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Tracer Diffusion in HEMA Based Polymer Hydrogels

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1. Introduction

Dependence of diffusion coefficients characterizing mutual diffusion and self-diffusion of oligomeric tracers on the composition of equilibrium swollen polymer hydrogels was studied. The hydrogels were characterized by their dynamic correlation lengths ξ measured by DLS and by concentrations of elastically active network chains ν determined by measurement of their elastic moduli. Diffusion coefficients of macroscopic translational diffusion of paramagnetic tracers (poly(ethylene glycol)s spin-labeled with nitroxides) in gels were measured by electron spin resonance imaging (ESRI) [1], self-diffusion and mutual diffusion coefficients of corresponding diamagnetic tracers (poly(ethylene glycol)s without nitroxides) were measured by pulsed-gradient stimulated NMR spin-echo (PGSTE) and dynamic light scattering (DLS), respectively.

2. Experimental

Hydrogels A, B, C, and D equilibrium-swollen with water were prepared by light-induced copolymerization of 2-hydroxyethyl methacrylate (HEMA) with 2-(2-hydroxyethoxy)ethyl methacrylate (DEGMA) using 2,3-dihydroxybutane-1,4-diyl dimethacrylate as crosslinker and 2-hydroxy-2-methyl-1-phenylpropan-1-one as initiator. Compositions of batches leading to equilibrium-swollen hydrogels given in the Table were selected in preliminary experiments. Copolymerization was performed in sealed sample tubes the diameter of which was designed to meet demands of particular experiments: thin glass capillary of o.d. $\approx$ 1 mm for ESRI, glass sample tube of o.d. 4 mm for PGSTE NMR and glass sample tube of o.d. 10 mm for DLS, gravimetry and measurement of elastic moduli. Possible differences between the water contents in the batch and equilibrium water contents in the hydrogels were checked gravimetrically in long-term swelling experiments.

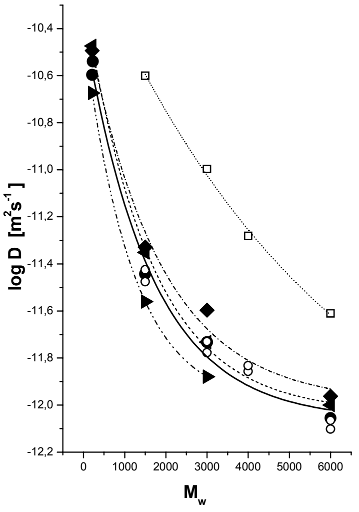
ESRI experiment was started by topping the hydrogel in the glass capillary (o.d. $\approx$ 1 mm, gel cylinder length 3 - 5 mm) with a drop of aqueous solution of the tracer (0.2 μL, 10^{-2} mol/L), the capillary was resealed and placed in the spectrometer cavity with the cylinder axis oriented vertically, parallel to the direction of the magnetic field gradient. Shapes of concentration profiles of the paramagnetic tracer inside the sample along the magnetic field gradient, approaching equilibrium distribution due to the tracer diffusion, were measured by ESRI [2] at suitable times after the diffusion start.

Diffusion coefficients of the paramagnetic tracers were found by analysis of the time dependence of the tracer concentration profiles, based on the solution of Fick's equation appropriate for the sample geometry [3]. Diffusion coefficients of the diamagnetic derivatives of the tracers added to the polymerization mixture before polymerization were determined using PGSTE NMR and DLS.

3. Results

Data presented in the Table clearly show that the concentration of elastically active network chains v increases and dynamic correlation length ξ decreases with increasing concentration of the crosslinker in gels. In addition to the expected dependence of the diffusion coefficients of the tracers on their molecular weight and on the polymer concentration in the gel shown in the Figure, the experiments revealed their dependence on the crosslinker concentration (concentration of elastically active network chains). The differences found in diffusion coefficients measured in gel D by ESRI and QELS compared with the coefficients measured by PGSTE indicate that these techniques measure different diffusion processes.

	Gel			
	A	B	C	D
$\frac{\text{HEMA}}{\text{HEMA+DEGMA}}$ [mol%]	54	30	54	54
Crosslinker [wt%]	0.52	1.45	1.30	4.20
Polymer fraction v_0	0.39	0.35	0.39	0.39
c_{polymer} [g/mL]	0.44	0.39	0.44	0.44
v [mol/m^3]	30	39	57	83
ξ [nm]	4.6	5.0	4.2	3.45



Diffusion coefficients of PEG tracers in gel A (▶), B (◀), and C (◆), determined by ESRI and in gel D determined by ESRI (●), PGSTE (○) and by QELS (□).

4. Conclusion

The presented data indicate complexity of diffusion processes in polymer gels. Elucidation of the dependence of the diffusion coefficients on the gel composition requires more experimental data measured by various techniques in well characterized gel matrices covering a broader range of polymer fractions, crosslinking densities, and ratios of permanent and temporary crosslinks.

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