Transient inhomogeneities in polymeric liquids and solutions: characterization by static and dynamic light scattering

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Low molecular weight liquid polyisoprenes and concentrated solutions of polystyrene in toluene were studied by static and dynamic light scattering. Besides the well known density and concentration fluctuations, both systems show an additional slow relaxation mode which is accompanied by a strong scattering at small angles. The relaxation rate of the process is proportional to the square of the scattering vector q. The process seems to be due to the motion of clusters inside the sample. Small angle light scattering experiments indicate a cluster size of the order of 10^{-7} m. After several months the clusters disappeared. For the samples under study, cluster formation therefore constituted a non-equilibrium phenomenon.

(Keywords: static and dynamic light scattering; inhomogeneities; concentrated solutions; polymeric liquids)

Introduction

In quasielastic light scattering experiments with a variety of samples, it has recently been reported that a slow relaxation mode occurs in the intensity correlation function, which appears simultaneously with a strong small angle scattering. The phenomenon was observed in concentrated solutions[1–3] as well as in pure polymer melts[4]. The anomalous scattering is also observed in low molecular weight liquids with a tendency to glass formation like *ortho*-ter-phenyl[5].

In this paper we not only present other examples for the occurrence of this phenomenon but show in particular that for the systems under study — low molecular weight polymer melts and concentrated solutions — it is of a transient nature.

Samples

Measurements were performed on polyisoprene ($M_w = 1400\,\mathrm{g\,mol^{-1}}$, $M_w/M_n = 1.1$, glass transition temperature $T_g = -80°\mathrm{C}$) and a solution of polystyrene ($M_w = 43\,000\,\mathrm{g\,mol^{-1}}$, $M_w/M_n = 1.05$) in toluene.

A basic requirement in light scattering is the purification of the samples, which can be difficult for viscous liquids. In a first step we dissolved all samples in freshly distilled dioxane. Then this solution was pressed through a fine filter (Millipore 0.2 μm) into a dust-free cell. In a further step this clean solution was freeze dried. The polyisoprene was decanted into a dust-free light scattering cuvette. Semidilute solutions of polystyrene in toluene were obtained from a dilute solution by controlled evaporation of the solvent in a laminar-flow box.

Static and dynamic light scattering experiments were conducted using a commercially available goniometer equipped with a photon correlator (ALV, Langen, Germany; model 3000). The light source was an Ar ion laser (Coherent, model Innova 90-3). The ampoule with the sample was placed into a silicon bath, which was index-matched with regard to the quartz-glass of the basin. All measurements were performed at room temperature.

Scattering experiments

The scattering of light is caused by fluctuations of the dielectric constant $\delta\varepsilon$ in the sample[6]. In a polarized light scattering experiment (equal directions of polarization of the initial and scattered electric field), fluctuations of the dielectric constant are observed in mixtures, arising from concentration and density fluctuations, δc and $\delta\rho$. Polymer melts show only density fluctuations. In our studies we found an additional slow fluctuation. In general the total intensity was composed of three parts:

$$I(q) = I(q)_{\delta\rho} + I(q)_{\delta c} + I(q)_{\mathrm{sm}} \qquad (1)$$

where q is the scattering vector and the subscript sm represents slow mode.

Using photon correlation spectroscopy it is possible to determine the intensity correlation function $G_2(q, t)$:

$$G_2(q, t) = \langle I(q, t) I(q, 0)\rangle \qquad (2)$$

G_2 can be related to the normalized field correlation function $g_1(q, t)$:

$$g_1(q, t) = \frac{\langle E_s(q, t) E_s(q, 0)\rangle}{I(q)} \qquad (3)$$

by use of the Siegert relation:

$$f g_1(q, t) = \sqrt{\frac{G_2(q, t) - I^2(q)}{I^2(q)}} \qquad (4)$$

Here f denotes an experimental factor ($0 \leqslant f \leqslant 1$), which is related to the size of the scattering volume.

