Dynamic behaviour of semidilute solutions and gels of poly(methacrylic acid)

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We have used photon correlation spectroscopy to compare the dynamic properties of poly(methacrylic acid) solutions and gels as a function of polymer concentration and degree of crosslinking. The slow diffusive mode, which is frequently observed in aqueous polyelectrolyte solutions, was not found in poly(methacrylic acid) gels or in solutions of branched macromolecules below the gel point. The intensity correlation function of samples at the gel threshold has a logarithmic time dependence $\sim t^{\phi}$ with ϕ lying between 0.3 and 0.25, which is consistent with the percolation prediction.

(Keywords: dynamic behaviour; poly(methacrylic acid); solutions; gels)

This paper is a continuation of our previous work[1–4] dealing with the dynamic properties of polyelectrolyte solutions and gels of poly(methacrylic acid) (PMA), under conditions of strong electrostatic interactions. This polymeric system has been selected because of the possibility of varying the charge per unit length of the molecules by neutralization with a suitable alkali. The first paper[1] dealt with the influence of the degree of neutralization, concentration, and molecular weight, the second[2] with the influence of temperature and the third[3] with the effect of solvent dielectric permittivity (methanolic solutions of PMA) on the polyelectrolyte solution dynamics. The fourth paper[4] is devoted to the swelling behaviour of PMA gels.

In this paper we report quasielastic light scattering (QELS) experiments performed with fully neutralized PMA solutions and chemically crosslinked gels. The purpose was to establish similarities and differences between the gel and analogous solutions.

The samples used in this study were made by copolymerizing sodium methacrylate (SMA) and bisacrylamide (Bis) using ammonium persulphate as initiator (40 mg per 100 ml), and TEMED (160 μl per 100 ml) as catalyst in the presence of water. Two series of samples differing in crosslink content, $f_{\mathrm{Bis}} = [\mathrm{Bis}]/([\mathrm{SMA}] + [\mathrm{Bis}]) = 0\%$ (linear polymer) and 4% (gel), respectively, with a total monomer concentration, $c = [\mathrm{SMA}] + [\mathrm{Bis}]$, varying from 0.05 to 0.1 g ml^{-1} were prepared. A third set of samples with total monomer concentration fixed at 10×10^{-2} g ml^{-1} and crosslink content varying from 1 to 4% was also investigated. By visual observation we could identify the samples with $c = 5 \times 10^{-2}$ g ml^{-1}, $f_{\mathrm{Bis}} = 4\%$ and $c = 10 \times 10^{-2}$ g ml^{-1}, $f_{\mathrm{Bis}} = 2\%$ as the gel threshold samples. The weight-average molecular weight of the linear PMA increases monotonically from 2×10^5 at $c = 5 \times 10^{-2}$ g ml^{-1} to 4×10^5 at $c = 10 \times 10^{-2}$ g ml^{-1}.

Measurements of the scattered light intensity autocorrelation function, $g_2(t)$, at a constant temperature of 20°C and scattering angle of 90° were performed using a standard laser light multi-angle spectrometer with an argon ion laser and a Brookhaven Instruments (model BI-2030AT) 256-channel digital correlator. The correlation functions were analysed by the CONTIN program[5].

Figure 1 compares the diffusion constant distributions for PMA solutions ($f_{\mathrm{Bis}} = 0\%$) with PMA gels ($f_{\mathrm{Bis}} = 4\%$) having the same total monomer concentration in the range of 0.05 to 0.1 g ml^{-1}. The distribution shown in *Figure 1a* for PMA solutions has a comparatively more complicated dynamic structure than that of the corresponding gels. Three well-separated peaks centred at the fast (f), D_{f}, medium (m), D_{m}, and slow (s), D_{s}, diffusion coefficients can be identified. The most intense peak in PMA solutions nearly coincides with the corresponding peak in gel samples and D_{f} decreases slightly with increasing concentration (cf. *Figure 1* and *Table 1*). This peak corresponds to the network (co-operative) diffusion mode, which reflects the concentration fluctuations of polyions and counterions. The m-mode, where the scattering amplitude decreases with increasing concentration, finally disappears at $c = 10\%$. Such modes can be observed in light scattering experiments as a consequence of the size polydispersity in the system[6]. In this particular case, the m-mode corresponds to the interdiffusion (self-diffusion) of PMA macromolecules in the polymeric matrix of entangled semidilute solutions. According to g.p.c. measurements, the polydispersity of PMA samples decreases with increasing concentration, which results in a decrease of the scattering amplitude of the m-mode. Both D_{s} and the

