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A Brillouin scattering study of a polymer blend showing upper critical solution temperature behaviour

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Summary

The Brillouin spectra of a polymer blend of poly(styrene-co-allyl alcohol) and poly(neopentyl glycol adipate), showing upper critical solution temperature behaviour, have been measured as a function of temperature. Conspicuous changes have been observed in the Brillouin width near the cloud point and have been interpreted as arising from composition changes in the two originally distinct low-temperature microscopically separated liquid phases towards a common high-temperature solution.

Introduction

Many miscible polymer blends undergo phase separation when they are heated, showing lower critical solution temperature (LCST) behaviour (1,2). Relatively fewer miscible blends, however, undergo phase separation when they are cooled, displaying upper critical solution temperature (UCST) behaviour (1,2). The latter behaviour is usually observed for blends in which one or both components have relatively low molecular weights. There are only a few blends which are known to show both UCST and LCST (3-5).

A simple method of detecting the onset of phase separation in a polymer blend is to heat the sample on a hot stage. The temperature at which a transparent blend develops cloudiness (for LCST behaviour), or a turbid blend turns clear (for UCST behaviour), is taken as the transition temperature (6-8). Such a visual detection of UCST/LCST behaviours lacks accuracy. More accurate determinations of the UCST/LCST behaviours are obtained by monitoring the changes in the intensity of light scattered elastically from the sample (3,9,10). The underlying principle of the latter method is, however, similar to that of the cloud point.

The technique of Brillouin light scattering simultaneously measures three quantities: the Brillouin shift ν; the Brillouin width Γ and ; the Landau-Placzek ratio LP. These quantities are related to a large number of physical properties including refractive index, elastic modulus, density, sound velocity and sound attenuation. Recently we have used this technique to study quite a variety of different types of transitions, including sol-gel transitions (11), glass-transitions (12) and crystalline melting (13). Although Brillouin scattering has been used to study polymer blends (see, for example, (14)), to our knowledge it has not been applied to investigate UCST/LCST behaviours. In our Brillouin studies special effort has been made to determine Γ accurately and this has yielded many interesting new results (11-13). This technique has potential to reveal considerably more information than the more conventional methods, mentioned above. In order to explore this potentiality, we undertook a Brillouin scattering study of polymer blends which show UCST behaviour.

Experimental

For the present initial Brillouin study and to serve as an inceptive demonstration of the technique, we chose, as an example of a typical blend showing UCST behaviour, binary blends of poly(styrene-co-allyl alcohol) and poly(neopentyl glycol adipate) (7). Poly(styrene-co-allyl alcohol) (SAA), with molecular weight 2300 and containing 5.7wt% of hydroxyl group, was obtained from Scientific Polymer Products Inc. Poly(neopentyl glycol adipate) (PDPA), with a molecular weight range of 1000-2000, was obtained from the Ruco Polymer Corporation. 6.0g of PDPA and 1.5g of SAA were vigorously stirred in a glass vial immersed in an oil bath at 130°C for ten minutes to ensure thorough mixing. The weight fraction of the resulting viscous solution was 0.20 of SAA (volume fraction 0.21). This weight fraction was chosen because it is close to the critical point of the system and its cloud point is known to be near 40°C (7). The solution was poured into a quartz scattering cell, which was then placed for 15 minutes in a vacuum oven at 100°C, to remove the air bubbles.

