Q_{bb} is obtained from this equation by exchanging a and b.

$$\Delta\cdot Q_{cc} = x_c^2 v_c + (v_a v_c - v_{ac}^2)x_a' + (v_b v_c - v_{bc}^2)x_b' + 2(v_c v_{ab} - v_{ac}v_{bc})x_{ab}' + (v_a v_b v_c + 2v_{ab}v_{ac}v_{bc} - v_a v_{bc}^2 - v_b v_{ac}^2 - v_c v_{ab}^2)(x_a'x_b' - x_{ab}'^2) \quad (A.5)$$

$$\Delta\cdot Q_{ab} = v_a x_a' x_{ab}' + v_b' x_b' x_{ab}' + v_{ab}(x_a'x_b' + x_{ab}'^2) + (v_a v_b - v_{ab}^2)(x_a'x_b' - x_{ab}'^2)x_{ab}' + (v_a v_c - v_{ac}^2)x_a'x_{ab}'x_c + (v_b v_c - v_{bc}^2)x_b'x_{ab}'x_c + (v_c v_{ab} - v_{ac}v_{bc})(x_{ab}' + x_a'x_b')x_c + (v_a v_b v_c + 2v_{ab}v_{ac}v_{bc} - v_a v_{bc}^2 - v_b v_{ac}^2 - v_c v_{ab}^2)(x_a'x_b' - x_{ab}'^2)x_{ab}'x_c \quad (A.6)$$

$$\Delta\cdot Q_{ac} = x_a' x_c v_{ac} + (v_b v_{ac} - v_{ab}v_{bc})x_b' + (v_{ab}v_{ac} - v_a v_{bc})x_{ab}' + x_{ab}'x_c v_{bc} + (v_a v_{bc} - v_{ab}v_{ac})x_a' + (v_{ab}v_{bc} - v_b v_{ac})x_{ab}' \quad (A.7)$$

Q_{bc} is obtained from this last equation simply by changing a to b. As already mentioned, this formulation is also valid for a mixture of three homopolymers A–C, and a copolymer AB changing only the definition of x_a', x_b', and x_{ab}'. In the absence of the copolymer, the system is reduced to three homopolymers and the corresponding values of Q_{ij} are immediately obtained by letting $x_{ab}' = 0$ and $x_a' = x_a$, $x_b' = x_b$.

References and Notes

(1) Benoit, H.; Benmouna, M. *Polymer* **1984**, *25*, 1059.
(2) Benoit, H.; Benmouna, M. *Macromolecules* **1984**, *17*, 535.
(3) de Gennes, P. G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979; Chapter IX.
(4) (a) Kirkwood, J. G.; Goldberg, R. J. *J. Chem. Phys.* **1950**, *18*, 54. (b) Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18*, 58.
(5) Kratochvil, P.; Vorlicek, J.; Stakova, D.; Tuzar, Z. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 2321.
(6) Benoit, H.; Leibler, L.; Koberstein, J. *Makromol. Chem., Suppl.* **1981**, *4*, 85.
(7) Benmouna, M.; Benoit, H. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 227.
(8) (a) Joanny, J. F. *C. R. Seances Acad. Sci., Ser. B* **1978**, *286B*, 89. (b) Leibler, L.; Benoit, H. *Polymer* **1981**, *22*, 195.
(9) (a) Schulz, G. V. *Z. Phys. Chem., Abt. B* **1939**, *B43*, 25. (b) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1099.
(10) Ionescu, L.; Picot, Cl.; Duval, M.; Duplessix, R.; Benoit, H.; Cotton, J. P. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1019.
(11) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1967; Chapter XII.
(12) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(13) Froelich, D.; Benoit, H. *Makromol. Chem.* **1966**, *92*, 224.
(14) Fetter, A. L.; Walecka, J. D. "Quantum Theory of Many Particles Systems"; McGraw-Hill: New York, 1971; p 154.
(15) Glinka, C. *AIP Conf. Proc.* **1982**, *No. 89*, 395.
(16) Duplessix, R.; Cotton, J. P.; Benoit, H.; Picot, C. *Polymer* **1979**, *20*, 1181.
(17) Roe, R. J.; Fishkis, M.; Chang, J. C. *Macromolecules* **1981**, *14*, 1091.
(18) Brandrup, J.; Immergut, E. H. "Polymer Handbook", 2nd ed.; Wiley-Interscience: New York, 1975; Vol. IV, p 40.

