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Relaxation Processes

Relaxation Fluctuations in Poly(2-Hydroxyethyl Methacrylate) Gels Swollen in Butanol

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Summary

Quasielastic light scattering measurements on transparent poly(2-hydroxyethyl methacrylate) (PHEMA) gels were performed under temperature equilibrium conditions at several temperatures from 40 to 80°C. All observed correlation functions departed from the single exponential decay with a long-time limit. The asymptotic value relaxation frequency Γ_a decreased steeply with decreasing temperature. The observed temperature dependence of Γ_a is interpreted as resulting from polymer fluctuations near the glass transition of weakly swollen PHEMA gels.

Introduction

Investigation of gels by quasielastic light scattering (QELS) experiments has been limited mostly to the study of dynamic properties of highly swollen gels. Experiments performed by many authors (see e.g. review 1) provided a persuasive confirmation of the analogy between the dynamical behaviour of gels and semi-dilute solutions of linear flexible polymers in good solvents.

Dynamic properties of highly swollen gels in poor solvents were studied by photon correlation spectroscopy (PCS) by TANAKA et al. (2) and TANAKA (3). It was shown that, as the spinodal temperature T_s was approached by fast cooling, the intensity of scattered light increased as a consequence of increasing concentration fluctuations in the gel and at the same time the relaxation frequency Γ (the decay rate of the correlation function) decreased to zero. The temperature dependence of Γ in the vicinity of T_s could be described adequately by the power law, in good agreement with theoretical predictions.

On the other hand, QELS experiments are frequently used for the study of dynamic properties of bulk polymers (see e.g. review 4) near the glass transition where the density and orientational fluctuations are slow enough. The correlation functions observed were highly non-exponential in all cases and could be adequately described by the empirical Williams-Watts relaxation function (5,6). The observed correlation functions for most polymers studied have been discussed in terms of primary glass-rubber relaxation- α motions (long-time data). The experimental relaxation data can be characterized by the average relaxation time $\bar{\tau}$ which is usually calculated from the composite correlation function covering a wide dynamic range (typically, from 10^{-6} to 100 s). The $\bar{\tau}$ values were found to increase dramatically as the sample was cooled toward the glass-rubber transition temperature T_g. The temperature variation of τ (α-motions) usually follows the Antoine-WLF empirical equation. In a narrower temperature range and sufficiently far from T_g the experimental data can be fitted to the Arrhenius equation with a constant activation energy (e.g., 7).

No rigorous theory of QELS exists and only one such experimental study has been reported by PATTERSON et al. (8) for weakly diluted polymers (polystyrene) where the average relaxation time was measured near the end of the thermal polymerization of styrene. The presence of only a few percent of diluent (styrene monomer) lowered the value of T_g, and this change in T_g was reflected in measured relaxation functions. As long as the concentration of small molecules was low (<5%), the scattered intensity due to concentration fluctuations was negligible, compared with the density or anisotropy fluctuations of the polymer.

The present study deals with QELS measurements of poly(2-hydroxyethyl methacrylate) (PHEMA) gels, weakly swollen in butanol slightly above T_g. The aim of the work is to characterize the fluctuations which predominantly contribute to the scattered light and to describe their temperature dependence.

Experimental

Transparent PHEMA gels were prepared by the crosslinking polymerization of HEMA with 0.2% (sample 1) and 2% (sample 2) of ethylene dimethacrylate (azo-bis-isobutyronitrile served as the initiator) and then swollen in butanol at room temperature for one year, a time in our experience more than sufficient for the samples to be homogeneously swollen to equilibrium. The respective volume fractions of the polymer in the swollen state were $\phi_1 = 0.74$ and $\phi_2 = 0.78$ for samples 1 and 2. Sample dimensions were about 30x10x5 mm.

The light-scattering system used in the present investigation is essentially the same as described in an earlier publication from this laboratory (9). Briefly, the incident light was the 632.8 nm line of Spectra Physics He-Ne laser (Model 125 A); the scattered light was detected by RCA C 31034 photomultiplier and photon counting system Spex PC 1. The photopulse signal was carried via a digital/analog converter to a 100-channel Hewlett-Packard 3721 A correlator. All measurements were performed at a scattering angle of 90°. The sample cell temperature was controlled with an accuracy better than 0.1 K by direct heating of a copper holder containing the scattering cell. The sample was placed vertically in the center of a high-quality rectangular cell filled with butanol serving as swelling solvent and immersion liquid simultaneously. Thus, stray light due to the reflection from various surfaces was minimized.

The correlation functions were measured at several temperatures within the range from 40 to 80°C. In order to prevent turbidity of the samples as a consequence of phase separation, the temperature was changed stepwise, starting at the lowest value (40°C). During the measuring cycle which lasted some 6 hours the overall volume fraction of the polymer, ϕ, changed only slightly, to wit, by 5 per cent with sample 1 and by 3 per cent with sample 2. As the light scattering probes the interior of the sample, we assume these changes to be still smaller in the scattering volume so that the measurements can be thought of as proceeding at a constant volume fraction ϕ.

