Molecular motion in concentrated solutions of spherical polystyrene microgels studied with the pulsed field gradient n.m.r.

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Results of a pulsed field gradient n.m.r. study of the motion of swollen spherical microgels in solution are presented. We have measured the echo attenuation (or the incoherent dynamic structure function) of the protons in the microgels in the dynamic range from $qR \ll 1$ up to $qR \approx 1.8$ (where q = scattering vector and R = particle radius), and in the timescale from a few milliseconds up to 100 ms. Rotational diffusion of the microgel spheres could not be detected with certainty. However, restricted diffusion of the spheres within a cage was observed, in particular for the large microgel with $R = 125$ nm, where the short-time diffusion could be monitored. For apparent volume fractions $\Phi > 0.6$, the diffusion is restricted within a space scale of root mean square displacement, $\langle z^2 \rangle^{1/2} \approx 120$ nm. With increasing volume fraction of the microgels in solution, $\Phi > 0.6$, the diffusion becomes increasingly restricted. This crossover corresponds to the dynamic glass transition observed by Bartsch *et al.* for a similar system using quasielastic light scattering.

(Keywords: polystyrene microgels; concentrated solutions; self-diffusion)

INTRODUCTION

The pulsed field gradient nuclear magnetic resonance (p.f.g. n.m.r.) technique is widely used for observation of the long-range dynamics of molecular systems[1,2]. P.f.g. n.m.r. is a generalized incoherent quasielastic scattering experiment; the measured quantity is the incoherent intermediate structure function $S(q, t)$ of the protons in the system[3], commonly called echo attenuation and denoted by Ψ or E_q. The generalized scattering vector q of p.f.g. n.m.r. is given by $q = \gamma \delta g$, where γ is the gyromagnetic ratio of the proton, δ the width and g the magnitude of the field gradient pulses. In a typical p.f.g. n.m.r. experiment $1/q$ is in the order of 1 μm, i.e. in homogeneous non-structured systems we measure in the diffusion limit and obtain the self-diffusion coefficients of the species in the system. However, with p.f.g. n.m.r. the observation of more complicated modes of motion and structures is possible, which in molecular systems mostly appear in space scales smaller than the micrometre region. Examples are the dynamics of polymer molecules and molecules in micellar solutions and porous systems. For this purpose it is necessary to increase the field gradient intensity and hence q. At present, pulsed field gradients of about 50 T m^{-1} are applied and values of $1/q < 100$ nm are reached[4-6]. A very promising development is n.m.r. in the stray field of a cryomagnet[7,8].

The motion of sterically stabilized spherical particles in solution has been studied intensively[9,10]. These particles show interesting features: different dynamic ranges of short-time and long-time diffusion, hydrodynamic interaction and direct hard-core interaction. The motion of these particles is also a matter of intense theoretical investigation. Quasielastic light scattering is a very convenient method to study these systems experimentally, preferentially in dilute solution under the condition $qR \ll 1$, where R is the particle radius. For large particles $qR \geqslant 1$ can be reached, and in dense systems the short-time diffusion can be detected in the experiment[9-11].

Antonietti and co-workers[12,13] have synthesized spherical crosslinked polystyrene beads; these beads swell in solution behaving like 'rubber balls', and no sterical stabilization is necessary. A p.f.g. n.m.r. study of these spherical particles in solution is possible since the nuclear magnetic relaxation times of the swollen network chains are long enough to provide a spin echo in the n.m.r. experiment. For solid latex spheres the short nuclear magnetic relaxation times prevent an n.m.r. signal in the

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