Dynamic light scattering from polymer solutions and gels at the gelation threshold

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(*Received 20 March 1990; revised 24 August 1990; accepted 24 August 1990*)

The purpose of this communication is to report relaxation time distributions derived from dynamic light scattering measurements, close to the gelation threshold, for PMMA gels swollen in butylacetate. The distributions are composed of contributions from two diffusive (K^2-dependent) modes corresponding to collective diffusion of the gel matrix and the interdiffusive modes of sol components inside the gel matrix. While the collective diffusion is typified by a unique value of the correlation length, the latter are described by a very broad distribution due to substantial polydispersity. K-independent structural relaxations, which are usually present in semidilute solutions in poor solvents, are not present.

(Keywords: polymer solutions; gels; dynamic light scattering; polymethylmethacrylate)

INTRODUCTION

A number of authors have used dynamic light scattering (d.l.s.) to investigate the properties of dilute gels[1–5]. For example, Tanaka *et al.*[2] used this technique to measure the collective concentration fluctuations in polyacrylamide (PA)/water gels and observed that the autocorrelation function of the scattered light is a single exponential with decay rate $\Gamma = D_c K^2$, where D_c is the collective diffusion coefficient and K is the scattering wave vector. These authors also presented a model in which the gel was considered as an elastic continuum and they derived relationships for the dynamic structure factor. D_c is then related to the high frequency longitudinal modulus M; $D_c = M/f$, where f is the total friction of polymer against solvent per unit volume. Single exponential autocorrelation functions have been reported by many groups for different gels in good solvents well above the gelation threshold[2,4]. However, non-exponential correlation functions have been mentioned for PA gels close to the gelation threshold and thus resemble in this respect polymers in semidilute solution in poor (Θ) solvents[6–8].

To further amplify the apparently complex behaviour at the gelation threshold, we report in this paper an analysis of time autocorrelation functions measured over eight decades of delay time for binary polymethylmethacrylate (PMMA)/butyl acetate solutions and gels as a function of the crosslinking degree and scattering vector. We observe a complex dynamic behaviour corresponding to the superposition of two diffusive processes: the collective diffusion mode of the gel (pseudogel) matrix; and the interdiffusive mode of a sol inside the gel matrix. Modes corresponding to the K-independent structural relaxations observed in semidilute solutions of linear polymers in poor (Θ) solvents[6–8] were not found.

EXPERIMENTAL

Sample preparation

The samples used in these experiments are PMMA solutions and gels obtained by copolymerizing methacrylate monomer (MMA) with small amounts of ethylene-dimethacrylate (EDMA) as the crosslinking agent in the presence of butyl acetate. A set of samples with total monomer concentration $C = 10\%$ (v/v) was prepared with different degrees of crosslinking: $f_e = [\text{EDMA}]/[\text{MMA}]$ varying between 0% (the linear polymer) to 6% (gel). The reaction was initiated with azobisisobutyro-nitrile (10 mg per ml of MMA) and allowed to proceed for seven days at 50°C in cylindrical light scattering cells. By the end of this period, the gelation reaction was complete with a conversion of about 95%. All monomer solutions were first filtered using 0.22 μm filters (Millipore). Because at f_e values greater than 5% further increase in crosslinking produces partial phase separation and the samples become opaque, only samples with $f_e < 5\%$ were used for light scattering.

Apparatus

Measurements were made using a dynamic light scattering apparatus in Uppsala previously described[9]. The light source was a 35 mW He Ne laser. An ALV-Langen, multibit, multi-tau autocorrelator was operated with 23 simultaneous sampling times covering approximately 8 decades in delay time. The samples were thermostated at 25°C in a refractive index matching liquid (decalin).

Data treatment

Two different methods were used to analyse the autocorrelation functions. Inverse Laplace transform (ILT) was performed using a constrained regularization calculation (REPES[10]) which is similar to that of CONTIN[11] to obtain a distribution $A(\tau)$ of decay times τ. This method uses an equidistant logarithmic grid of fixed components (here a grid of 90 components) and determines their amplitudes.

The correlation functions were also fitted to the sum of two distributions. One is Gaussian in $\log \tau$ and represents the fast K^2-dependent peak

$$w_1(\tau) = \pi^{-1/2}(\tau\sigma)^{-1} \exp[-(\log(\tau/\tau_d)/\sigma)^2] \qquad (1)$$

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0032-3861/91/061077-03

The other is the so-called generalized exponential (GEX) distribution representing the total of all slow components[18]

$$w_2(\tau) = |s|\tau^{p-1}\tau_0^{-p}\exp[-(\tau/\tau_0)^s]/\Gamma(p/s) \qquad (2)$$

With $s=-1$ and p negative, the distribution is of the Pearson type V. τ_d and τ_0 are relaxation times which position $w_1(\tau)$ and $w_2(\tau)$ on the log (time) axis; σ characterizes the width of the Gaussian and the parameters p and s determine the shape and width of the GEX distribution. The general shape of the relaxation time distributions obtained in this way is very similar to that using ILT but with the slow modes replaced by a smooth broad distribution. A more comprehensive discussion has been given in ref. 12.

