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Diffusive properties of solvent molecules in neighborhood of polymer chain as seen by Monte-Carlo simulations

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An influence of both polymer chain length and concentration on mobility of solvent molecules in polymer solutions was studied by Monte Carlo simulations with use of Dynamic Lattice Liquid (DLL) model. The poly(vinylmethylether)-water system was used as a model. Two different solvent (water) states differing on mobility were distinguished in polymer solutions. The first one with high molecular mobility independent of polymer concentration corresponds to bulk solvent in real systems. The second state relates to so called bound solvent. In this case the solvent diffusivity decreases with polymer content. For diluted solutions the diffusion of bound solvent is affected by polymer chain length, precisely, by ability of polymer chain to coil formation.

Introduction

Significant difference in size of solvent and polymer molecules results in important difference in their mobility. In consequence, many polymer systems (concentrated solutions, membranes, gels) deviate from normal (Fickian) diffusion.¹⁻⁷ Diffusion is especially important issue in stimuli responsive gels exhibiting Volume Phase Transition (VPT). In such systems, molecular mobility (diffusivity in a case of water and molecular relaxations of polymer segments) is one of the key factors that determine dynamics of VPT.^{8,9} VPT and other phase transitions are accompanied by drastic change in local polymer concentration and by change in character of diffusion.^{8,10-14} Poly(vinylmethylether) (PVME) is a perfect candidate for a model of stimuli responsive polymer, because of its simple chemical structure and many experimental results collected for neat PVME as well as for its solutions and gels.^{8,10-27} Moreover, the PVME-water systems may be easily considered by the coarse-graining procedure with conservation of the natural scale of objects and distances between them²⁸ – see also Fig. 1.

According to model proposed by Maeda²⁹, water in hydrogels may be classify as:

- strong (primary) or weak (secondary) bound water depending on a type of intermolecular interactions between water and polymer network,
- interstitial water closed in confined space of entangled chains,
- bulk water distant from polymer segments.

Similar classification may be introduced also for water in solution of linear polymers. Water in various states differs on ability for crystallisation and on rotational and vibrational dynamics.^{11-13,16,17,21,24,25,30-32} Thus, these states may be

distinguished by some experimental methods such as differential scanning calorimetry³⁰, neutron scattering^{33,34}, vibrational^{16,17,31,32} and dielectric spectroscopies.^{29,35,36} The diffusive properties of water as well as various useful additives (tracers, drugs, ionic and non-ionic solutes, nanoparticles) in polymer systems have been still explained insufficiently.^{1-7,37} Experimental techniques useful to characterise diffusive properties - like fluorescence correlation spectroscopy (FCS)³⁻⁶, dynamic light scattering³⁸, nuclear magnetic resonance^{2,39,40} - give only average picture of the sample, without distinction between water in various states. However, recently two fractions of diffusant differed on mobility were distinguished by FCS.^{4,6,7} Thus, presented problem seems to be especially attractive for computer simulations.

Recently, it was shown that the presence of polymer chains in the direct neighbourhood of solvent (water) molecule significantly reduced their mobility.²⁸

In this work an influence of polymer chain length and polymer concentration on mobility of solvent molecules in various states will be discussed in light of theoretical models as well as experimental data.

Theoretical background

The classical approach to diffusion bases on Fick's laws originated from an assumption that the particle movements are governed by Brownian motions. In that case the mean-squared displacement $\langle r^2 \rangle$ is proportional to time t :

$$\langle r^2 \rangle = kt, \quad (1)$$

where k is a constant dependent on temperature and diffusant size.^{1,2} To describe properly complex systems (concentrated polymer solutions or gels), formula (1) should be used in more general form:^{1,2}

$$\langle r^2 \rangle \sim t^\alpha, \quad (2)$$

where exponent α is a parameter related to the diffusion mechanism. If $0 < \alpha < 1$ the subdiffusion occurs, while for $\alpha > 1$ the superdiffusion takes place. The anomalous diffusion originates from the breakdown of the central limit theorem caused by broad distribution or long range correlations (for more details see^{1,2}).

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Many factors influence molecular mobility in polymer systems: temperature, pressure, molecular mass of a polymer and its dispersion, polymer concentration, polymer topology, diffusant size and shape, inter- and intramolecular interactions and others.^{1,2,5} Such wide variety of variables resulted in many models proposed in this field. These models may be grouped into three main classes:

(a) models based on free volume theory⁴¹⁻⁴⁷ assuming that the free volume is a key factor controlling molecular mobility; rearrangement of free volume creates the holes being a transport channels for diffusant;

(b) models based on obstruction⁴⁸⁻⁵² – where macromolecules are regarded as motionless; in consequence both mean path length and self-diffusion coefficient of a diffusant increase;

(c) models based on hydrodynamic theories⁵³⁻⁵⁸ taking into account hydrodynamic interactions such as friction.

Some other models as well as detailed presentation and comparison of mentioned above ones are available in literature.⁵

Coarse-graining procedure

Presented herein studies concerned a model system that reflects well the aqueous solutions of PVME. In order to transfer the real PVME-water system to the lattice simulations, the coarse-graining procedure was applied. It is schematically presented in Fig. 1 and has been described in details elsewhere.²⁸ Three types of united-atoms (grains) such as: water (H-O-H), main chain (-CH-CH₂-) and pendant group (-O-CH₃) were introduced. Only two types of water acting as a solvent were distinguished: bound water directly interacting with polymer by excluded volume and bulk water located in further distances (see Figures 1 and 2). Distinction between strong and weak bounded water requires taking under consideration electrostatic interactions in the system, and additional energetic tests should be introduced to the algorithm. Such approach, although interesting, results in significant increase in computing time. Thus, in this paper only excluded volume interactions were taken into account.

