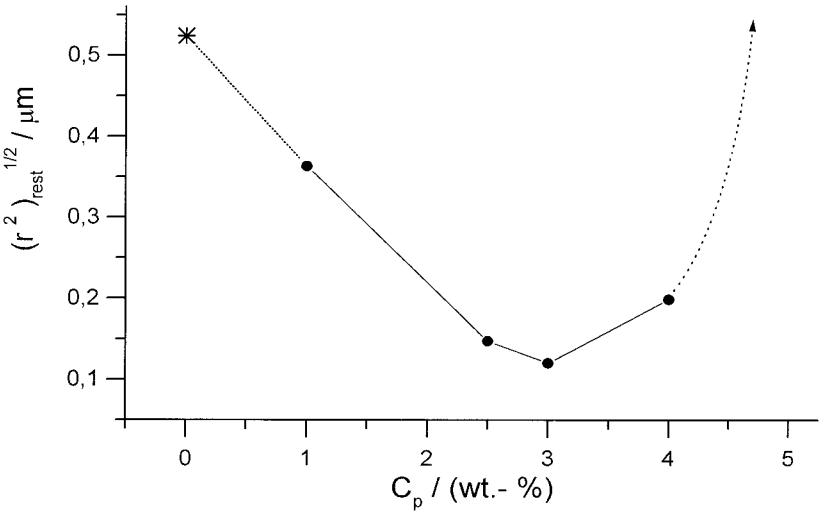

Fig. 5. The dependence of mean-square displacements of PEG macromolecules in the system PMAA gel/PEG on the diffusion time at various polymer concentrations. These values are determined from D^*_{sp2} (●). The value marked by ∗ corresponds to zero concentration of PEG, i.e., it is determined from the value of D^*_{spm} (see Eq. (4)). This value of the mean-square displacement characterizes the scale of the restrictions of the mobility of elements of the three-dimensional network of PMAA

As to PMAA gel/PEG samples (samples A), in the swollen gel at C_p = 5−15 wt.-% the self-diffusion coefficient of PEG inside the gel and in the solution is almost the same (cf. curves B and C in Fig. 4). The close values of the self-diffusion coefficients indicate that the values of PEG concentrations in these samples are practically the same. This is consistent with the data obtained earlier[4, 10].

Now let us consider the behavior when the PEG concentration was below 5 wt.-%. At C_p = 4−5 wt.-% the gel shrinks. The shape of the curve E shows that this leads to a sharp decrease of the value of self-diffusion coefficient of PEG macromolecules. A comparison of the curves A, B and E shows that, to achieve such a significant drop of the self-diffusion coefficients, the concentration of PEG inside the gel should be increased by more than one order of magnitude, which seems unrealistic. An additional argument in favor of such a statement comes from the comparison of the relative contributions of PEG components in diffusion decays for samples A, B and C: in all types of samples the relative contribution of PEG is almost the same. The question about the concentration of PEG inside the hydrogel will be considered in detail below, but the drop of the self-diffusion coefficients of PEG at the shrinking transition cannot be connected only with the change of PEG concentration in the gel.

The most important fact is that for the collapsed gel samples (at C_p = 1−4 wt.-%) we observe not only the quantitative, but also the qualitative change in the behavior of the self-diffusion coefficients of PEG: one part of PEG macromolecules is characterized by free diffusion D_{sp1} (curve D),while another part of them has a self-diffusion coefficient $D^*_{sp2}(t_d)$ (curve E) which is dependent on the diffusion time t_d. Such an effect can be observed[13–16] in the restricted self-diffusion of the polymer network chains. In the samples under study a network indeed exists (PMAA gel), but here the effect of restricted self-diffusion is observed for linear PEG sol macromolecules. Most probably this is due to the formation of PMAA/PEG complex, as a result of which the translational mobility of PEG macromolecules becomes connected with that of the PMAA network chains. In turn this allows us to use the data on the translational mobility of PEG to take insight about the state of the PMAA gel/PEG system.

The observed regime $D^*_{sp2} \propto t_d^{-1}$ for the part p_{p2} of PEG molecules at concentrations C_p = 1−4 wt.-% indicates a independence of the mean-square displacements of the diffusion time, and allows us to find the mean-square size of restrictions: $\langle r^2(t)\rangle^{1/2}_{rest} = (6 t_d D^*_{sp2})^{1/2}$. The results so obtained are given in Fig. 5.

It is seen that the most "rigid" gel (with minimum values of $\langle r^2(t)\rangle^{1/2}_{rest}$) is formed at PEG concentration of about 3 wt.-%. As the concentration of PEG decreases to 1 wt.-%, the possibility of translational displacements of PEG macromolecules connected with PMAA chains increases by a factor of three. As has been already mentioned, for all PEG concentrations higher than 5 wt.-%, no indications of PMAA gel/PEG complex formation have been detected. It should be noted that the value $\langle r^2(t)\rangle^{1/2}_{rest} = (6 t_d D^*_{sp2})^{1/2}$ (point ∗) derived from data for PMAA chains in hydrogel at zero PEG concentration correlates quite well with the data obtained for restricted self-diffusion of PEG macromolecules. This fact counts