RESULTS AND DISCUSSION

Column A in *Figure 1* shows a typical series of multisampling time autocorrelation functions, $g^2(t)$, for several values of f_e below ($f_e < 2$) and above ($f_e > 3$) the gelation threshold. There is a distinct trend in the slope of the autocorrelation function with change in f_e. Beneath the gel point, the long-time tail of $g^2(t)$ becomes increasingly pronounced with increasing f_e and diminishes slightly above the gel point. These changes are clearly seen in *Figure 1* columns B and C showing the corresponding decay time distributions. Results of the REPES calculations gave broad distributions having a complex structure with many peaks (column B, *Figure 1*). However, because the recent testing[12] of REPES and CONTIN shows that the inversion tends to replace an asymmetric distribution by many symmetric ones, we presume that the indicated fine structure is not real but is an artifact of the calculation procedure. For this reason we fitted the experimental autocorrelation functions to a sum of two distributions. The following considerations suggested this:

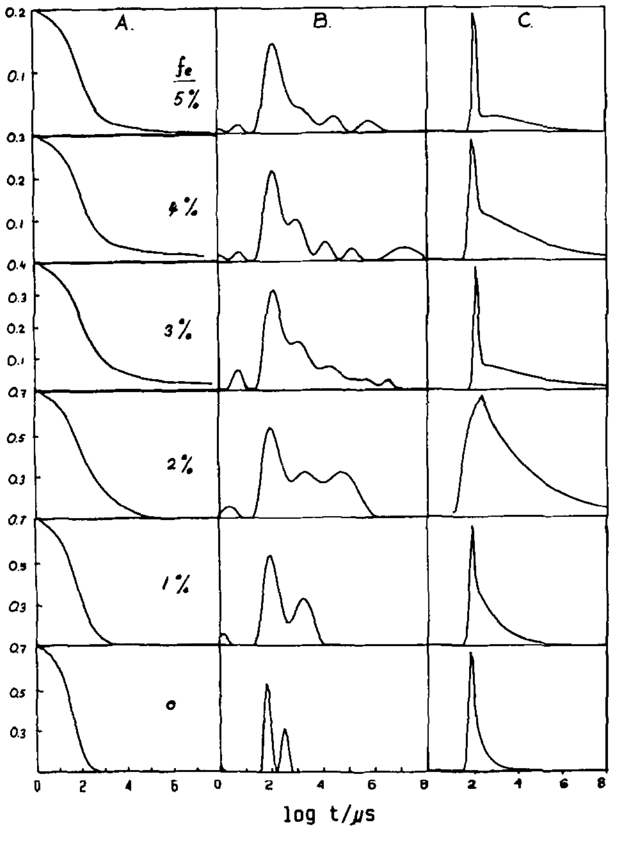

Figure 1 Column A, autocorrelation functions for PMMA solutions and gels, for samples with $f_e = 0$–5% as indicated, in butyl acetate. Temperature 25°C; angle 90°; column B, relaxation time distributions by Laplace inversion of the functions in column A by means of REPES; column C, the correlation functions have been fitted to the sum of a Gaussian distribution plus a GEX distribution[18] (see Data treatment section)

> One contribution to the scattered light should come from the collective concentration fluctuations in gels and thus the corresponding A(τ) is expected to approximate a narrow Gaussian distribution with characteristic relaxation time $\tau_c = 1/D_cK^2$.
>
> The other contributions should come from the interdiffusion of a sol inside the gel matrix. This should reflect a broad distribution of molecular sizes of sol particles.