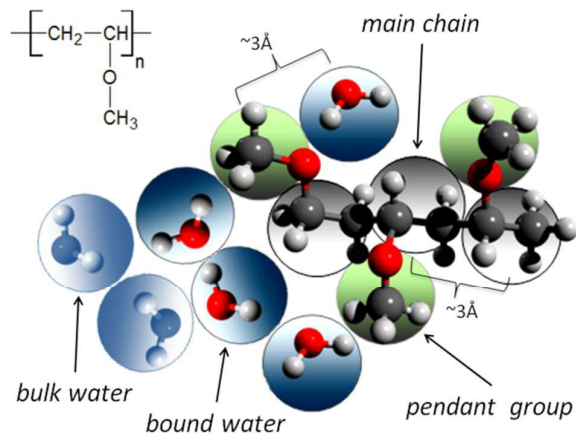


Fig. 1. Chemical structure of PVME and scheme of the coarse-graining procedure applied to transfer real PVME-water system to the lattice simulations.

Dynamic Lattice Liquid model

Dynamic Lattice Liquid (DLL) model was first published in 1997 by T. Pakula.⁵⁹ This model treats a matter as a large set of grains (united-atoms, super-atoms) representing molecules or their parts. The grains are located in the nodes of the network representing their temporary positions. To form bigger molecules, like polymer chains, stars, brushes and others, the grains may be joined by the non-breakable and inextensible (over length of one lattice constant) bonds. It is assumed that each bead have some free excess volume to vibrate around its temporal position. Each bead displacement is considered as an attempt of movement to neighboring lattice site. A set of possible vectors of movement attempts is equal to lattice coordination number for simplicity. In dense system long range motion can take place only by cooperative displacement due to caging effect of neighbors. One of the most powerful advantages of DLL model is possibility to work in dense system (full occupation of lattice) without any holes of molecular size. It has been achieved by the assumption that the translation of the elements over larger distances than vibration range take place only in cooperative manner – in frame of closed “cooperative loops” as Fig. 2 presents (the 2D system is presented in Fig. 2 for clarity).

The DLL model fulfills the continuity equation and provides the correlated movements of ‘molecules’ as in a real liquid. The excluded volume is preserved for beads – only one molecule can be present in lattice node at any time, and for bonds – molecules cannot move crossing the bonds. DLL model does not reproduce all properties known from the liquid mechanics but it is sufficient for studies of coarse-grained models. Moreover, the dynamic properties, which it produces, are in good agreement with those established for liquids in general.^{60,61} DLL model has been successfully used to characterize many complex phenomena, like: diffusion limited aggregation⁶², reaction diffusion front problems⁶³, polymer solution dynamics⁶⁴, gelation in cross-linked polymeric systems⁶⁵⁻⁶⁸, spinodal decomposition^{69,70} and diffusion in crowded environments.⁷¹

The Monte Carlo Step (MCS) applied to realize the DLL model in athermal case reflects discrete time. The single MCS unit includes four operations: (1) Random generation of movement attempts vectors (represented in Fig. 2 by arrows) assigned to every lattice bead simultaneously. (2) Immobilization of elements which cannot be moved, e.g. elements engaged in movement attempts leading to: violation of the excluded volume, creation of a vacant site or breaking a bond; examples are presented in Figure 2 as scenarios 1, 2 and 4 respectively. (3) Selection of groups of vectors (from remaining elements) coinciding with contours of closed continuous paths (loops). (4) Movement of elements along these loops by one lattice constant.

To relate defined above MCS unit to real time and length scales the comparison of diffusion constant of pure water determined from DLL algorithm with experimental data is possible. Taking into account that the valuable data for DLL calculations (see ref. [60]) related to athermal case (the electrostatic interactions were neglected) the experimental data should be considered for relatively high temperatures (to minimize influence of water-water H-bonds on diffusivity). Such rough estimation leads to conclusion that 1 MCS is near about 6·10⁻¹³ s. This value should be similar for diluted polymer

systems analyzed in this paper. However, one should be aware of that time scaling will be different for higher polymer concentration due to conformational constraints.

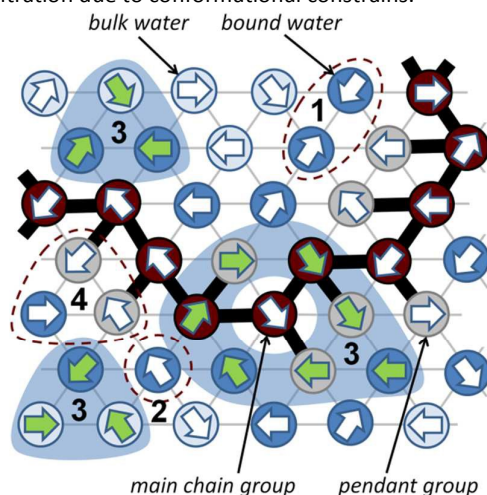


Fig. 2. Water-PVME system in DLL model - dynamics illustrated on 2D triangular lattice (for clarity). Numbers indicate various local movement scenarios: 1 – an attempt of a movement that violates the exclude volume (unsuccessful), 2 – an attempt that creates a vacant site (unsuccessful), 3 – successful movement attempts forming cooperative loops, 4 – an attempt that breaks a bond (unsuccessful).