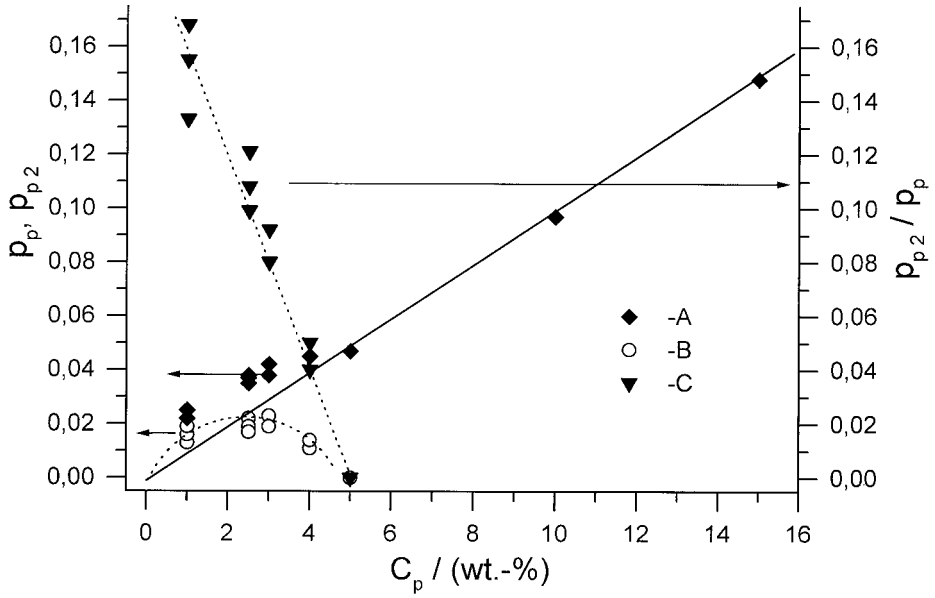

Fig. 6. The real populations p_p (curve A (◆)) and p_{p2} (curve B (○); left y-axis) and their ratio p_{p2}/p_p (curve C (▼), right y-axis) in the PMAA hydrogel/PEG samples as a function of the initial concentration of PEG C_p. The solid line corresponds to the condition $p_p = C_p$

in favor of the suggestion about the formation of the interpolymer complex PMAA gel/PEG, that as a result of the complex formation the PEG macromolecules acquire translational characteristics similar to those of PMAA chains.

When studying the systems PMAA hydrogel/PEG, it is important to allow for the absorption of PEG macromolecules from the external solution. This information can be obtained from an analysis of populations in Eq. (4). There is a problem of taking into account the nuclear relaxation in apparent values of populations (2b) $p_i' = f(\tau, \tau_1)$ because of the impossibility of establishing zero values for τ and τ_1. In order to find the real parameters p_{p1}, p_{p2} and the total fraction $p_p = p_{p1} + p_{p2}$ of PEG in a hydrogel, the double procedure[22] of extrapolation of $p_i' = f(\tau, \tau_1)$ measured at various values of τ and τ_1 in the stimulated echo sequence is used: $p_i = \lim_{\tau,\tau_1 \to 0} p_i'(\tau, \tau_1)$. The obtained results are given in Fig. 6.

At PEG concentrations $C_p \geq 5$ wt.-% the fraction of polymer p_p in the hydrogel is strictly the same as in the external solution (curve A). At lower concentrations of PEG the fraction of PEG in the hydrogel exceeds the corresponding value of C_p, so for the sample with $C_p = 1$ wt.-% the concentration of PEG in the gel is almost twice its concentration in the solution. The curve B shows the values of the fraction of p_{p2}, which characterize the PEG macromolecules in the interpolymer complex. One may perceive a maximum on this curve, at $C_p = 3$ wt.-%, the same concentration as the minimum in the of value $\langle r^2(t)\rangle_{rest}^{1/2} = (6 t_d D^*_{sp2})^{1/2}$ we saw in Fig. 5. This again suggests that the dynamic characteristics of the gel chains are related to the amount of PEG in the complexed state.

We consider the most interesting results are provided by curve C, demonstrating the dependence of the fraction of PEG macromolecules included in the complex on their total amount inside the hydrogel. It is seen that the value of p_{p2}/p_p tends to zero at $C_p \approx 5$ wt.-%. Therefore, this value of the initial PEG concentration in a given system can be supposed to be critical for the formation of interpolymer complex and hence for the observation of the gel collapse. At the decrease of C_p the part p_{p2}/p_p of PEG macromolecules in the complex increases and practically approaches to 1 at $C_p < 1$ wt.-%.

Conclusions

In the collapsed gel (at PEG concentrations $C_p < 5$ wt.-%), for part of PEG molecules, the regime of completely restricted diffusion is realized, which is characteristic for polymer chains constituting a three-dimensional network[13]. The peculiarity is that in this case the network is formed by PMAA chains, but the effect is observed for linear PEG macromolecules. The only reason for this is a complex formation between PMAA gel and PEG, so that the translational mobility of PEG macromolecules becomes restricted to that of the PMAA chains. It should be noted that the PMAA is chemically cross-linked and therefore must have restricted diffusion at all concentrations. However, we failed to determine the lifetime of PMAA/PEG complex because of too limited range of diffusion times (as a result of a sharp decrease of spin-lattice relaxation). One can only state that the lifetime of the complex PMAA gel/PEG in the collapsed state exceeds 50 ms – a maximum value of the diffusion time used in

the experiments. An important result of this study is that not all PEG macromolecules form the interpolymer complex PMAA gel/PEG. A part of them remains free, although this part decreases when the initial PEG concentration C_p becomes smaller. Therefore, we can suppose that in the collapsed gel the PMAA/PEG complex is formed according to the rule "all or none", i.e., some of PEG molecules are completely bound and others are completely free. It is interesting to note that the translational characteristics of such "free" PEG macromolecules are close to those of PEG macromolecules in PMAA gel / PEG sample with C_p = 5 wt.-%.

The observation of only free diffusion regime at PEG concentrations $C_p \geq 5$ wt.-% indicates either the complete absence of interpolymer complex formation at these concentrations or the short lifetime of these complexes.

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