Because gel chromatography analyses have shown that the molecular weight distributions of the sol samples below the gel point are asymmetric with a high molecular weight tail, we have selected a Pearson distribution as a plausible approximation. Plots of residuals to these fits showed that the distribution used well approximates the experimental data apart from a small systematic deviation (<0.5%) which was only observed in the vicinity of τ_c. Using these criteria for the analysis, the contributing dynamic processes may be adequately reduced to two main components. Column C in *Figure 1* shows the correlograms in column A fitted to a sum of a Gaussian distribution and a Pearson distribution with relaxation time τ_{max}. Both dynamic processes have diffusive character because both τ_c^{-1} and τ_{max}^{-1} are linearly dependent on K^2 as is demonstrated for samples with $f_e = 2$ and 3% in *Figure 2*. This conclusion is also supported by *Figure 3* which shows typical correlation functions for a sample with $f_e = 3$% displaced as a function of K^2t for scattering angles 60° and 120°. The correlation functions thus scale with K^2. The diffusion coefficients D_c ($=(\tau_cK^2)^{-1}$) and D_p ($=(\tau_{max}K^2)^{-1}$) thus describe the dynamical behaviour in the present gels.

D_c is attributed to the collective diffusion of the gel. This is supported by the observation that this diffusive process is essentially single exponential and τ_c is practically independent of the degree of crosslinking, i.e. the correlation length (ξ) for the concentration fluctuations is independent of f_e. These findings are in agreement with the literature.

Although the samples with $f_e = 1$ and 2% may have sufficiently high molecular weight for formation of the gel, intramolecular branching may inhibit topological entanglements and thus there will be relatively small contributions to the collective mode. Below the gel point, the broad distributions at longer times may reflect the collective diffusion of branched and linear macromolecules in solvent. As the gel point is approached, the polydispersity in size increases leading to a broadening of this part of $A(\tau)$. Below the gel point, the broad distributions at longer times may reflect the diffusion of branched clusters in the solvent. As the gel point is approached, the polydispersity in size increases leading to a broadening of this part of $A(\tau)$.

Recently, similar results for silica gels below the gel point were given by Martin and Wilcoxon[13]. The correlation functions accumulated over an extended range in delay time showed an initial exponential

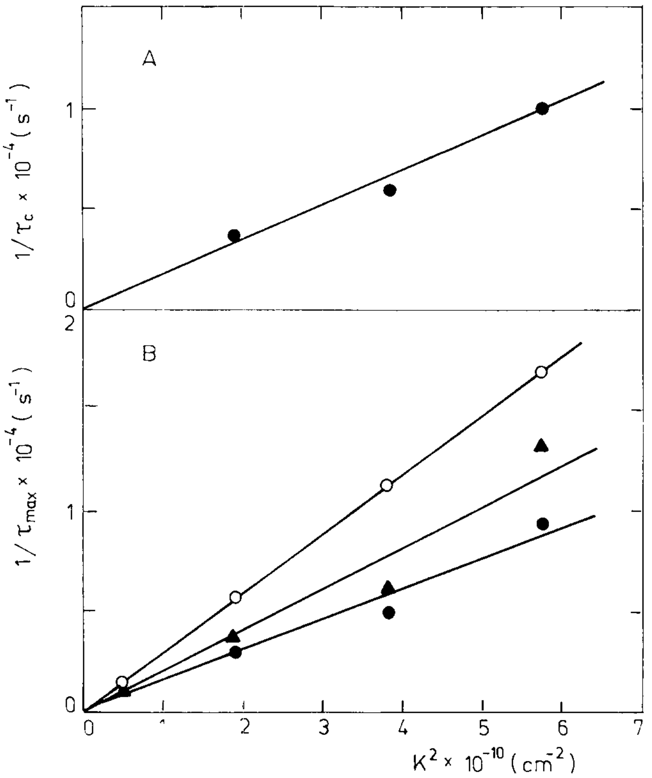

Figure 2 (a) Plot of relaxation rate for the fast mode ($f_c = 3\%$) and (b) for the slow mode as a function of K^2 (where K is the scattering vector). Points represent different levels of crosslinking: (●) 3%; (▲) 2% and (○) 0%

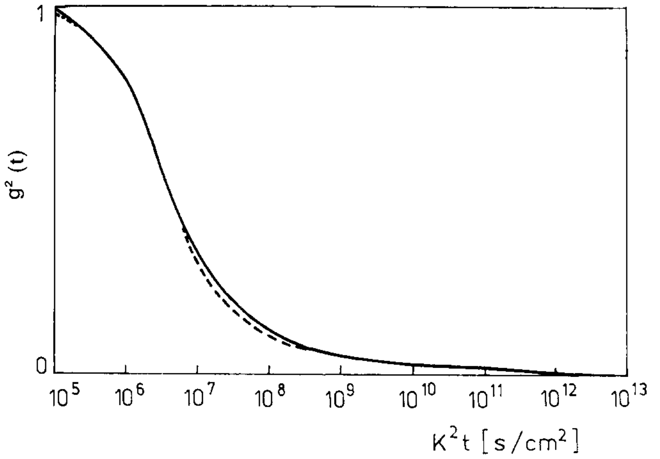

Figure 3 Plots of the normalized autocorrelation function, $g^2(t)$, for $f_c = 3\%$ as a function of $\log(K^2t)$ where the curves represent data at two angles: (----), 120°; (———), 60°