Experimental

All simulations were carried out on 3D 50^3 FCC lattice (coordination number = 12) with periodic boundary conditions. Various lengths of PVME macromolecules (from 5 to 360 polymer units) in different concentration were studied. A wide range of concentrations and polymer molecular masses allowed to obtain systems differ on morphology and diffusive properties. In the most extreme case, there was only 1 chain with length of 360 polymer units in computational box (1 %wt. solution). Contrarily, for the shortest PVME chains, 6693 macromolecules were necessary to reach highly concentrated systems – 65 %wt.. Polymer chains were virtually synthesized by well-known pseudo-living controlled polymerization method.^{28,65} Kinetic chains were killed when the tailored length of particular macromolecule was achieved. Therefore, for all samples molecular mass dispersity was exactly 1. Of course, this is inaccessible value of molecular mass dispersity in real synthesis, nevertheless, it is not far from the values (1.02-1.05) found for polymers prepared by Controlled Radical Polymerization methods, like Atom Transfer Radical Polymerization ATRP.⁷²⁻⁷⁵ This simplification used in proposed approach is useful to separate effects related to polymer chain length from effects related to polymer concentration.

The character of diffusion in polymer systems often depends on the observation time scale. For long time scales the $\langle r^2 \rangle$ increases usually with time according to Einstein relation – proportionally to self-diffusion coefficient D_{self} :

$$\langle r^2 \rangle = \frac{1}{N_x} \left\langle \sum_i (r_i(t) - r_i(t_0 = 0))^2 \right\rangle = 6D_{self}t, \quad t \rightarrow \infty, \quad (3)$$

where N_x is a total number of analyzed molecules, calculated as difference between molecule position at time $t - r_i(t)$ and at start $r_i(t_0 = 0)$. In short and intermediate time scales diffusion

in complex system is rather anomalous, especially in semi-diluted and concentrated systems. Taking into account equation (2), the α parameter can be determined from logarithmic derivative:

$$\alpha = \frac{d \log \langle r^2 \rangle}{d \log t}. \quad (4)$$

For qualitative comparison of solvent mobility in different vicinity of polymer, the time-dependent position autocorrelation function $A(t)$ was introduced. It was defined as a change of position of solvent molecule at time t in respect to its initial position:

$$A(t) = \frac{1}{N_R} \sum_i \delta_i, \quad (5)$$

where: N_R – number of solvent molecules in analyzed region, δ – is equal to 1 if the same solvent molecule occupied site i at time t and $t_0 = 0$, otherwise $\delta = 0$. Next, $A(t)$ dependences determined from DLL simulations were fitted using KWW⁷⁶ function:

$$A(t) = A_0 \exp(-(t/\tau)^\beta), \quad (6)$$

where τ – diffusion relaxation time of solvent, A_0 – prefactor close to 1 and β – fitting parameter.

To characterize morphology (homogeneity) of polymer solutions differed on polymer chain length and their concentration radial pair correlation function $g_{xy}(r)$ was defined as follow:

$$g_{xy}(r) = \frac{1}{M\Delta V} \left\langle \sum_r \sum_{r'} [\sigma_x(r') \sigma_y(r'+r)] \right\rangle, \quad (7)$$

where x, y stands for types of analyzed pair, r is distance between them, M is the total number of lattice sites and ΔV is space volume limited by range of distances $r + dr$ used to build the histogram. FCC lattice generates itself characteristic peaks in $g_{xy}(r)$ function. To exclude them, obtained results were subtracted and normalized to pure solvent lattice spectrum g_0 . The characteristic correlation length ξ was estimated for polymer-polymer correlation, to describe homogeneity of particular systems numerically, according to the formula:

$$g_{pp}/g_0(r) = R_0 \exp(-(r/\xi)) + y_0, \quad (8)$$

where p – stands for polymer, and R_0 and y_0 are fitting parameters.

Results and discussion

A. Comparison with theoretical models and experimental results

In the first approach to analysis of DLL simulation results all solvent molecules were treated *en masse*, without the differentiation between the bulk and bound states. It was the only way to validate used method because of lack of experimental data as well as theoretical models distinguishing various states of solvent in polymer systems. However, strong intermolecular interactions play an important role in aqueous solutions of PVME especially below lower critical solution temperature.^{13,17} Results presented herein neglected all electrostatic and friction interactions. They may be considered as a limiting case where excluded volume effects are more important than electrostatic interactions. It is also necessary to underline that an introduction of interactions to DLL algorithm-based simulations leads to a new variable – temperature – and results in significant increase in computing

time (by 2-3 orders even for the most simple isotropic form, like Ising type interactions). Moreover, presented results are more universal and may be expanded (scaled) to other polymer systems with the ratio of size of monomer unit to solvent close to 2.

The presented simulations cover relatively broad range of polymer concentrations and chain lengths. Most of samples are in diluted or semi-diluted regimes. Taking into account that the solvent molecules are the main object of presented herein investigation, it is also worth noting, that for all systems water molecules percolate forming continuous phase.

Mean-squared displacement of solvent molecules $\langle r_{sol}^2 \rangle$, measured in lattice spacing units, as a function of time t expressed in Monte Carlo Steps (MCS) units for different PVME weight fraction and one selected chain length ($N = 90$) is shown in Fig. 3a. For long time scales $\langle r_{sol}^2 \rangle$ increases with time according to Einstein relation (see Eq. (3)).

Increasing PVME concentration slightly slows down solvent diffusion. Inset in Fig. 3a presents solvent diffusion for different polymer chain length N in the systems with 15 %wt. of polymer. Differences due to chain length are negligible. Self-diffusion coefficients for solvent were calculated for times over 1000000 MCS i.e. in a range of normal diffusion (where α was close to 1). Solvent diffusion coefficients in PVME solutions calculated and normalized in relation to self-diffusion coefficient in pure solvent (D_{self}/D_{self}^0) are presented in Fig. 3b. The dependence of D_{self}/D_{self}^0 in a function of polymer content is linear in whole range of concentrations, independently of polymer chain length.