Rayleigh–Brillouin Spectra of Poly[(phenylmethyl)siloxane] under High Pressures

George Fytas,[*,†] Gerd Meier,[‡] and Thomas Dorfmüller

Faculty of Chemistry, University of Bielefeld, D-4800 Bielefeld 1, West Germany.

Received July 12, 1984

ABSTRACT: We report polarized Rayleigh–Brillouin spectra of bulk poly[(phenylmethyl)siloxane] (PPMS) with a molecular weight of about 2500 in the temperature range 20–150 °C and in the pressure range 1–950 bar. The frequency of the hypersonic waves, f_B, and the temperature T_{max} at which the Brillouin line width has its maximum value, are both increasing functions of the hydrostatic pressure P. On the other hand, the relaxation strength, R, is virtually independent of the hydrostatic pressure. The plane (P,T_{max}) consists of an isokinetic curve, which is in agreement with previous high-pressure photon correlation measurements. It appears that the two light scattering techniques monitor the same physical process.

Introduction

Brillouin scattering (BS) and photon correlation spectroscopy (CS) have been applied to study relaxation processes in bulk polymers.[1-4] Above the glass transition temperature, the so-called local primary glass–rubber relaxation dominates the highly nonexponential photon correlation functions of the scattered light from density fluctuations. The corresponding mean relaxation time, $\bar{\tau}$ (1 to 10^{-6} s), exhibits a strong temperature and pressure dependence.[5] On the other hand, the same structural relaxation process affects, in principle, the high-frequency (and hence high temperature) Brillouin spectra via the stress correlation function.[6] The frequency shift, f_B, and the line width, $2\Gamma_B$, of the Brillouin doublet exhibit a dispersion with respect to temperature. The calculation of the relaxation time τ ($={}^1/_2\pi f_{max}$, where f_{max} is the frequency shift at temperature T_{max} at which $2\Gamma_B$ has its maximum value) involves the simplest type of analysis.[3] An alternative approach to analyze the Brillouin spectra[4,6] leads to the temperature dependence of τ, which requires knowledge of the adiabatic ultrasonic frequency f_0. The extent of the information which can be extracted by studying hypersonic dispersion has recently been examined by taking into account the temperature dependence of the Brillouin spectra.[7] In this paper, we performed high-pressure Brillouin scattering measurements on bulk polymers using Fabry–Perot interferometry. The objective is to investigate the pressure effect on f_B and $2\Gamma_B$ of the Brillouin doublet. We have chosen poly[(phenylmethyl)siloxane] (PPMS) for this study on account of the convenient temperature range and the existence of photon correlation high-pressure measurements.[8] Thus, the characteristic times for the structural relaxation process obtained by the two light scattering techniques can be compared in terms of their pressure dependence.

[†] Permanent address: Department of Chemistry, University of Crete, Iraklion, Greece.

[‡] Present address: Institute of Physical Chemistry, University of Mainz, D-6500 Mainz, West Germany.

0024-9297/85/2218-0993$01.50/0

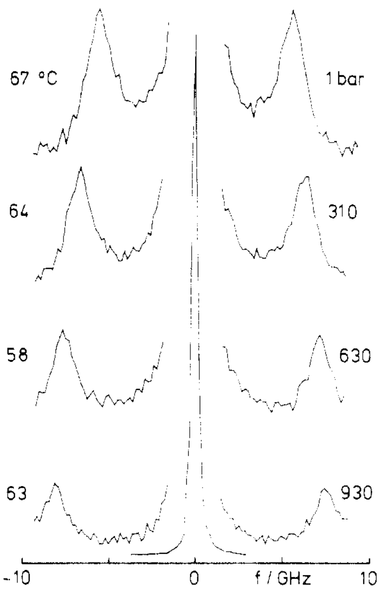

Figure 1. Polarized Rayleigh–Brillouin spectra of PPMS around 63 °C for different pressures.

Experimental Section

The polarized scattering spectra were taken at a scattering angle of 90° using the spectrometer described elsewhere.[4] The light source was an argon ion laser operating at a single mode at 514.5 nm with a power of 200 mW. The scattered light from the dust-free sample contained in a rectangular Hellma cell was spectrally analyzed with a piezoelectrically scanned Fabry–Perot interferometer. The operating finesse was 60, and the spectra were taken over a free spectral range of 17.94 GHz. Experimental Brillouin spectra were fitted to three Lorentzian functions considering the overlap of the neighboring orders. After subtraction of the instrumental line width (0.3 GHz), the full width $2\Gamma_B$ and the shift f_B of the Brillouin peak were obtained. The line widths are reproducible to better than 10%, whereas the uncertainty of f_B is less than 2%.