Although the initial components of the polymerizing system were filtered in order to remove the undesirable light scattering impurities, the resulting gel samples contained a number of inhomogeneities resulting from the polymerization process itself. The intensity of light scattered on these inhomogeneities was considerably higher than that originating in fluctuations of the polymer itself, and changes in their local concentration gave rise to a spectrum with a characteristic time much longer than that of polymer fluctuations. It was shown experimentally that this stray light, which can be considered as a local oscillator, heterodynes with the light scattered by the polymer fluctuations (e.g., 10). In this situation it was practically impossible to employ sampling times longer than 10 ms, in particular in view of both the duration of the measuring cycle and spurious signals produced probably by streaming of the solvent under the non-equilibrium conditions of the gel.

Results and Discussion

The observed heterodyne correlation functions at all measured temperatures could not be represented by a single exponential, contrary to the case of highly swollen gels (e.g., 11). Fortunately, the correlation functions possess a long time limit. Values of the relaxation frequency obtained by a forced single exponential fit at different sampling times (ST), approached an asymtotic value with increasing ST. The values of this quantity, Γ_a, form the basis of subsequent discussion.

The values of Γ_a as a function of temperature are plotted in Fig.1 for both samples. The experimental curve for sample 2 is shifted to higher temperatures in comparison with that for sample 1.

For highly swollen gels and bulk polymers, similar steep temperature changes in the characteristic relaxation time were ascribed to concentration fluctuations near T_s, and to density and orientational fluctuations near T_g, respectively. In principle, both types of fluctuations could be observed in our PHEMA gels: (a) Butanol is not a good solvent for PHEMA gels in the temperature range <40°C where a microphase separation of butanol inside the PHEMA gels takes place after fast cooling from 80°C (12,13). The characteristic relaxation time of concentration fluctuations increases with decreasing solvent quality (decreasing the measuring temperature). (b) The glass transition temperature of solid PHEMA gels, which is about 100°C, can be decreased by swelling of the gel and, at the volume fraction $\phi \sim 0.75$ employed, the T_g value seems to be about 10°C (14). The temperature range used (40-80°C) is slightly above the T_g temperature. It means that effects similar to those in bulk polymers could be expected.

Fortunately, both processess differ in the temperature dependence of Γ_a. Therefore, we tried to fit the experimental data to both the power law and Arrhenius equation. The temperature dependences of the asymptotic relaxation times τ_a ($\tau_a = 1/\Gamma_a$) can be quite adequately described by the Arrhenius equation with an apparent activation energy of 136 kJ/mol and 133 kJ/mol for samples 1 and 2, respectively, practically equal within the limits of experimental error (see Fig.2). It means that the scattering intensity due to concentration fluctuations is negligible compared with the density or anisotropy fluctuations of the polymer, similarly to weakly diluted polystyrene (ϕ > 0.95) (8).

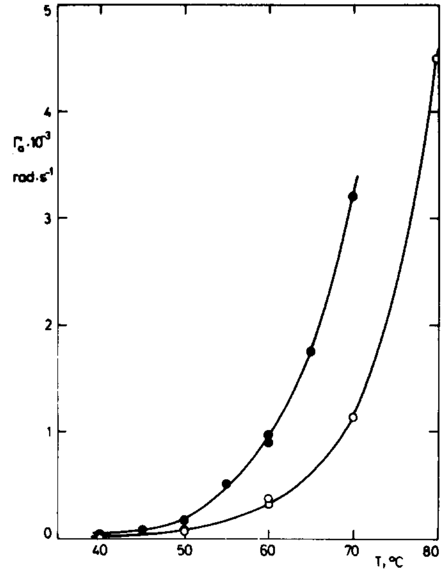

Fig.1. The asymptotic value of the relaxation frequency Γ_a of PHEMA gels as a function of temperature;
● sample 1, o sample 2.

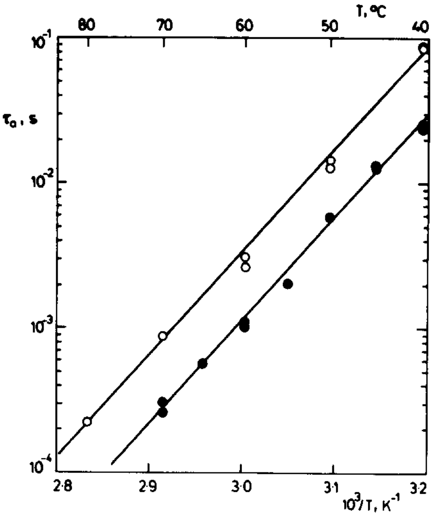

Fig.2. Arrhenius plot of the Γ_a values from Fig.1;
● sample 1, o sample 2.

The shift of the Γ_a(T) curve for sample 2 to higher temperatures can be explained by the shift of T_g to higher temperatures, T_g increases with ϕ (14) and for our samples $\phi_2 > \phi_1$.

We may conclude that the observed relaxation times Γ_a reflect the density or anisotropy fluctuations of the gel rather than the concentration ones.

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