Figure 4a and b shows an impact of polymer concentration and chain lengths on solvent diffusion parameter α in short and intermediate time scales (below 10^5 MCS). In this range results were averaged over 30 independent runs. As it was mentioned in Theory section, $\alpha < 1$ indicates anomalous character of the solvent diffusion. This slowed-down diffusion is called sub-diffusion and is observed in fractal or porous environments.¹ A convenient way to analyze the time dependent exponent α is to plot the logarithmic derivative of $\langle r^2 \rangle$ defined in Eq. (4). The results for different polymer content and one selected chain length ($N = 90$) are presented in Fig. 4a. Low PVME fraction (1% wt.) does not influence the dynamics of solvent (α is close to 1 in whole investigated region).

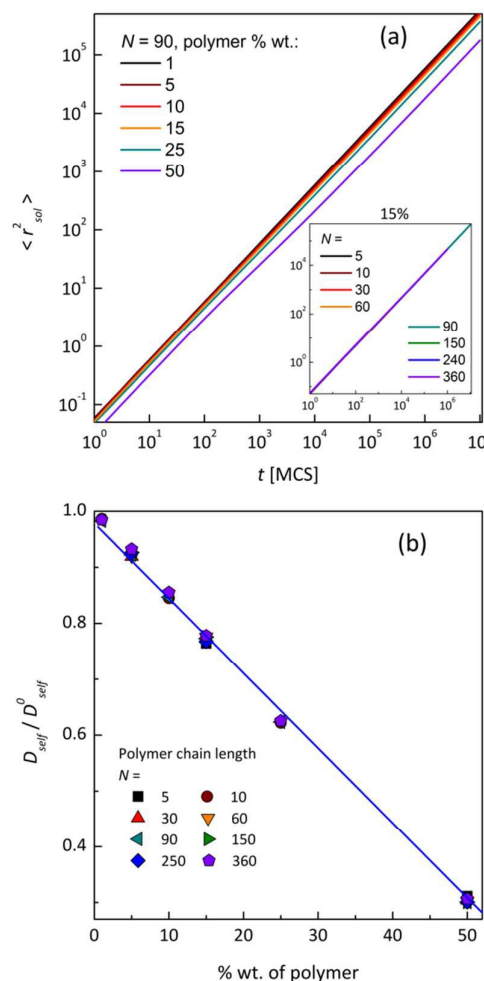


Fig. 3. (a) Mean-squared displacement $\langle r_{sol}^2 \rangle$ of solvent molecules as a function of time for different polymer concentrations. Inset shows exemplary $\langle r_{sol}^2 \rangle = f(t)$ dependences for one selected polymer concentration (15 %wt.) and various chain lengths; (b) Normalized (to pure solvent) self-diffusion coefficients obtained from Einstein relation for different polymer concentrations and different polymer chain lengths.

If polymer concentration increases, slowing down effect is more significant and reaches maximum (minimum of α exponent) near $t = 10^3$ MCS independently on polymer content. In longer time scales normal diffusion is recovered. Described above dynamic behaviour of solvent can be explained by a smaller amount of excluded volume from polymer grains and bonds than in concentrated solutions. Figure 4b presents the results for one selected polymer concentration (15 %wt.). Slight shift of minimum of $\alpha = f(t)$ dependences towards shorter times and less slowing down effect were found only for short chains ($N < 60$). For longer chains character of solvent diffusion is independent of polymer molecular mass.

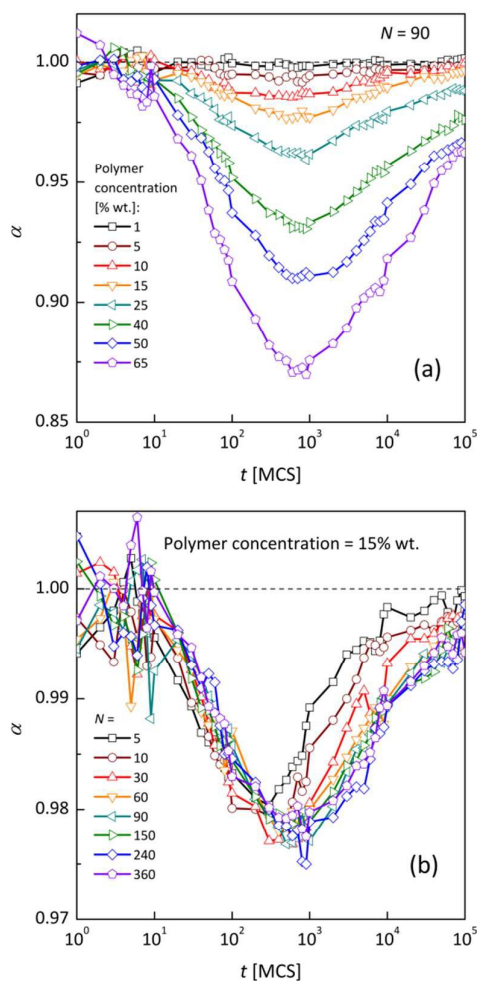


Fig. 4. Exponent α as a function of time: (a) for different polymer weight concentrations and (b) for various chain lengths N .

The polymer beads dynamics in short and intermediate time scales was also analyzed to confirm an influence of polymer chain length on solvent mobility in highly diluted systems. Figure 5 presents mean square displacement $\langle r_p^2 \rangle$ of unites-atoms (grains) averaged over all elements representing polymer without differentiation between “main chain” and “pendant group” elements. Expressed this way polymer mobility offers higher sensitivity to sub-diffusion effect than the center of mass diffusion, as Polanowski and Pakula showed [61]. Unfortunately, it is difficult to compare these results with experimental data because they do not correspond directly neither to segmental motions (accessible for broadband dielectric spectroscopy or dynamical mechanical analysis) nor to diffusion of macromolecule center of mass.