Brillouin spectra of PPMS were recorded at temperatures between 20 and 150 °C and pressures of 1, 310, 630, and 930 bar. Typical polarized Brillouin spectra around 63 °C are shown in Figure 1 at four different pressures. The measurements were performed with the high-pressure light scattering cell shown in Figure 2. Six optical windows (float glass SF 57 NSK, Schott, Germany), four of them in 90° geometry for alignment purposes and an additional two in 45° geometry lying opposite to each other to allow angular-dependent measurements, are incorporated in the main body of the vessel. The float glass windows have an extremely low Pockels coefficient,[9] so that with this setup depolarized measurements are also possible besides Brillouin spectroscopy. Further studies on appropriate systems are in progress. A more detailed description of the high-pressure cell is indicated in Figure 2. For reasons of simplicity only one window is explicitly shown. The thermostating liquid was circulated through a jacket surrounding the main cell body, and the temperature was measured by means of a thermocouple located very close to the sample position. The pressure was generated with a Nova Swiss membrane compressor and was measured with a Heise gauge. The pressurizing medium was nitrogen.

Poly[(phenylmethyl)siloxane] with a molecular weight of ~2500 was purchased from Petrarch Systems. The sample was filtered through a 0.45-μm Millipore filter directly into the dust-free 10-mm-o.d. Hellma cell. In order to retard the diffusion of nitrogen into the scattering volume (close to the bottom of the Hellma cell), a capillary (0.5 mm × 5 mm) was incorporated in the top of the Hellma cell.

Results and Discussion

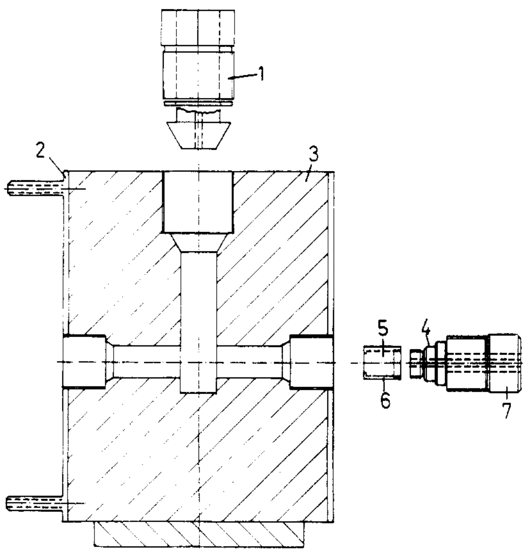

Figure 2. (1) Top screw with inlet for nitrogen; (2) surrounding jacket for thermostating liquid; (3) main high-pressure vessel (stainless steel 4057); (4) window holder (seals to vessel with Viton O-rings); (5) float glass window; (6) cap to fix the window onto (4) (between glass and steel is 0.1-mm-thick Teflon); (7) screw to fix (4) in (3).

Table I
Shift f_B and Line Width $2\Gamma_B$ of the Brillouin Doublet of PPMS

T/°C	P/bar	f_B/GHz	$2\Gamma_B$/GHz
21.2	1	6.92	1.10
35.5		6.40	1.45
48		6.01	1.70
67		5.53	1.67
87.7		5.05	1.42
23.5	310	7.67	0.96
41.2		7.04	1.10
52.5		6.66	1.49
64		6.41	1.64
77.7		6.13	1.72
97		5.68	1.60
140		5.10	1.10
30.8	630	8.16	0.86
43.2		7.80	0.96
57.5		7.37	1.13
73		6.99	1.30
92.5		6.45	1.67
112.5		6.15	1.45
147		5.60	1.25
44	930	8.40	0.76
63		7.82	0.86
80		7.42	1.12
99		6.99	1.55
118		6.65	1.56
147		6.23	1.38

The values of f_B and $2\Gamma_B$ of PPMS as a function of temperature at different external pressures are listed in Table I. The shift, f_B, is a decreasing function of temperature and increasing function of pressure (Figure 3). The effect of pressure is mainly due to a decrease of the free volume, V_f, according to the relation $f_B \sim (V_0/V_f)^{1/3}$,[10] where V_0 is the closest packing molar volume of the polymer. In the absence of relaxation effects f_B measurements can be used to monitor free volume changes. Alternatively, the line width, $2\Gamma_B$, in Figure 4 displays a bell-like form, which is typical for structural relaxation processes. The temperature T_{max}, at which $2\Gamma_B$ has its maximum value, is found to increase with increasing hydrostatic pressure.

