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ORIGINAL CONTRIBUTION

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Concentration fluctuation dynamics of concentrated aqueous hydrophobically-modified acrylic copolymer solutions

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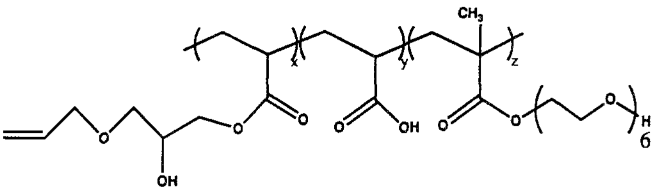
Abstract The dynamics of concentration fluctuation in concentrated aqueous solutions of a poly(hexaethylene glycol monomethacrylate-co-acrylic acid/allyl glycidyl ether) copolymer were studied by means of the time-resolved low angle laser light scattering (LALLS). Concentrated aqueous solutions in the range 30–55% w/w showed a lower critical solution temperature behaviour (LCST). A peak was observed in the scattered light profile with time, $I(q,t)$, when a temperature jump above the coexistence curve was performed. The peak shifted to lower q values with time in a logarithmic mode. Only at low q values and very short times did the solutions obeyed Cahn's linear spinodal decomposition kinetics, subsequently slowing down.

Key words Aqueous – hydrophobic – acrylic – spinodal – phase separation – dynamics – low angle light scattering

Introduction

Aqueous polymers constitute a significant class of materials which are highly relevant to biomedical/biochemical systems (1) and increasingly attractive in view of the environmental need for organic solvent replacement. Acrylic copolymers offer a wide scope for structure-property design by incorporating readily comonomers with different and specific contributions to the polymer properties including functionality for cross-linking and water/solvent solubility. Applications of these polymers involve, almost invariably, highly concentrated systems. A relatively restricted body of experimental data (2) and theoretical predictions (3) is available in this particular area compared with the extensive studies of the dynamics of phase decomposition in polymer melts. In this paper we present low angle light scattering data on the phase diagram and kinetics of phase decomposition of concentrated aqueous solutions of a hydrophobically-modified acrylic copolymer. The acrylic copolymer consisted of a hydrophilic backbone of acrylic acid and hexaethylene glycol monomethyl methacrylate. Part of the acrylic acid was reacted with allyl glycidyl ether to introduce hydrophobic pendant groups. The final product was soluble in water producing clear concentrated solutions.



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Experimental

Low-angle laser light scattering (LALLS)

The light from an unpolarised 5 mW He-Ne laser gun (632.8 nm) (Newport Ltd) scattered through the sample was detected by a photodiode attached to a goniometer arm equipped with a position encoder, travelling at a variable speed through 5° to 50° angles. A pre-amplifier and amplifier enhanced the signal which was subsequently converted to digital through an AD converter and stored as an ASCII file. The light source, sample holder, goniometer arm, detector and pre-amplifier were enclosed in a light-tight box to eliminate noise from environmental light. The intensity of the incident beam was monitored by a reference photodiode and a beam splitter. Neutral intensity filters (Newport Ltd) were used to avoid photodiode flooding. The system was very carefully aligned optically prior to each run. The sample holder was a HT6000 microscope stage and PR6000 temperature controller capable of heating rates from 0.1 to 90 deg/min. The solutions were placed between two microscope cover slips. The scattering angle was determined with a position transducer attached to the goniometer arm and was calibrated and checked using the intensity peak of polyethylene terephthalate (PET) films as described by Stein and coworkers (4).

Materials

The copolymer studied (*I*) was a poly(hexaethylene glycol monomethyl methacrylate-co-acrylic acid/allyl glycidyl ether) (PEM6/AA/AGE) copolymer with weight composition of 45/26.5/28.5 and final acid value of 57.8 mgKOH/g copolymer. The monomer hexaethylene glycol monomethyl methacrylate (PEM6) was obtained from BP Chemicals. The poly(PEM6-co-AA) prepolymer was prepared in propylene glycol monomethyl ether (Dowanol PM) by continuous feed free radical polymerisation under reflux with a diazo initiator. The AGE was reacted with part of the AA at 125–130 °C with benzyl trimethyl ammonium hydroxide as the catalyst. The propylene glycol monomethyl ether was removed by careful steam stripping. The samples tested were aqueous solutions of this polymer in the concentration range from 30 to 50% w/w. The copolymer had $\bar{M}_n \approx 2\,000$ and $\bar{M}_w/\bar{M}_n = 2.5$ as measured by GPC with tetrahydrofuran as the carrier solvent and with polystyrene standards calibration.