In Fig. 5a samples with various chain lengths (for polymer content = 15% wt.) are presented. Inset shows diffusion exponent α determined according to Eq. (4), for some selected samples. Three different diffusion regimes can be distinguished. Below 10^1 MCS normal diffusion is observed (slope = 1). Then, up to $10^5 - 10^6$ MCS, large slowing down is present (sub-diffusion zone). After that the normal diffusion starts to recover again. For the shortest chains minimal α is close to 0.4, for the longest ones – 0.3. Similar value ($\alpha = 0.5$)

was found for neat PVME (without any solvent) by Molecular Dynamics simulations.³⁴ Higher polymer concentration results in lower displacement of polymer elements. The differences in diffusion character vanish for chain lengths close to 90 polymer units. This corresponds well to chain length dependence of solvent relaxation times for short chains – Fig. 4b. Figure 5b shows the $\langle r_p^2 \rangle = f(t)$ dependences for one selected chain length ($N = 90$) and different polymer contents. Higher polymer concentrations result in lower diffusion of polymer elements. No threshold value can be observed. Such behavior relates to nonlinear increase of relaxation times of bound solvent in function of polymer content, what will be discussed in next section (compare Fig. 8).

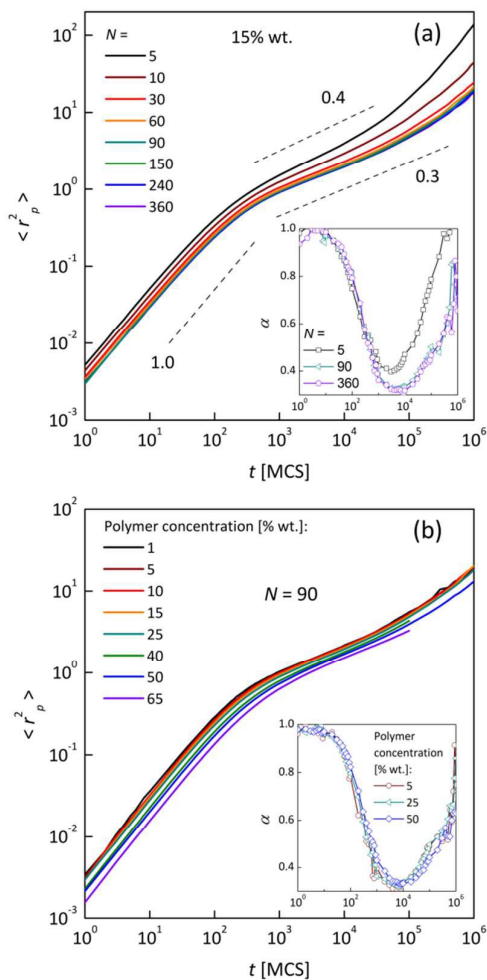


Fig. 5. Mean square displacement of polymer units as a function of time: (a) for different chain length and 15% wt. of polymer, (b) for various polymer weight concentration and $N = 90$. Insets show α exponent for selected cases. Dashed lines show slope values.

To validate the DLL simulation results, the relation presented in Fig. 3b was analyzed in frame of various models known from literature.⁵ Thus, the results were recalculated for easier comparison with experimental data as well as with theoretical predictions. In Fig. 6 the D_{self}/D_{self}^0 ratio is shown in semi-logarithmic representation as a function of polymer volume fraction (ϕ_p) on the background of experimental data collected for methyl methacrylate (MMA) – poly(methyl methacrylate)

(PMMA) and ethylbenzene (EtPh) – polystyrene (PS) systems. Additionally, a line representing Mackie-Meares model was added (dotted lines in Fig. 6). This model is one of the simplest and of the most popular models. It assumes, that the diffusion coefficient of small solvent molecule (D_{SM}), of the same size as the monomer unit is given by the equation:

$$\frac{D_{SM}}{D_{SM}^0} = \left(\frac{1 - \varphi_p}{1 + \varphi_p} \right)^2, \quad (9)$$

where D_{SM}^0 is a self-diffusion coefficient in pure solvent. Good agreement between the DLL results and experimental data (especially in a case of MMA – PMMA system) is well visible. Small deviation between DLL results and Mackie-Meares model results probably from three facts:

(a) Mackie-Meares model belongs to the diffusion models based on obstruction effect, what means that the polymer chain is treated as immobile; in the case of performed simulations macromolecules could move freely.

(b) In mentioned model diffusant (solvent) was assumed to be equal in size to polymer unit, while in simulations its size was two times smaller in comparison to the polymer unit.

(c) Mackie-Meares model does not take into account the free volume interactions in the system.

The free volume models seem to be more appropriate to describe the results of DLL simulations. However most of them introduce also other interactions. The Fujita's model⁴¹ assumes that the diffusion coefficient of small solvent molecule relates to the average free volume per molecule, temperature and size of diffusant. However, this model was used to characterize diffusion of various particles (including oligomers) in polymer solutions^{2,77,78}, gels⁷⁹ and even in solid state⁴², Massaro and Zhu⁵ stated that it is adequate to describe diffusion of small-sized molecules, mostly organic, in diluted and semi-diluted polymer solutions. Model proposed by Vrentas and Duda⁴⁴⁻⁴⁶ takes into account several physical parameters such as temperature, polymer concentration, solvent size and its molecular weight, activation energy for a solvent "jump" and even glass temperatures of both polymer and a solvent. One of the biggest disadvantages of this model is number of independent parameters (14) needed to apply it. It is also worthy to notice about Peppas and Reinhart model.⁴⁷ It is especially useful to describe hydrogel systems and polymer membranes, as it considers a mesh size of polymer network and hydrodynamic radius of a diffusant.⁸⁰