In the Brillouin experiment, the dispersion of the longitudinal hypersonic waves for a single relaxation pro-

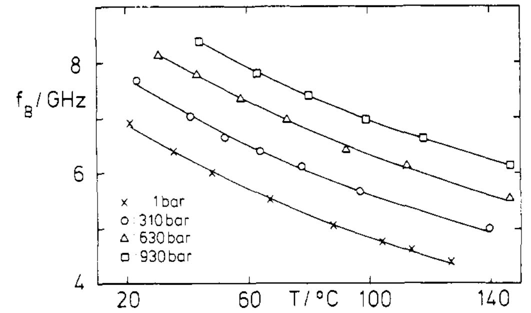

Figure 3. Hypersonic frequency shift f_B in PPMS vs. temperature at different pressures. The lines are to guide the eye.

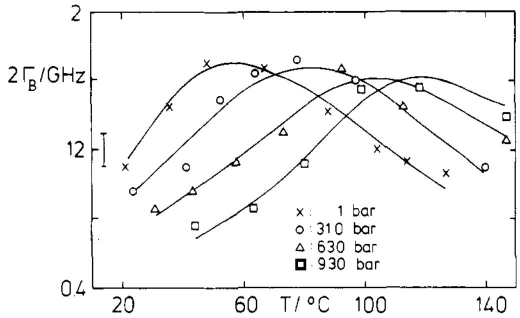

Figure 4. Brillouin line width $2\Gamma_B$ vs. temperature at different pressures. The solid lines represent the fit of eq 2 to the experimental data.

cess can be approximately described by[6,11]

$$\frac{\omega_B^2}{\omega_0^2} - 1 = \frac{(R-1)\omega_B^2\tau^2}{1+\omega_B^2\tau^2} \quad (1)$$

$$2\Gamma_B = \frac{(R-1)\omega_0^2\tau}{1+\omega_B^2\tau^2} \quad (2)$$

where $R = (u_\infty/u_0)^2$ is the relaxation strength and u_∞ and u_0 are the limiting sound velocities at high and low frequencies, respectively. According to eq 2, $2\Gamma_B$ has its maximum value at T_{max} when $\omega_B\tau \sim 1$. With increasing pressure in the range 1–1000 bar the maximum line width region is shifted to higher temperatures (Figure 4). Since ω_B is an increasing funtion of P (Figure 3) but a decreasing function of T, the two effects cancel each other to a large extent. The value of ω_B for each pair (T_{max},P) is virtually constant and amounts to 6.4 GHz, which yields $\tau = 2.5 \times 10^{-11}$ s. A plot of T_{max} vs. P (Figure 5) is an isokinetic curve which is defined as the locus of equal value of τ in the (P,T) plane. The slope $(\mathrm{d}T/\mathrm{d}P)_\tau$ at constant Brillouin time τ is found to be 8.4×10^{-2} K/bar. The corresponding values at $\bar{\tau} = 6.2 \times 10^{-5}$ s and 0.13 s obtained from high-pressure photon correlation measurements are 2.4×10^{-2} and 2.0×10^{-2} K/bar, respectively.[8] The temperature–pressure dependence of $\bar{\tau}$ can be described well by[5,12]

$$\bar{\tau} = \bar{\tau}_0 \exp\frac{B + aP}{T - T_0} \quad (3)$$

According to eq 3, $(\mathrm{d}T/\mathrm{d}P)_{\bar{\tau}} = a/\ln(\bar{\tau}/\bar{\tau}_0)$ should increase with decreasing $\bar{\tau}$. The slopes in Figure 5 do indeed conform to this prediction. Furthermore, if the pressure dependence of the structural relaxation time $\bar{\tau}$ and the Brillouin time τ is the same, then the slopes of the curves in Figure 5 should scale with $\ln(\tau/\tau_0)$. Taking $\bar{\tau}_0 = 10^{-13}$ s, the ratio $(\mathrm{d}T/\mathrm{d}P)_\tau/(\mathrm{d}T/\mathrm{d}P)_{\bar{\tau}}$ is indeed within 5% close to the value of the ratio $\ln(\bar{\tau}/\bar{\tau}_0)/\ln(\tau/\tau_0)$. This observation suggests that the same physical process is probed by photon correlation at low temperatures and Brillouin scattering at high temperatures.