Results and discussion

The coexistence curve

The part of the coexistence curve relevant to our studies was constructed by monitoring the intensity of the light scattered at 30 degrees angle while heating the polymer solution at 2 deg/min. The scattered light intensity remained almost constant up to a critical temperature thereafter increasing fast following the clouding of the polymer solutions due to phase separation. The coexistence curve in the concentrated region constructed by this procedure is shown in Fig. 1. The experimental coexistence curve is anticipated to have been shifted to lower temperatures compared to the true thermodynamic equilibrium corresponding to infinitely slow heating rates. However, it was sufficient for defining the critical region for studying the phase decomposition kinetics.

Dynamical studies

The dynamics of phase decomposition were studied by means of the technique of time-resolved light scattering. Phase separation was thermally induced by a temperature-jump from room temperature (ca. 21 °C) to a temperature above the coexistence curve (see Fig. 1); the heating rate of the temperature-jump was 90 °C/min. Figure shows the evolution of the scattering profile with time $I(q, t)$ for the 50% polymer solution. The intensity data have not been smoothed. A peak was clearly observed at very early times in the scattered light intensity, $I(q)$, persisting to relatively longer times. The magnitude of the scattering vector q is given by:

$$q = (4\pi/\lambda) \sin\theta \qquad (1)$$

where 2θ is the scattering angle and $\lambda = 632.8$ nm. The magnitude of the scattering vector corresponding to the maximum intensity, $q_{\max}$, shifted to lower q values with time reflecting the anticipated coarsening of the morphology with time (Fig. 3). Using Bragg's expression, the

Fig. 1 Coexistence curve in the concentrated polymer region, 30–55% w/w; heating rate 2 °C/min. Arrows indicate the temperature-jumps for the 40% w/w sample (A → B) and 50% w/w sample (C → D)