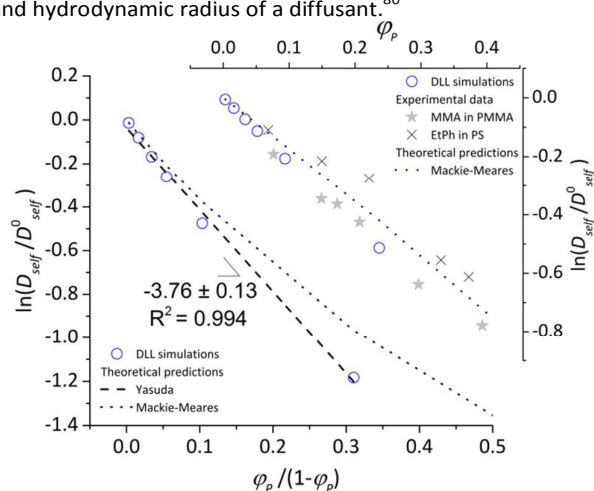


Fig. 6. Comparison between results of DLL simulation for selected polymer chain length $N = 90$, experimental data from⁴⁸ and theoretical predictions.^{42,50}

In performed studies only excluded volume interactions are taken into account. Thus, mentioned above models seem to be not fully appropriate to describe properly obtained simulation results. One of the simplest models based on free volume theory was proposed by Yasuda.⁴² Their main assumptions are very similar to those of DLL algorithm, as follow:

- polymer is less mobile than the solvent,
- the effective free volume is contributed mainly from a solvent,
- there is no additional interactions between polymer and the diffusing molecule,
- solvent diffusion decreases with increasing polymer concentration.

In result, the self-diffusion coefficient of small solvent molecule may be expressed as follow:

$$D_{self} = D_{self}^0 \exp\left(-\frac{B}{f_v^*} \left(\frac{\varphi_p}{1 - \varphi_p}\right)\right), \quad (10)$$

where f_v^* is a solvent free volume in the polymer solution. As Figure 6 shows, Yasuda's model can be well fitted to results obtained from simulations. Good agreement between obtained simulation results with both experimental data as well as theoretical model confirms the correctness of the DLL simulations results.

B. Diffusion of bulk and bound solvent

Figure 7 shows some exemplary autocorrelation curves $A(t)$ (defined according to Eq. (5) – see Experimental section) for solvent in polymer solutions differ on concentration. It is clearly visible that the autocorrelation functions of bulk solvent are independent of polymer concentration.²⁸ The autocorrelation functions for bound solvent are sensitive to polymer concentration. The higher polymer concentration the lower diffusivity of bound solvent.

To qualitative comparison of solvent mobility in different vicinity of polymer the characteristic diffusion relaxation times of solvent in various states were calculated using KWW equation (see Eq. (6)). Relaxation times for various solvent states as a function of polymer content are presented in Fig. 8a. Relaxation times for bulk solvent increase very slightly with polymer concentration. This effect insignificantly relates to cooperativity of movement and results from large slowing down of both polymer and bound solvent (compare to Fig. 5).

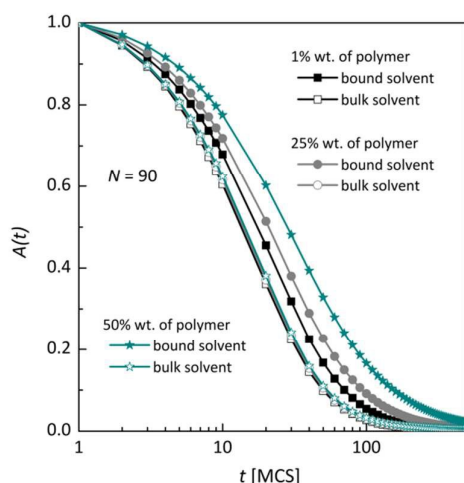


Fig. 7. Autocorrelation functions for bound and bulk solvent for solutions differ on polymer concentration. Polymer chain length was 90.

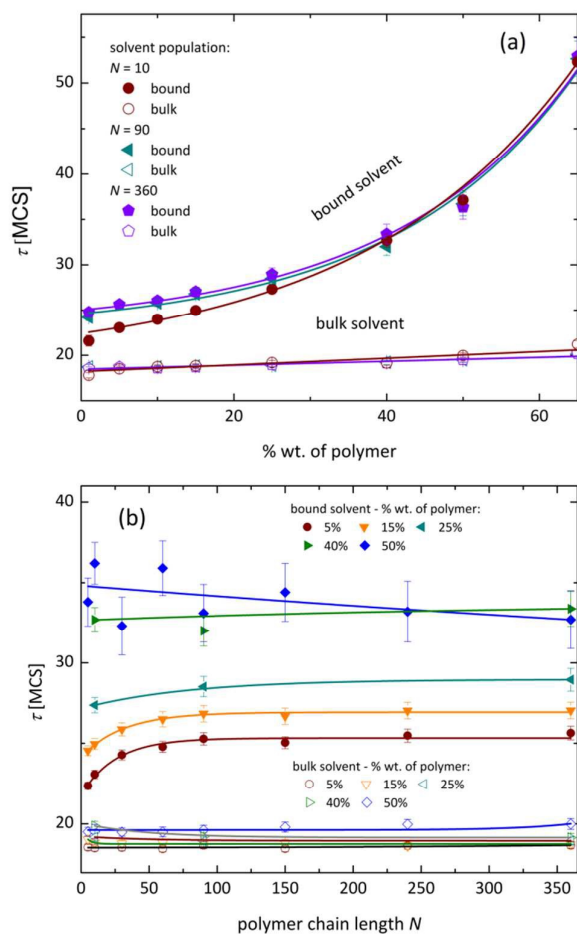


Fig. 8. Diffusion relaxation times for bound and bulk solvent as a function of (a) different polymer concentration for selected polymer length, (b) different polymer chain length for selected polymer contents.