The phase behaviour at the cloud point of this PDPA/SAA blend was reversible, although the kinetics varied greatly depending on the direction of temperature change (7). On heating, it became clear very quickly, but, when cooled again, took days to turn into a hazy blend. This thermally-induced phase separation is primarily dominated by spinodal decomposition (7) and is on a microstructural level only. The prepared sample was subsequently kept at room temperature for a week during which the hazy blend did not alter appreciably. Hence, the microscopically phase-separated state could be considered to be stable over practical time-scales. Before measurements were made, the sample was first cooled from room temperature to about 283K. Its Brillouin spectrum was then measured as a function of temperature, which was increased in steps from ~ 283K to ~ 333K. The steps of increment in temperature were ~ 5K, except when the temperature was near the cloud point, in which case the steps were ~ 2K. A heating, rather than cooling, sequence was chosen because of the difference in kinetics described above. At each temperature, the sample was held for an equilibration time of typically 20 minutes. Single mode laser light at 514.5nm (100mW) was scattered through 90° from the sample held at a fixed temperature (± 0.01K) and analysed using a Burleigh DAS-1 five-pass Fabry-Perot interferometer system operated with a spectral range of 26GHz, as described previously (11). Any measured Brillouin spectrum is the result of an unavoidable convolution between the true Brillouin lineshape and the instrumental response. In the present study, the effects of instrumental resolution were removed from the measured spectrum by using the technique of Bayesian iterative deconvolution (11). The Brillouin shift ν and true width Γ (f.w.h.m.) were then obtained by least-squares fitting of a Lorentzian profile which accurately describes the true Brillouin lineshape for underdamped acoustic modes (11).

Results

The Brillouin shift, ν, for the PDPA/SAA blend is shown, as a function of temperature, in fig. 1. In general, ν decreases roughly linearly with increasing temperature. No pronounced abrupt changes are observed near the cloud point. There is perhaps, at best, a very slight change of slope. Linear regressive fits to two different portions of data, well below and just above the cloud point, show that the slopes are respectively -0.0365 ± 0.0001 GHz K^{-1} and -0.0343 ± 0.0003 GHz K^{-1}.

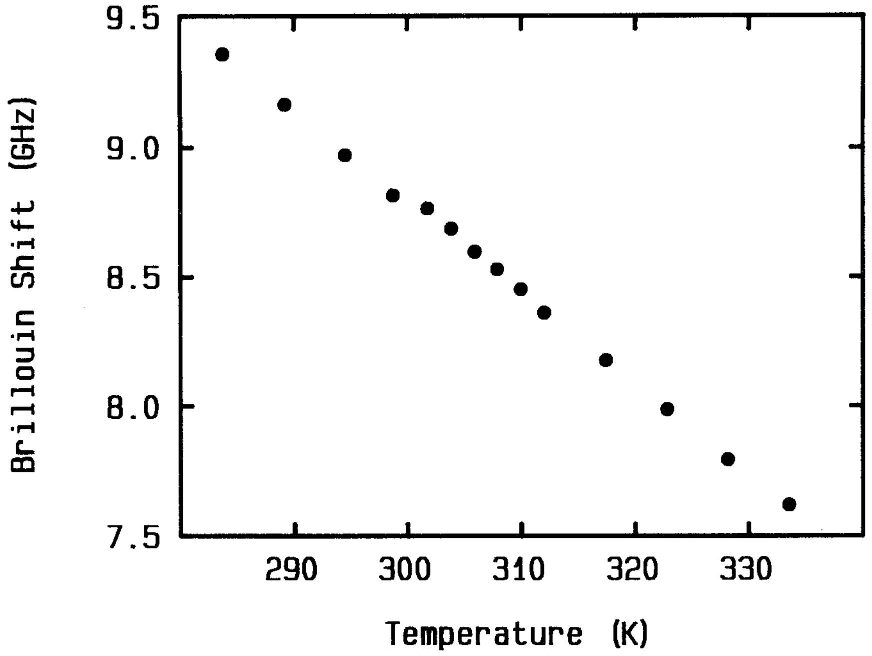

Fig. 1. The Brillouin shift, ν, of the PDPA/SAA blend as a function of temperature. The error bars are too small to show.