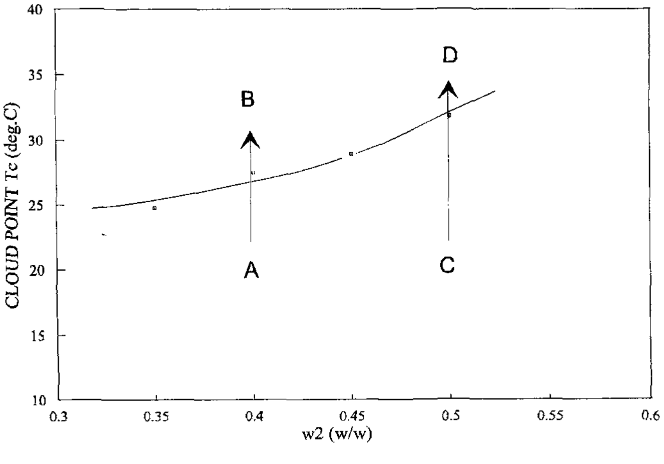
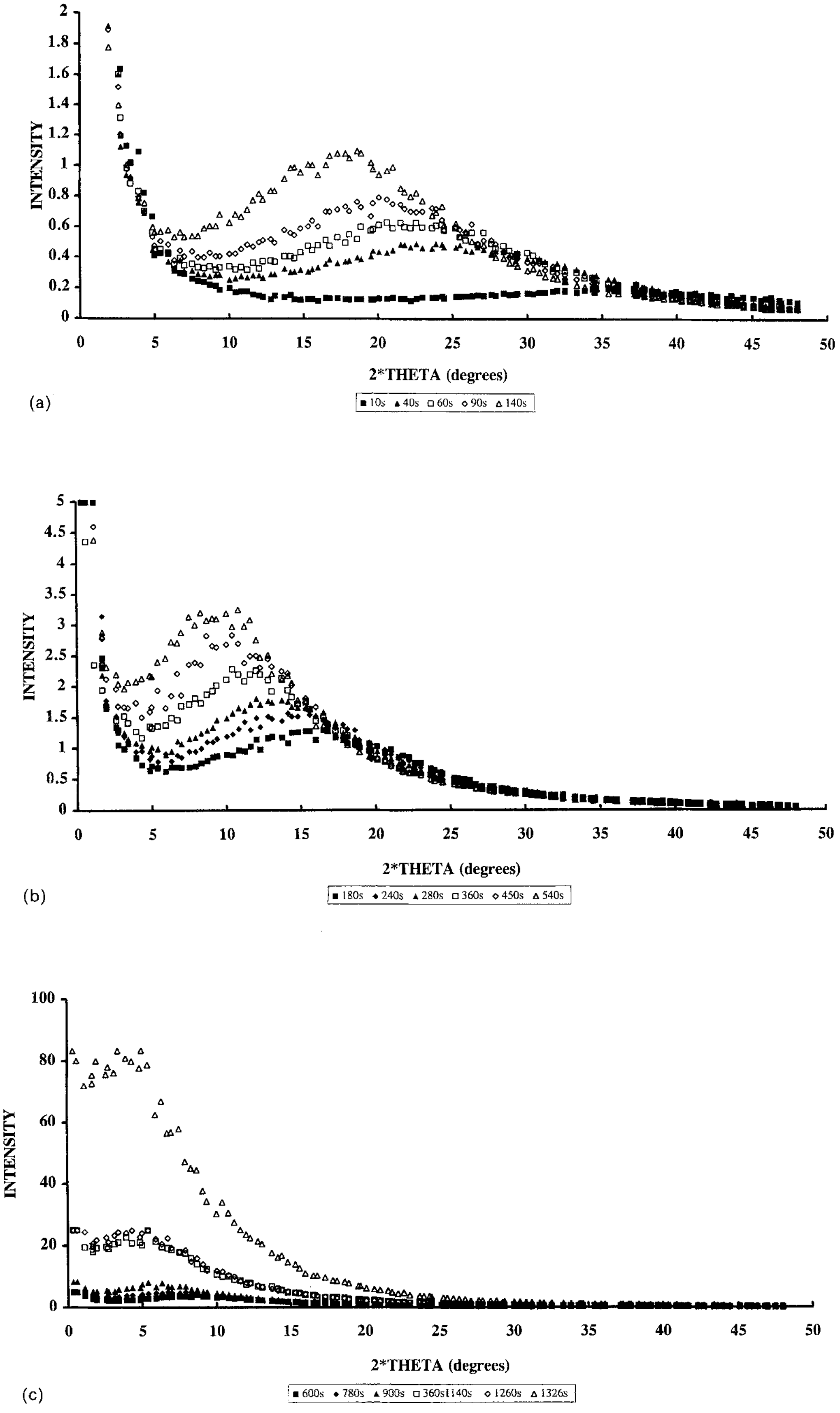


Fig. 2 Time evolution of the scattering intensity $I(q, t)$ for a temperature jump from 20 °C to 34.3 °C of a 50% w/w copolymer solution (a) ■ 10s ▲ 40s □ 60s ◇ 90s △ 140s; (b) ■ 180s ◆ 240s ▲ 280s □ 360s ◇ 450s △ 540s; (c) ■ 600s ◆ 780s ▲ 900s □ 360s1140s ◇ 1260s △ 1326s



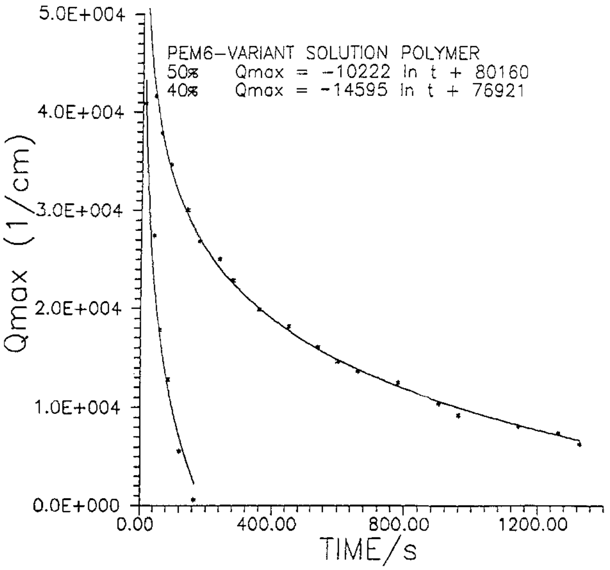


Fig. 3 Variation of $q_{\max}$ with time for the 40% and 50% copolymer solutions. Continuous lines represent the fitted data

