diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

ESRI Study of Diffusion Processes in Poly(2-Hydroxyethyl Methacrylate) Gels and Concentrated Solutions

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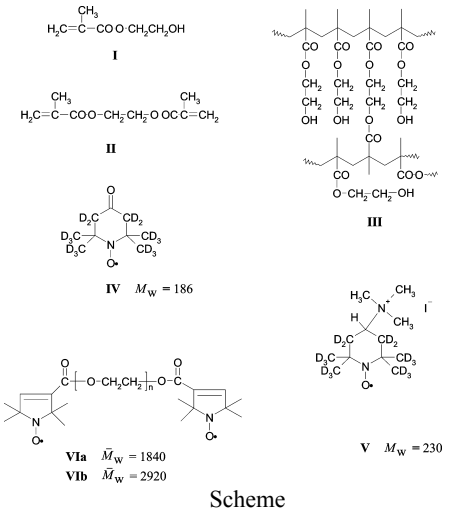
1. Introduction

Electron spin resonance imaging (ESRI) can provide information on macroscopic translational diffusion of paramagnetic tracers in various matrices.[1,2] For the purpose of estimation of tracer diffusion coefficients it is sufficient to measure and simulate time dependence of one-dimensional (1D) tracer concentration profiles in the sample. Each of the profiles can be determined by deconvolution of the ESR spectrum taken with the gradient coils-off out of the spectrum taken with gradient coils-on. Macroscopic measurements are interpreted in terms of the description of diffusion given by Fick's second law.[3]

The contribution is devoted to study of diffusion in the interesting region of semidilute and concentrated polymer solutions as well as in swollen polymer gels. Despite several diffusion models[4,5] trying to explain diffusion of low-molecular weight tracers in concentrated solution, a consensus has not been attained yet.[6] Especially in the case of gels, reliable data are comparatively sparse and diffusion mechanisms are unsatisfactorily explained.

2. Experimental

For ESRI measurements we used poly(2-hydroxyethyl methacrylate) (poly(HEMA)) gels **(III)** swollen with methanol and concentrated methanolic solutions of linear poly(HEMA) as matrices. The samples were filled in glass capillary tubes (i.d. ca 1 mm), sample lengths ranged from 3 to 10 mm. The diffusion was started by topping the sample with ca 0.2 μL of 0.05 M methanolic solution of one of the paramagnetic tracers **(IV-VI)**. The capillary was then placed, with its axis parallel to the vertical gradient direction, in the cavity of ESR spectrometer.



Scheme

3. Results

The dependence of diffusion coefficients of the tracers on the poly(HEMA) concentration in methanolic solution was analyzed in the frame of Petit's[4] and Phillies'[5] models. The respective equation for the tracer diffusion coefficient is given by relations

$D = D_0 \exp(-\alpha_1 c^{\nu_1})$ and $D = D_0/(1+\alpha_2 c^{2\nu_2})$, where D_0 is the diffusion coefficient of the tracer in the absence of the polymer, c is the polymer concentration and α,ν are the model parameters. Both models fit the experimental data well at a similar level of accuracy as shown in Fig. 1 (fits to the Phillies' and Petit's models are shown by solid and dashed lines, respectively).

Lower diffusion coefficients measured in HEMA gels (given by empty symbols in Figure 1) compared with poly(HEMA) solutions in matrices with the same polymer concentration follow from Fig. 1. Practically the same relative decrease in diffusion coefficients for all four tracers was observed when comparing both mentioned matrices.

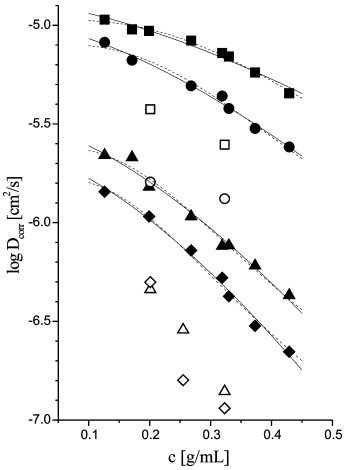


Fig.1: Dependence of the diffusion coefficients of the tracers on the polymer concentration in solutions of poly(HEMA) (■ **IV**, ● **V**, ▲ **VIa**, ◆ **VIb**) and in HEMA gels (empty symbols).

4. Conclusion

Experimental arrangements for ESRI experiments aimed at determination of macroscopic translational diffusion of paramagnetic tracers in polymer solutions and gels and methods of treatment of experimental data based on deconvolution and fitting procedures were elaborated. Diffusion coefficients for four paramagnetic tracers in nondilute poly(HEMA) solutions in methanol and in HEMA gels equilibrium-swollen with methanol were determined. Both solution and gel matrices were characterized by the hydrodynamic correlation length measured by DLS technique. The dependences of the diffusion coefficients on the poly(HEMA) concentration in methanolic solutions were well fitted within the frame of both Phillies' and Petit's models at approximately the same level of accuracy. Lower values of diffusion coefficients for all four tracers were found in HEMA gels compared with polymer solutions containing the same concentration of the polymer. The data found indicate that slowing down of the tracer diffusion in gels depends not only on the presence of additional permanent crosslinks as demonstrated by shortening hydrodynamic screening length of the matrix but also on microscopic heterogeneities always present in gels.

References

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