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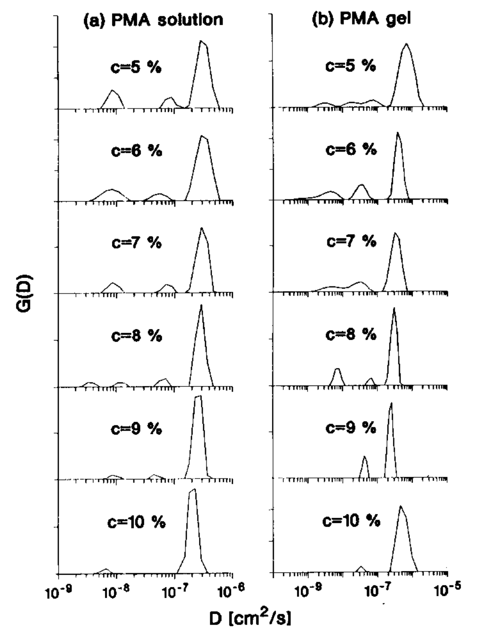

Figure 1 Comparison of diffusion constant distributions for poly (methacrylic acid) solutions ($f_{Bis} = 0\%$) (a) and gels ($f_{Bis} = 4\%$) (b). Data obtained by Laplace inversion of QELS autocorrelation curves measured at $\theta = 90°$ and $T = 20°C$

Table 1 D_f, D_s and A_s/A_f for a series of linear PMA solutions ($f_{Bis} = 0$), and D_f and the relative amplitude A_f for a series of gel samples ($f_{Bis} = 4\%$)

	Linear PMA solutions			PMA gels	
$c \times 10^2$ (g ml^{-1})	$D_f \times 10^7$ (cm^2 s^{-1})	$D_s \times 10^9$ (cm^2 s^{-1})	A_s/A_f	$D_f \times 10^7$ (cm^2 s^{-1})	A_f
5	3.26	8.99	0.21	5.55	0.59
6	3.28	8.78	0.22	4.50	0.66
7	3.02	8.64	0.14	3.59	0.74
8	2.86	7.17	0.11	2.98	0.76
9	2.63	8.81	0.04	2.47	0.82
10	2.66	6.24	0.03	2.79	0.85

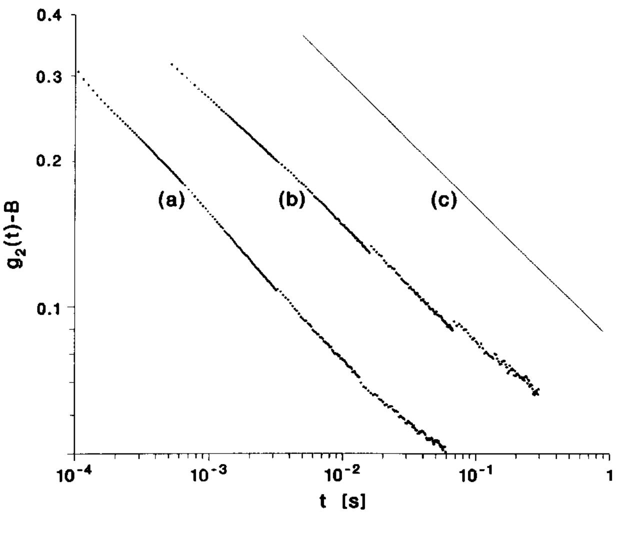

Figure 2 Long-time tail of the autocorrelation function plotted logarithmically (after subtracting baseline, B) for gel threshold samples: (a) $c = 5 \times 10^{-2}$ g ml^{-1}, $f_{Bis} = 4\%$ and (b) $c = 10 \times 10^{-2}$ g ml^{-1}, $f_{Bis} = 2\%$. Also shown in (c) is the line with slope = 0.27

ratio of scattering amplitudes A_s/A_f decreases (cf. *Table 1*) with increasing concentration. This slow mode can be attributed, by analogy with our previous findings[1], to slow concentration fluctuations with large correlation length, probably due to the formation of clusters or domains. Such slow modes are frequently found in aqueous polyelectrolyte solutions[1,2] and the origin of these modes is not well understood, as yet.