approximate scale of the heterogeneity in both samples was calculated to vary from 1.5 μm to just over 10 μm, before the peak disappeared under the incident beam signal. The $q_{\max}$ was determined accurately by fitting the experimental data to a quadratic equation to the scattering peak. The shift of $q_{\max}$ with time can be successfully described by a logarithmic function:

$$q_{\max} = A \ln t + B \qquad (2)$$

with constants A and B equal to − 1.04E04, 8.02E04 and − 1.46E04, 7.69E04 for the 50 and 40% w/w polymer solutions, respectively (see Fig. 3). In agreement with the expected behaviour, system heterogeneity coarsening was strongly dependent on polymer concentration, decreasing with increasing polymer content and hence viscosity. This is understood to be caused by the reduced polymer mobility in the solution. The intensity peak indicates some degree of regularity of the two-phase structure in the concentrated solutions, perhaps similar to spinodal decomposition.

According to Cahn's linear theory of spinodal decomposition, the increase in the scattered light intensity is described by an exponential function:

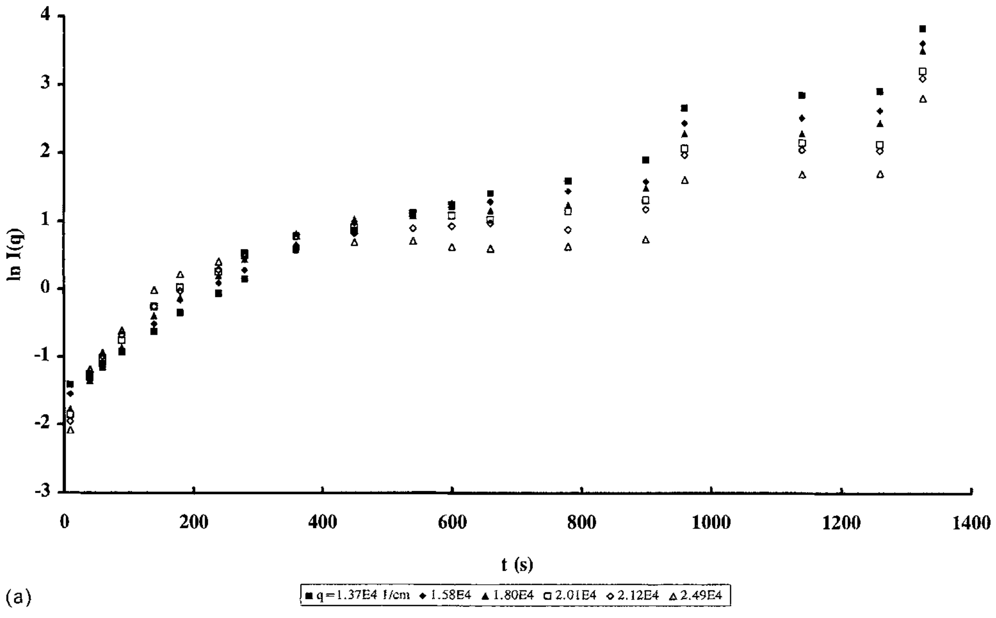
$$I(q, t) \propto \exp[2R(q, t)] \qquad (3)$$

where $R(q)$ is the growth rate of concentration fluctuation having wavenumber q and is given by:

$$R(q) = -Mq^2(\partial^2 f/\partial c^2 + 2kq^2) \qquad (4)$$

where M is the mobility, k is the concentration-gradient energy coefficient, f is the free energy of mixing and c the concentration of the solution. According to equation 3 a plot of $\ln I(q)$ against time at a fixed q should yield a straight line with $2R(q)$ as the slope. Figures 4 and 5 illustrate the variation of $\ln I(q)$ with time for our two copolymer solutions. In both cases the experimental behaviour deviated quickly from the linear prediction indicating that phase decomposition does not follow linear kinetics in agreement with observations reported by other workers (5–7). They also showed that at later stages the growth is expected to become non-exponential and that $q_{\max}$ moves to smaller values as the phase separation

Fig. 4A Plot of $\ln I(q)$ vs t for the 50% copolymer solution for q in the region from 1.37×10^{-5} to 2.49×10^{-5} cm^{-1}.
■ q = 1.37E4 1/cm ◆ 1.58E4
▲ 1.80E4 □ 2.01E4 ◇ 2.12E4
△ 2.49E4;