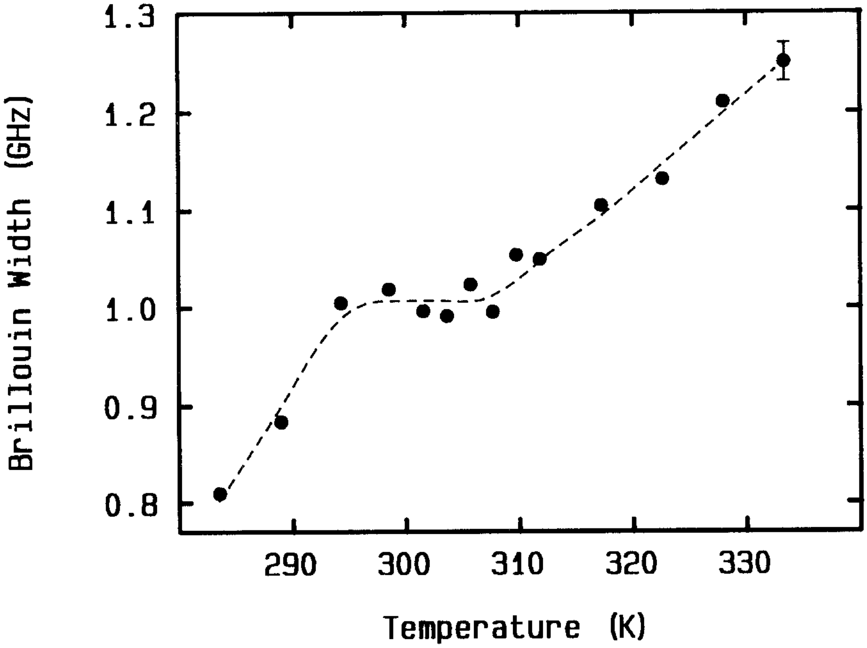

Fig. 2. The Brillouin width, Γ, of the PDPA/SAA blend as a function of temperature. The broken line is a guide to the eye. Typical experimental uncertainties are shown by the error bar.

The Brillouin width, Γ, is shown, as a function of temperature, in fig. 2. In contrast to ν, the behaviour of Γ is considerably more interesting. At first, Γ increases with increasing temperature, then it becomes almost a constant up to the cloud point, beyond which, it increases with temperature again.

The Landau-Placzek ratio, LP, computed by dividing the integrated Rayleigh intensity by twice the integral of the deconvolved Brillouin lineshape, is shown in fig. 3, as a function of temperature. Contrary to the behaviour of Γ, in the temperature range where Γ is almost a constant, LP drops drastically by about three orders of magnitude. The abrupt changes in the LP ratio are mostly due to the corresponding decrease in the integrated Rayleigh intensity, reflecting the visibly obvious reduction observed in the elastic scattering when the sample becomes a solution. The arrow sign indicates the temperature which would conventionally be regarded as the cloud point. This temperature, ~ 310K, agrees well with the result obtained by cloud point method (7).