In addition to the strong f-peaks, the results of CONTIN analysis for gel samples gave broad distributions having a complex structure with several peaks (cf. *Figure 1b*), especially at lower concentrations. According to our previous results[7,8], these distributions may be interpreted as an interdiffusion mode for the sol in the gel matrix. Since the sol content inside the gel decreases with increasing c, the corresponding scattering amplitude decreases, too. We note that in the weakly gelled samples ($c = 5$–7%) this slow mode spans a range of D values of almost two orders of magnitude, suggesting that there may be a continuous spectrum of dynamical modes in the gel threshold sample.

To further test this idea, *Figure 2* shows the baseline subtracted autocorrelation function plotted logarithmically for the gel threshold samples ($c = 5 \times 10^{-2}$ g ml^{-1}, $f_{Bis} = 4\%$ and $c = 10 \times 10^{-2}$ g ml^{-1}, $f_{Bis} = 2\%$). The long-time tail follows a power law with exponent $\Phi = 0.3$ and 0.25, respectively, which is close to $\Phi = 0.27 \pm 0.03$ reported for silica[9] and $\Phi = 0.34$ for poly(methyl methacrylate) gels[10] at the gel point. Such autocorrelation functions correspond to the dynamics of interacting polymer clusters having mass distribution of the percolation type[9].

Contrary to neutral solutions and gels, where the co-operative diffusion coefficient D_c increases with polymer concentration, in PMA solutions and gels D_c ($\equiv D_f$) decreases for a given degree of ionization (cf. *Table 1*). This decrease is somewhat more pronounced in gel samples than in solutions. A similar c dependence of D_c has also been reported for poly(acrylic acid) gels[11], where a qualitative explanation based on concentration dependences of the longitudinal modulus and the friction coefficient was given. D_c is insensitive to the variation of the degree of crosslinking (f_{Bis}) for concentrations well above the gel threshold.

The slow mode was not found in PMA gels or in solutions of branched PMA molecules below the gel point. This means that the presence of crosslinks prevents the formation of intermolecular domains (clusters), and thus also the occurrence of the slow mode.

REFERENCES

1 Sedlák, M., Koňák, Č., Štepánek, P. and Jakeš, J. *Polymer* 1987, **28**, 873
2 Sedlák, M., Koňák, Č., Štepánek, P. and Jakeš, J. *Polymer* 1990, **31**, 253
3 Sedlák, M., Koňák, Č. and Labský, J. *Polymer* 1991, **32**, 1688
4 Koňák, Č. and Bansil, R. *Polymer* 1989, **30**, 677
5 Provencher, S. W. *Makromol. Chem.* 1979, **180**, 201
6 Phillies, G. D. J. *J. Chem. Phys.* 1974, **60**, 983; 1983, **79**, 2325; Pusey, P. N., Fijnaut, H. M. and Vrij, A. *J. Chem. Phys.* 1982, **77**, 4270
7 Fang, L., Brown, W. and Koňák, Č. *Polymer* 1990, **31**, 1960
8 Koňák, Č., Jakeš, J., Brown, W. and Fang, L. *Polymer* 1991, **32**, 1077
9 Martin, J. E. and Wilcoxon, J. P. *Phys. Rev. Lett.* 1988, **61**, 373
10 Fang, L., Brown, W. and Koňák, Č. *Macromolecules* 1991, **24**, 6839
11 Schosseler, F., Ilmain, F. and Candau, S. J. *Macromolecules* 1991, **24**, 225