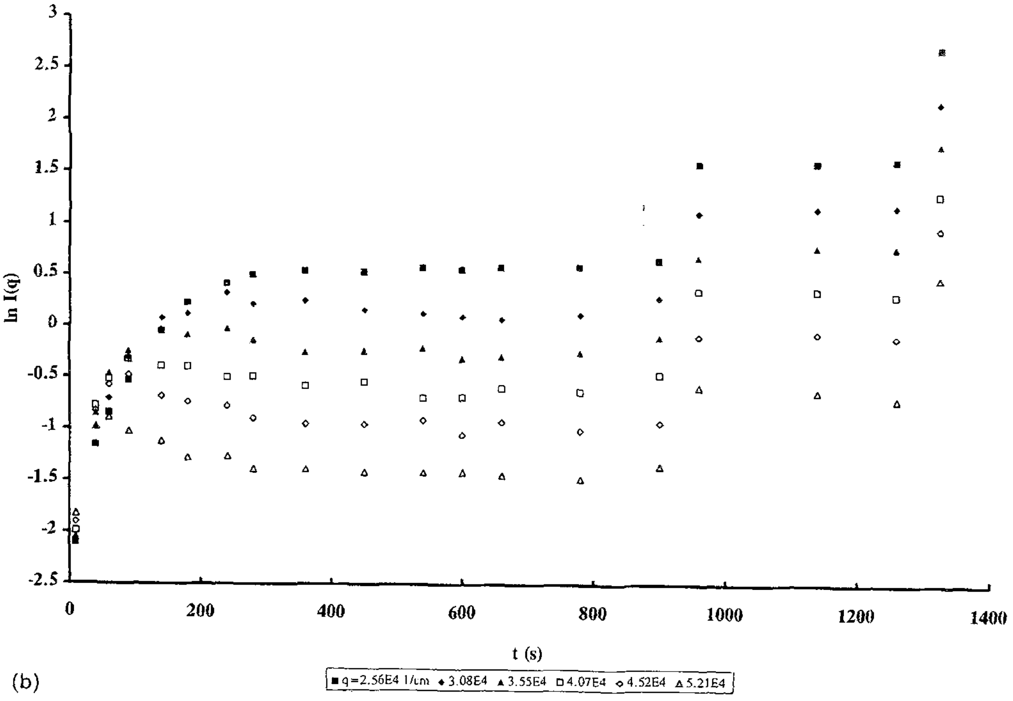


Fig. 4B Plot of $\ln I(q)$ vs t for the 50% copolymer solution for q values from 2.56×10^{-5} to $5.21 \times 10^{-5}\,\mathrm{cm}^{-1}$. ■ $q = 2.56\mathrm{E}4$ 1/cm ◆ 3.08E4 ▲ 3.55E4 □ 4.07E4 ◇ 4.52E4 △ 5.21E4