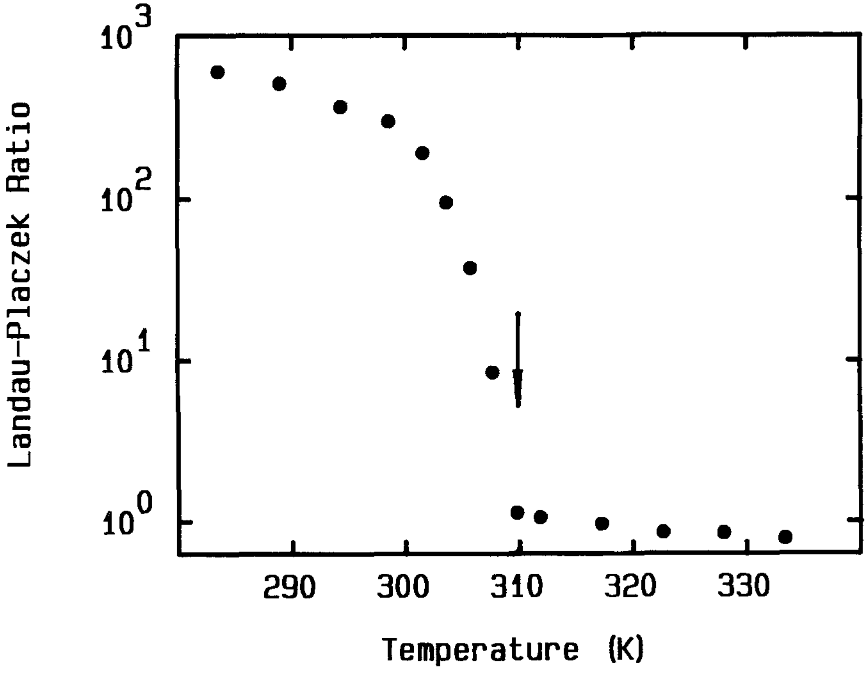

Fig. 3. The Landau-Placzek ratio, LP, of the PDPA/SAA blend as a function of temperature. The arrow sign indicates the temperature which would be conventionally regarded as the cloud point.

Discussion

The Brillouin shift, ν, is related to the velocity of sound, v, in the light-scattering system by $\nu = 2nv \sin(\theta/2)/\lambda$, where λ is the wavelength of light in vacuum, n the refractive index of the system and θ the scattering angle. The sound velocity is given by $v = (M/\rho)^{1/2}$, where M is the longitudinal elastic modulus and ρ the density of the system. In the microscopically separated two-phase state, the observed Brillouin shift represents an average behaviour of the particular mixture through its elastic modulus and density. In this region, these quantities, and hence the Brillouin shift, depend on the respective compositions of the two distinct phases, which are constantly changing as the temperature is raised. The fact that there are no obvious abrupt changes in ν at the cloud point implies that both M and ρ (and therefore the volume) of the PDPA/SAA blend do not vary at the phase separation. We can, therefore, rule out volume change as a possible factor which favours mixing at high temperature for this polymer blend. The probable slight change in the temperature coefficient of ν well below and above the cloud point may be attributed to the change in the temperature coefficient of the specific volume (thermal expansion coefficient) (15).

The Brillouin width, Γ, is given by $\Gamma = \gamma v/\pi$, where γ is the sound attenuation coefficient. The unusual behaviour of Γ may be interpreted as follows. The general increase in $\Gamma(\gamma)$ with temperature well below and above the cloud point can be ascribed to the increase in phonon scattering at higher temperatures due to increases in the molecular mobility (12). Near the cloud point, however, this general rising trend becomes increasingly counterbalanced by an opposing effect; as the cloud point is approached, the compositions of the two microscopically separated phases become more and more similar (1). Consequently, the contribution to sound scattering from the dissimilarity of these phases decreases rapidly. In contrast to the increase in Γ due to enhanced molecular mobility, this effect tends to cause Γ to decrease with rising temperature. Evidently, it happens that the two opposing influences on Γ roughly cancel each other over a range of temperatures just below the cloud point and Γ is almost constant. Beyond the cloud point, the blend turns into a solution, this cancellation effect ends and Γ resumes its increase with temperature again.

The propagation of sound in microscopically inhomogeneous media has been discussed in detail by M.A. Isakovich (16). According to his treatment, non-local relaxation processes could lead to an additional sound absorption and a dispersion of the sound speed. However, these effects are not particularly helpful in interpreting our results, as they are probably masked by the stronger effects, described above, of phase dissolution near the cloud point.

The sample of PDPA/SAA blend is optically hazy in the two-phase mixture state because of the difference in the refractive index of the two phases. However, as the cloud point is approached, this difference decreases, for the same reasons as given above, and the sample becomes less turbid. The sample turns clear at the cloud point as it becomes a solution. The abrupt decrease in the LP ratio near the cloud point region is a reflection of this effect. Furthermore, the fact that it happens in roughly the same temperature range as that in which Γ is constant, reinforces our interpretation of the behaviour of Γ.

In conclusion, the results of this paper have clearly demonstrated the usefulness of the Brillouin light scattering technique in the study of the upper critical solution temperature behaviour in polymer blends. In particular, our accurate determination of the Brillouin width has revealed subtle influences on this quantity, which can be clearly interpreted as arising from gradual, but ever more rapid, composition changes in the two originally distinct low-temperature microscopically separated liquid phases, towards a common high-temperature solution. We believe this is the first observation of such an effect.

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