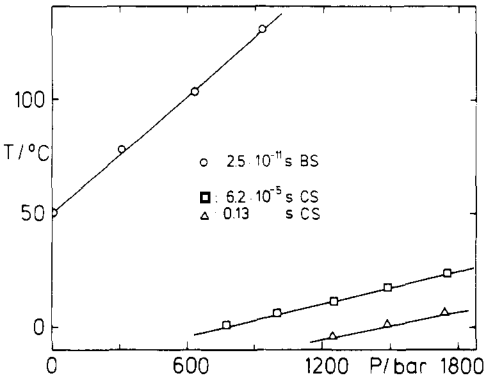

Figure 5. Temperature vs. pressure plot for a given value of the relaxation time for PPMS for three different relaxation times: (○) BS (Brillouin scattering); (△, □) CS (photon correlation spectroscopy).

A rigorous test of this proposal would be the direct comparison of the value a (eq 3) obtained from CS (photon correlation) measurements and the present Brillouin experiment. However, apart from the inherent difficulties in fitting the hypersonic dispersion,[7] the extraction of the Brillouin time requires a knowledge of the parameters R and ω_0 ($=u_0k$; k is the amplitude of the scattering vector) and their temperature and pressure dependence entering into eq 1 and eq 2.

The hypersonic dispersion in PPMS at ambient pressure has been represented by eq 1 and eq 2 with fixed ω_0 as obtained from ultrasonic measurements.[7] From the fit of the temperature dependence of $2\Gamma_B$ and f_B at 1 bar we have obtained the relaxation strength R:

$$R = 1.66 - 2 \times 10^{-3}T \quad (4)$$

where T is given in °C. A rough estimate of R at high pressure can be deduced from eq 2. At $T = T_{max}$, $2\Gamma_B \sim (R-1)/\tau$, and R is virtually independent of pressure, as both the maximum value of $2\Gamma_B$ and τ were found to be the same in the plane (P,T_{max}). However, since R is a decreasing function of temperature (eq 4), the value of $2\Gamma_B$ at T_{max} is slightly lower at high pressures. Thus, is seems reasonable to handle R as a fixed parameter in fitting eq 2 to the experimental line width data at high pressures. By floating R, we obtained values which obey eq 4. Furthermore, an estimate of ω_0 for each isobar curve of Figure 3 is obtained from the high-temperature value of f_B assuming a pressure-independent temperature coefficient $(\mathrm{d}\omega_0/\mathrm{d}T)/2\pi = 0.0133$ GHz/K.[7] This crude estimate is, however, adequate as the line width fit is less sensitive to ω_0.

On the ground of these estimations, we fitted eq 2 with an Arrhenius temperature dependence of τ to the experimental line width data of Table I. From the pressure dependence of the activation parameter, B, we computed $a = 0.7 \pm 0.2$ K/bar. The corresponding value obtained from the pressure dependence of the structural relaxation time $\bar{\tau}$ using the CS technique amounts to 0.81 K/bar.[8] Thus, the characteristic times for the structural relaxation obtained by the BS and CS techniques show similar pressure dependence. This finding suggests that the two light scattering techniques monitor the same physical process. As to the relation between the absolute value of the times τ and $\bar{\tau}$, one should be cautious, because of the differences in the probe emphasis, the extremely broad time distribution of the structural relaxation process, and the frequency limits in Fabry–Perot interferometry and CS. While the probe emphasis is a theoretical problem, the frequency gap between the two light scattering techniques can be almost covered by extrapolation of high-pressure measurements.[8]

Finally, the fit of eq 1 to the Brillouin shift f_B at high pressures is ambiguous, because the measurements above 330 bar are in the range where $\omega_B\tau \gg 1$ and ω_0 is not precisely known.[13]

Note Added: After this paper was submitted for publication one other reference on the pressure dependence of the hypersonic attenuation in poly(dimethylsiloxane) appeared.[14] The reported shift of the hypersonic loss maximum at elevated pressure to higher temperature is in agreement with the present results on poly[(phenylmethyl)siloxane]. We also received a preprint by Wang and Fischer,[15] who provide a theoretical framework for the determination of the longitudinal compliance using both light scattering techniques.

Acknowledgment. We gratefully acknowledge the financial support of the Deutsche Forschungsgemeinschaft (D.F.G.) and E. Lükkeville for making the high-pressure cell. Thanks are also due to I. Schiller for typing the manuscript.