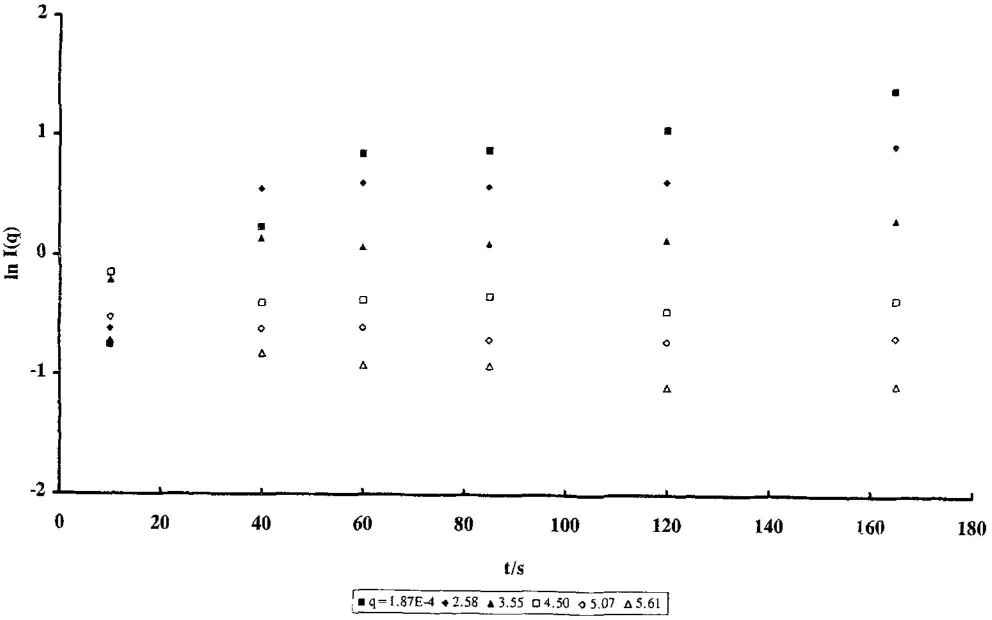


Fig. 5 Plot of $\ln I(q)$ with time (s) for the 40% w/w copolymer solution. ■ $q = 1.87\mathrm{E}4$ ◆ 2.58 ▲ 3.55 □ 4.50 ◇ 5.07 △ 5.61

progresses. The critical point for this deviation would be a function of the mobility in the system and the magnitude of the $(T - T_S)$, where T_S is the spinodal temperature.

In the case of the 50% solution, this deviation appeared more pronounced at higher q values. Using the lower q data for this sample, we calculated an effective interdiffusion coefficient, D, corresponding to the linear decomposition kinetics region:

$$D = -M(\partial^2 f/\partial c^2) \qquad (5)$$

Figure 6 illustrates the plot of $R(q)/q2$ vs $q2$ for this sample, the slope of which, according to Eq. (4), yields the diffusion coefficient. At low q values where the kinetics obey Cahn's linear prediction, the diffusion coefficient was

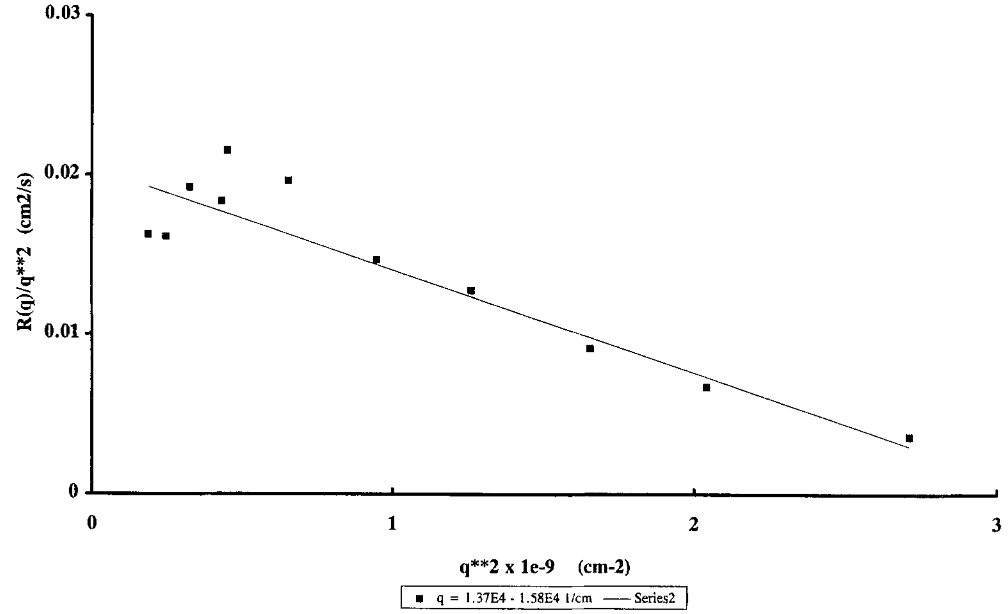


Fig. 6 Plot of $R(q)/q^2$ vs q^2 for the linear $I(q, t)$ region.
■ q = 1.37E4–1.58E4 1/cm

negative in agreement with the spinodal mechanism. The value calculated from Fig. 6 was -2.0×10^{-11} cm^2/s, higher than values quoted for polystyrene/polyvinyl methyl ether blends (5–6) (ca. -2.8×10^{-13} cm^2/s at ca. 150–160 °C) and considerably higher than aqueous polyvinyl alcohol (30% w/w) solutions (-2.6 to -7.0×10^{-14} at 20–30 °C) (7). This is consistent with the lower molecular weight of our copolymer compared to the polymers in the reported systems and the gel state in the case of the 30% w/w PVA solution.

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