followed by a stretched exponential. In agreement with the present communication, the relaxation of density fluctuations was described by these authors as the sum of a normal cooperative diffusion component and an anomalous contribution arising from the self-diffusion of clusters. Even in the present gels, the long-time tails of the correlation functions are well described by a stretched exponential function below the gel point as is demonstrated by the data for the sample with $f_c = 2\%$ in *Figure 1*. The Pearson distribution of decay times used to fit the long time tails of the correlation functions differs only slightly from the Williams–Watts function corresponding to the stretched exponential time correlation functions. Our results are thus qualitatively consistent with those of Martin and Wilcoxon[13]. A significant difference, however, between their results and the present ones is that we do not observe a significant power law decay of the time correlation function at the gel point. While it may be possible to approximate a limited portion of the time domain in terms of a power law (some 1.5 decades), this appears highly tenuous and a smooth curve is at least as plausible.

The D_p mode above the gel point may be interpreted as an interdiffusion mode for the sol in the gel matrix. This interpretation derives from our experience with ternary polymeric systems (polymer 1/polymer 2/solvent). There we showed that the interdiffusion mode of one linear chain in semidilute solutions of the other[14] and in gels[15] can be reliably measured using d.l.s.

We do not observe here any trace of K-independent structural relaxations which dominate the decay time distributions in theta state[9] and marginal quality semidilute solutions. Butyl acetate ($\Theta = 20°C$) is a marginal solvent for PMMA[16] at 25°C.

Suppression of these relaxational modes thus results from the structure of the chemically crosslinked polymer, the latter consisting of a set of closely packed coils connected through the crosslinks. de Gennes[17] postulated that the equilibrium polymer concentration of a swollen network may be expressed in terms of the overlap concentration (C^*) for a polymer solution having the same molecular weight as the chains connecting crosslinking junctions in the gel (C^* theorem). Therefore, by analogy to the corresponding solution, structural relaxations may be expected to be very weakly represented at C^* and to be masked by the sol diffusional mode.

ACKNOWLEDGEMENTS

Financial assistance from the Bo Rydin Fund (SCA, Sundsvall, Sweden) is gratefully acknowledged. We would also like to thank the Swedish Board for Technical Development (STU) for support of this project. Göran Svensk is thanked for his assistance during the experiments. We are grateful to Drs S. W. Provencher and J. Jakeš for allowing use of their Laplace inversion programs.

REFERENCES

1 Prins, W., Rimal, L. and Chompff, A. J. *Macromolecules* 1972, **5**, 104
2 Tanaka, T., Hocker, L. O. and Benedek, G. B. *J. Chem. Phys.* 1973, **59**, 5151
3 Munch, J. P., Candau, S. J., Duplessix, R., Picot, C. and Benoit, H. *J. Phys. (Paris) Lett.* 1974, **35**, 239
4 Candau, S. J., Bastide, J. and Delsanti, M. *Adv. Polym. Sci.* 1982, **44**, 27
5 Hecht, A. M. and Geissler, E. J. *J. Phys. (Paris)* 1978, **39**, 631
6 Adam, M. and Delsanti, M. *Macromolecules* 1985, **18**, 1760
7 Štěpánek, P., Koňák, C. and Jakeš, J. *Polym. Bull.* 1986, **16**, 67
8 Brown, W., Johnsen, R. M., Štěpánek, P. and Jakeš, J. *Macromolecules* 1988, **21**, 2859
9 Nicolai, T., Brown, W., Johnsen, R. M. and Štěpánek, P. *Macromolecules* 1990, **23**, 1165
10 Jakeš, J. personal communication
11 Provencher, S. W. *Makromol. Chem.* 1979, **180**, 201
12 Jakeš, J. *Czech. J. Phys. B* 1988, **38**, 1305
13 Martin, J. E. and Wilcoxon, J. P. *Phys. Rev. Lett.* 1988, **61**, 373
14 Brown, W. and Zhou, P. *Macromolecules* 1989, **23**, 4031
15 Bansil, R., Pajevic, S., Koňák, C. and Jakeš, S. *J. Non-cryst. Solids* in press
16 Brandrup, L. and Immergut, E. H. (Eds) 'Polymer Handbook', Wiley Interscience, New York, 1967
17 de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, New York, 1979
18 Nicolai, T., Brown, W., Hvidt, S. and Heller, K. *Macromolecules* 1990, **23**, 5088