References and Notes

(1) Patterson, G. D. *Adv. Polym. Sci.*, **48**, 128 (1983).
(2) Y. Y. Huang and C. H. Wang, *J. Chem. Phys.*, **64**, 4738 (1976).
(3) G. D. Patterson, *Annu. Rev. Mater. Sci.*, **13** (1983).
(4) G. Fytas, Y. H. Lin, and B. Chu, *J. Chem. Phys.*, **74**, 3131 (1981).
(5) G. Fytas, A. Patkowski, G. Meier, and Th. Dorfmüller, *Macromolecules*, **15**, 870 (1982).
(6) Y. H. Lin, and C. H. Wang, *J. Chem. Phys.*, **70**, 681 (1979).
(7) A. Onabajo, G. Fytas, and Th. Dorfmüller, *J. Polym. Sci., Polym. Phys. Ed.*, in press.
(8) G. Fytas, Th. Dorfmüller, and B. Chu, *J. Polym. Sci., Polym. Phys. Ed.*, **22**, 1471 (1984).
(9) D. M. Cantor, J. Schröder, and J. Jonas, *Appl. Spectrosc.*, **29**, 393 (1975).
(10) J. V. Champion and D. A. Jackson, *Mol. Phys.*, **31**, 1159 (1976).
(11) R. D. Mountain, *J. Res. Natl. Bur. Stand., Sect. A*, **70**, 907 (1966).
(12) G. Fytas, Th. Dorfmüller, and C. H. Wang, *J. Phys. Chem.*, **87**, 5041 (1983).
(13) Th. Dorfmüller, G. Fytas, and W. Mersch, *Ber. Bunsenges. Phys. Chem.*, **80**, 389 (1976).
(14) G. D. Patterson, P. J. Carroll, J. R. Stevens, W. Wilson, and H. E. Bair, *Macromolecules*, **17**, 885 (1984).
(15) C. H. Wang and E. W. Fischer, *J. Chem. Phys.*, **82**, 632 (1985).

Neutron-Scattering Investigation of the Interaction between Components in Concentrated, Miscible, Amorphous Polymer Blends

C. T. Murray, J. W. Gilmer, and R. S. Stein*

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003. *Received August 13, 1984*

ABSTRACT: Small-angle neutron-scattering (SANS) experiments were performed to investigate the composition and temperature dependence of the interaction between components in the amorphous miscible blend of deuterated poly(styrene) and poly(*o*-chlorostyrene). Recent neutron-scattering theories[1,2] were modified by using an enthalpy-corrected Flory–Huggins theory and an empirical interaction function. The measured interaction function was found to be composition and temperature independent. The results of this investigation are compared to previous theoretical[2–4] and experimental data[2–4,38] on the blends of hydrogenated poly(styrene) and poly(*o*-chlorostyrene).

Introduction

The miscible amorphous blend of poly(styrene) (PS) with poly(*o*-chlorostyrene) (POCS) has been a subject of considerable investigation, primarily due to the large molar mass dependence of the phase diagram[3–5] and the positive heat of mixing measured for this blend system.[3] The heat of mixing results indicate that the PS/POCS blend has no net attractive interactions,[5] yet the system is miscible. In that instance, McMaster has shown that the system can exhibit UCST and LCST behavior,[6] although experimental conditions usually prevent observation of the UCST phase boundary. In a previous study, Zacharius et al.[5] concluded that the experimental evidence pointed to the existence of a critical double point (CDP) for the PS/POCS blend system.

Figure 1 shows the Flory equation of state calculated temperature dependence of the interaction function $\chi_{12}(T)$ for the system of indicated molecular weight poly(styrenes) mixed with M_w 100 000 POCS.[3] This figure illustrates the typical behavior of $\chi_{12}(T)$ for blend components that show no net attractive interactions. The critical value of the interaction between the components, χ_c, is indicated in Figure 1 by the solid horizontal lines. The $\chi_{12}(T)$ curve is assumed to be independent of molecular weight and χ_c is given as

$$\chi_c = (r_1^{-1/2} + r_2^{-1/2})^2/2$$

where r_1 and r_2 are the degrees of polymerization for each blend component. If the blend exists in a state where χ_c is larger than the minima in the $\chi_{12}(T)$ curve, a UCST and LCST will be found at temperatures where $\chi_c = \chi_{12}(T)$. Increasing either component's r value decreases χ_c until, eventually, the critical value coincides with the minima of the $\chi_{12}(T)$ curve. The UCST and LCST then merge in a critical double point. Figure 2 represents the phase diagram as a function of molecular weight resulting from the situation described above.

The critical double point hypothesis put forth by Zacharius et al. requires that the interaction function between components be independent of composition. In this study,