As expected, bulk solvent dynamics do not depend on polymer chain length – see Fig. 8b. In the case of bound solvent, effect of polymer content is clearly seen. Higher relaxation times of

bound solvent in comparison to bulk solvent were found even for highly diluted solutions. For diluted systems relaxation times of bound solvent depends also on polymer chain length. Relaxation times of bound solvent for samples containing short chains are smaller than for samples with longer chains. The threshold chain length, where no further differences between relaxation times are observed, is close to 90, as Fig. 8 presents. The differences in relaxation times of bound solvent vanish for higher polymer contents, and are not observed for system with polymer concentration higher than 40% wt.. Such behaviors suggest that large polymer content reduces long-distance mobility of short chains and, in consequence, influences solvent dynamics.

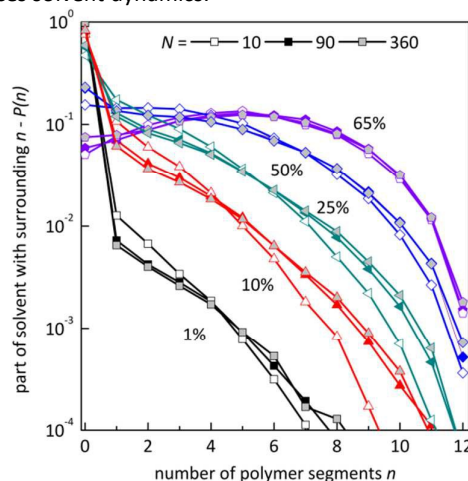


Fig. 9. Histograms of normalized number of solvent molecules surrounded by n number of polymer elements for different polymer content (in %wt.) and for selected chain lengths.

As it was shown, diffusion relaxation times of bound solvent are significantly influenced by polymer concentration and, in limited range, also by chain length. This can be explained taking into account that the molecular mobility is governed by system morphology and assuming cooperativity of movements. Thus, the polymer mobility influences solvent mobility in direct proximity of polymer chains. Higher mobility of short chains is suppressed in samples with high polymer concentration. This fact can be confirmed by analysis of an average neighborhood in the samples.

Figure 9 presents the histograms of normalized number of solvent molecules surrounded by n number of polymer elements for systems with different polymer content and for selected chain lengths. In diluted solutions containing short chains the fraction of solvent with small number of neighboring polymer elements (< 4) is more pronounced than in solutions containing longer chains. Also, the fraction of solvent with larger number of polymer elements in neighborhood (> 6) is smaller for chains of length 10 than for 90 and higher. No significant differences are seen for systems containing chains of length 90 and longer. It means that in the system with low polymer concentration short chains are surrounded more uniformly by solvent than the longer ones. The reason is different homogeneity of the systems. Long chains form coils where solvent “inclusions” are surrounded mainly by polymer. The shorter the chains the better dispersion of polymer chains.

This observation is confirmed by analysis of computational box snapshots for various polymer concentration and chain lengths (some exemplary snapshots are presented in Fig. 10). The solutions of PVME with chain length 360 are clearly more heterogeneous in comparison to solutions of PVME with chain length 10. The regions of high polymer content and empty spaces (pores) filled with solvent are well visible for systems containing longer polymer chains. Contrarily, for short polymer chains systems are homogenous even for relatively high polymer concentrations.

Figure 11a shows normalized radial polymer–polymer (pp) pair correlation function prepared according to Eq. (7). Systems containing various chain lengths are shown for one selected polymer content (15 %wt.). Values close to 1 stands for pure solvent, while 0 for pure polymer. For short chains uniform solvent concentration is reached faster than for longer ones. The chain length effect vanishes for macromolecules containing more than 90 polymer units. Also, for the shortest measurable distance (equal one lattice constant) shorter chains are statistically surrounded by more solvent molecules than the longer ones.

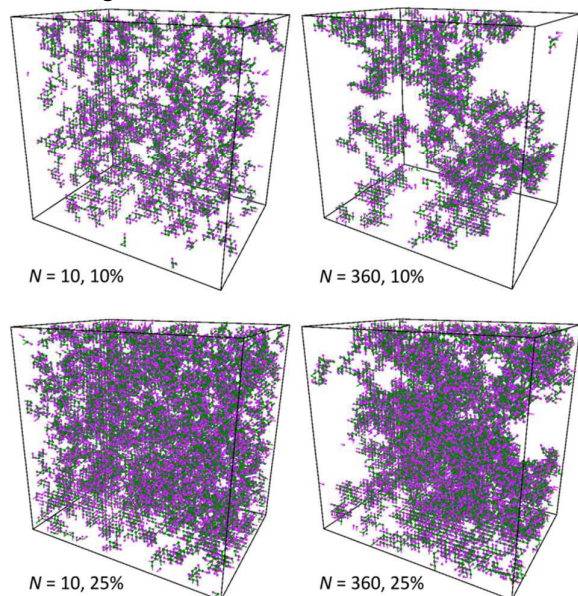


Fig. 10. Examples of system snapshots for various polymer weight content and chain lengths N . Main chain and pendant groups are presented with different colors. Solvent molecules are not shown for clarity.

This fact also indicates enhanced homogeneity in that case. Figure 11b presents the dependence of diffusion time for bound solvent as a function of characteristic parameter ξ for the solutions containing 15 %wt. of polymers with different lengths. The ξ parameter was determined according to Eq. (8) and may be used as a measure of system homogeneity. High correlation between these two parameters is well visible. It means that the bound solvent diffusivity is strictly joined with the morphology (homogeneity) of polymer system.