Often $g_1(q, t)$ can be represented by a Williams–Watts function:

$$g_1(q, t) = \mathrm{e}^{-(t/\tau)^{\beta}} \qquad (0 < \beta \leqslant 1) \qquad (5)$$

where τ is the relaxation time and β a distribution parameter. For diffusing particles of equal size a simple relaxation process ($\beta = 1$) is expected. The relaxation time

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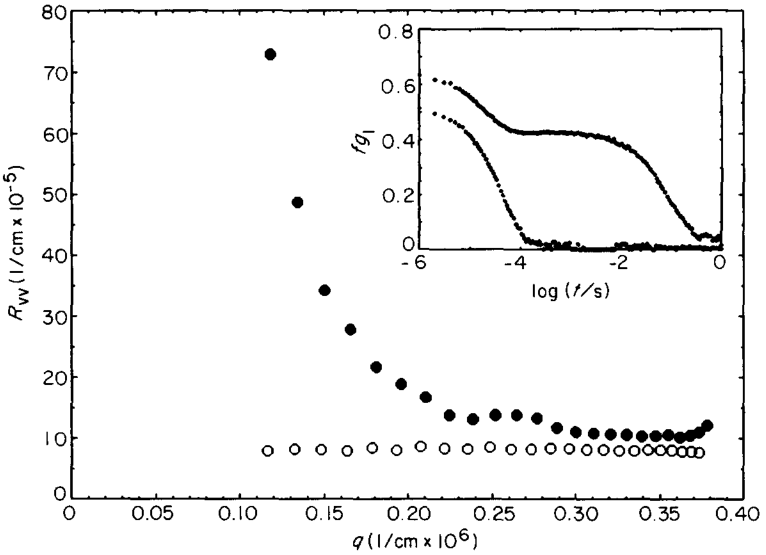

Figure 1 Static structure factor (Rayleigh ratio) and field correlation function $fg_1(q, t)$ (insert) of a dilute (○, $c = 0.011\ \mathrm{g\,cm^{-3}}$) and a concentrated solution (●, $c = 0.214\ \mathrm{g\,cm^{-3}}$) of polystyrene in toluene

of the concentration fluctuations then varies with q:

$$\tau^{-1} = Dq^2 \tag{6}$$

where D denotes the diffusion coefficient.

Results and discussion

Static and dynamic light scattering studies were performed on two different systems: concentrated solutions of polystyrene in toluene and low molecular weight polyisoprene. Both systems showed the anomalous scattering.

Polystyrene in toluene. Going from dilute to more concentrated polymer solution, a pronounced change occurs in the static structure factor $I(q)$ as well as in the field correlation function $g_1(q, t)$. *Figure 1* shows the Rayleigh ratio for a dilute and a semidilute solution together with the corresponding correlation functions. The fast relaxation is due to the concentration fluctuations associated with the diffusion of single molecules (in dilute solution) or the network dynamics (in semidilute solution).

In the semidilute solution an additional relaxation process is evident, leading to a slow fluctuation of the dielectric constant. The q-dependence of its characteristic time is shown in *Figure 2* together with the β parameters of the Williams–Watts fits. The parameter β is near to unity. The q-dependence of the relaxation rate, $\tau^{-1} \sim q^2$, is indicative of a diffusive process. Authors have associated this process with slow moving 'clusters' inside the sample[5].

After several months the anomalous scattering vanished. Even when the cuvette was shaken vigorously it did not reappear. This means that the specific kind of density fluctuations reflected in the anomalous scattering for our samples constitutes a non-equilibrium property. Obviously it has been introduced into the sample by the mode of preparation.

Low molecular weight polyisoprene. Similar observations were made in the case of oligomeric liquid polyisoprene. For the as-prepared sample we found a strong increase of the static intensity at small angles. We used a specific diffractometer to register the scattering at small angles. As shown by *Figure 3*, scattering curves could be evaluated on the basis of the Ornstein–Zernike equation:

$$I(q) = I(0)/(1 + q^2\xi^2) \tag{7}$$

yielding a correlation length of $\xi = 0.35\ \mu\mathrm{m}$.