The homogeneity of studied systems should be also reflected in percolation threshold (one can expect that for more homogenous systems the percolation threshold for polymer chains should be shifted to lower values). As Adamczyk et al.⁸¹ showed for 2D systems, the percolation threshold is an

important factor influencing anomalous diffusion in polymer solutions. Performed herein rough estimation of percolation thresholds showed that for polymer concentrations higher than 20 %wt., polymer chains always percolate independently of chain length. For the concentrations lower than 7–8 %wt., percolation of polymer chains was not observed in any sample. It was also impossible to detect any specific correlation between diffusive properties and percolation for investigated 3D systems. Nevertheless, determination of reliable phase diagram of studied system seems to be very interesting problem for future studies. Moreover, solvent molecules percolated in all investigated systems independently of polymer concentration and chain length.

Finally, it is necessary to underline the consistency between presented results and FCS data^{4,6,7} showing a deviation from the single Fickian diffusion model in PNIPAAm cross-linked systems.

It was shown that two types of diffusion processes may be distinguished in the PNIPAAm gels under the volume phase transition. The authors correlated them with two possible diffusant trajectories in heterogeneous systems:

(a) through solvent-rich region only – related to fast diffusion contribution in the experimental autocorrelation function and to normal diffusion,

(b) through polymer-rich regions – related to slow diffusion contribution in the experimental autocorrelation function and to sub-diffusion.

However, referred FCS experiments relate to the diffusion of small tracer molecules, while the reported herein results of MC simulations correspond to solvent diffusion, their qualitative comparison seems to be fully rational. Especially, taking into account much lower size of both solvent and tracer molecules in comparison to significantly larger and less mobile macromolecules or networks.

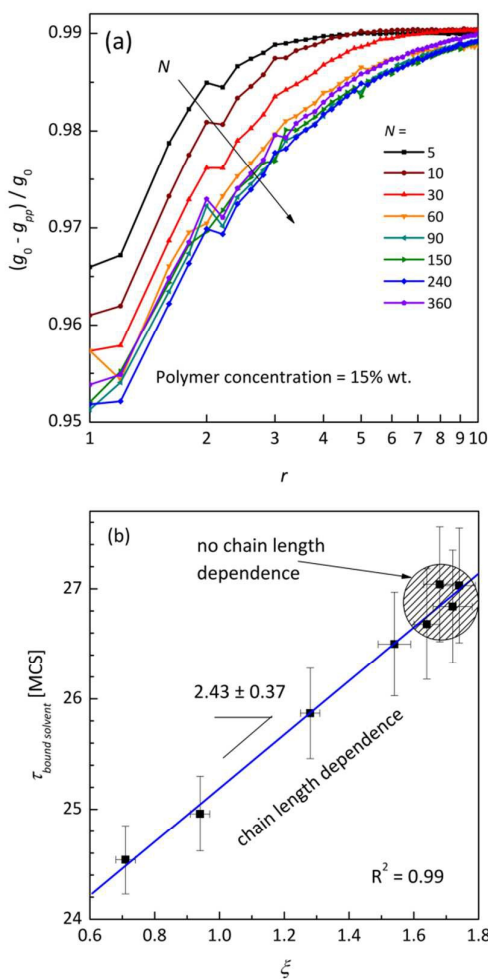


Fig. 11. (a) Normalized (to pure FCC lattice g_0) radial polymer–polymer pair correlation function presented as difference function. Various chain length are shown for selected polymer weight content (15% wt.). (b) Correlation between diffusion relaxation time of bound solvent and ξ parameter describing the homogeneity of polymer-solvent systems from Eq. (8).

Conclusions

Results of simulations performed with use of DLL model are consistent with experimental data^{4,6,7} as well as with theoretical predictions (Yasuda's model based on free volume concept)^{39,42}. Two different solvent states differed on mobility were evidently distinguished in polymer solutions. The first one with high molecular mobility independent of polymer concentration corresponds to bulk solvent in real systems. The second state relates to so called bound solvent. In this case the solvent diffusivity strongly depends on polymer content in the system. Moreover, in diluted solutions, the bound solvent diffusion is affected by polymer chain length. These specific behaviours were correlated to the homogeneity of polymer systems. The solutions contain long chains are more heterogeneous in comparison to solutions with short lengths due to the coil formation. In result, short chains are surrounded more uniformly by solvent than the longer ones in the diluted solutions. For concentrated solutions length chain effect is lost because a fraction of bulk solvent significantly

decreases and most of solvent molecules are surrounded by polymer elements.

Presented results are a good introduction to study polymer systems with complex architecture such as dendrimers, stars, brushes, networks. Thus, the further investigations focused on an influence of various topology of macromolecules on solvent diffusion are planned.

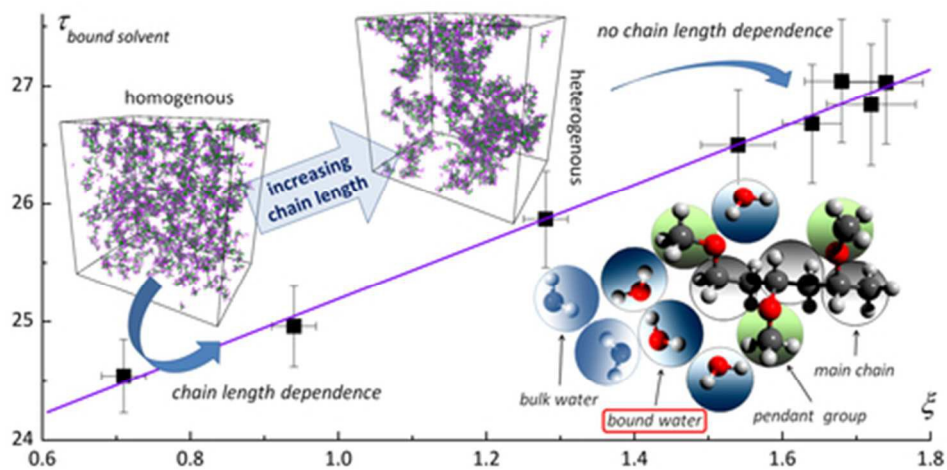
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