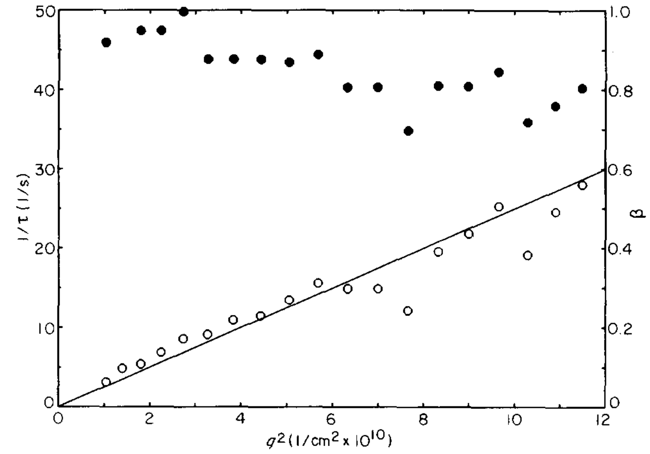

Figure 2 Solution of polystyrene in toluene ($c = 0.214\ \mathrm{g\,cm^{-3}}$). Relaxation rates $1/\tau$ (○) and β (●) parameters in dependence on q

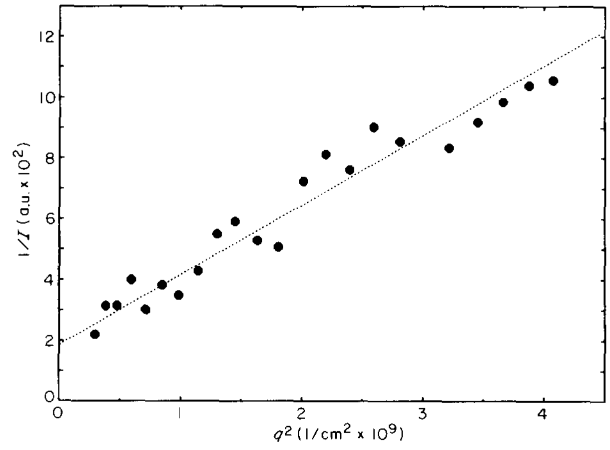

Figure 3 Low molecular weight polyisoprene. Small angle light scattering intensity in a plot $1/I$ *versus* q^2

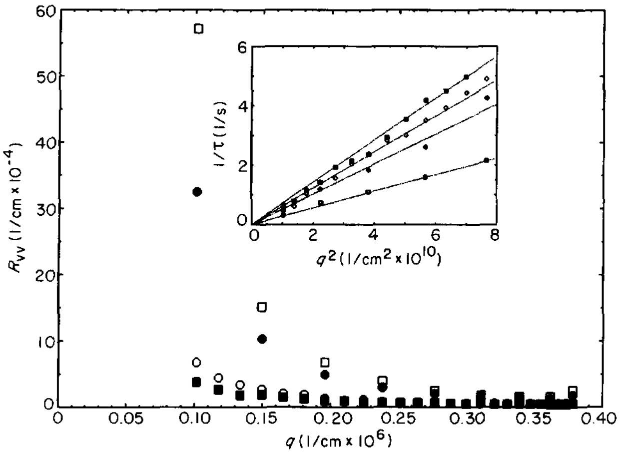

Figure 4 Low molecular weight polyisoprene. Changes of the static structure factor and the relaxation rate with time: □, start of experiment; ●, 3 days later; ○, 2 months later; ■, 4 months later

Simultaneously a slow mode showed up in the correlation function $g_1(q, t)$. Again the process turned out to be of a diffusive nature, with $\tau^{-1} = Dq^2$.

As in the first case, the phenomenon showed transient character. This is demonstrated in *Figure 4*. The static intensity decayed slowly and could be observed over several months. The relaxation frequencies as derived from $g_1(q, t)$ ($\beta \approx 0.9$) are plotted *versus* q^2 in the same figure. They indicate a steady increase of the diffusion coefficient.

Hence, in both systems the same phenomenon was observed. In addition to the concentration and density fluctuations, slowly diffusing clusters were detected. These clusters were not stable; if they disappeared they did not form again.

It appears that through the preparation of the samples a special initial state with additional free volume was prepared, which does not correspond to the thermodynamic equilibrium. Relaxation to equilibrium needs several months at ambient temperature.

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