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Phase Separation Curves of Poly(α-methylstyrene) in Methylcyclohexane

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We report new measurements of the liquid−liquid phase separation curves of poly(α-methylstyrene) + methylcyclohexane, for three well-characterized samples of the polymer with number average molecular weights of (A) 19 700, (B) 32 300, and (C) 72 000 g/mol. Sample A (polydispersity index PI = 1.02) has a critical point at a mass fraction m_c of polymer of 0.20 ± 0.02 and a critical temperature T_c at (305.70 ± 0.09) K. The critical point for sample A is not at the apex of the phase separation curve, which indicates that the polymer was not sufficiently monodisperse to behave as one component. Sample B (PI = 1.02) has $m_c = 0.15 \pm 0.02$ and $T_c = (318.3 \pm 0.4)$ K; this critical point is at the apex of the phase separation curve within our resolution. Sample C (PI = 1.05) has $m_c = 0.11 \pm 0.02$ (not the apex of the curve) and $T_c = (328.9 \pm 0.4)$ K. From these measurements, we find a theta temperature Θ of (357 ± 5) K and an entropy of dilution parameter ψ_1 of 0.49 ± 0.06. The polymer/solvent interaction parameter χ_1 at T_c for each sample is (A) 0.54 ± 0.01, (B) 0.56 ± 0.01, and (C) 0.58 ± 0.01. The uncertainties for Θ, ψ_1, and χ_1 are given as one standard deviation.

Introduction

Poly(α-methylstyrene) is a polymer of interest both in basic polymer science (Selser, 1985) and in industrial processes, such as the fabrication of laser fusion targets (Letts et al., 1995). So far as we can determine, the only published report of a liquid−liquid phase diagram of poly(α-methylstyrene) in a poor solvent is that of Saeki et al. (1983). We present here new measurements of the liquid−liquid phase separation curves of poly(α-methylstyrene) + methylcyclohexane, using three well-characterized samples of poly(α-methylstyrene). We compare our data with the data of Saeki (1983) and find poor agreement.

Experimental Methods

1. Sample Preparation. The poly(α-methylstyrene) samples were obtained from Polymer Source, Inc. (Quebec, Canada). The polymers had been prepared by anionic polymerization, using *sec*-butyllithium as the initiator. Size exclusion chromatography by Polymer Source showed unimodal peaks for all three samples. Polymer A had a number average molecular weight M_n of 19 700 and a weight average molecular weight M_w of 20 100, giving a polydispersity index (PI = M_w/M_n) of 1.02. Polymer B had $M_n = 32\,300$, $M_w = 32\,900$, and PI = 1.02. For Polymer C, $M_n = 72\,000$, $M_w = 75\,600$, and PI = 1.05. The methylcyclohexane (Aldrich Chemical Co., Milwaukee, WI), 99.9% pure, was shipped in a sealed bottle and used without further purification.

All solutions were prepared by weight, in volumes of 2 to 3 mL, in glass vials with Teflon-lined silicone cap liners (Pierce Chemical Co., Rockford, IL). Polymer A was studied in three sets of samples: In set A-a, the samples were prepared on the benchtop, with no further drying of polymer or solvent; set A-b samples were prepared by the dilution of set A-a; set A-c was prepared from polymer that had been dried in a desiccator (over P_2O_5 for 2 weeks).

Polymer B was studied in two sets of samples: In set B-a, samples were prepared on the benchtop, using the materials as purchased, with no further drying of either the polymer or the solvent, and using a cannula and argon pressure to transfer the MCH. For sample B-8, three drops of water were *added* to the sample, as a test of sensitivity to water as an impurity. In set B-b, eleven samples were made with some attention to removing water as an impurity. The preparation was done in a high-purity, argon-atmosphere drybox (<4 ppm water), using polymer that had been dried in the drybox for several days, using a fresh bottle of MCH from which transfers were made in the drybox by syringe, and sealing the vials in the drybox.

Samples of polymer C were prepared either (set C-a) by mixing on the benchtop as for A-a or (C-b) by drying the polymer in a desiccator (over P_2O_5 for 2 weeks), followed by mixing on the bench, with MCH transferred by cannula from a sealed bottle.

2. Temperature Control and Measurement. Sample vials were placed in a bath of water and ethylene glycol, the temperature of which was controlled to ±1 mK (Greer, 1989). The temperature was measured with a platinum resistance thermometer (Guildline Instruments, Inc., Orlando, FL) with a precision of 0.001 K and an accuracy of 0.01 K.

3. Procedure. Samples were placed in the water bath, in a holder that allowed them to be rotated for mixing. The temperature was raised, and the samples were mixed until the samples were homogeneous. Then the temperature was lowered in steps. At each step, the samples were inspected for the appearance of cloudiness or a liquid−liquid meniscus. Most samples were allowed to equilibrate for about 24 h at a given step. Samples near the critical composition required at least 24 h for phase separation, while those further from critical separated within 1 h. Several such

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Table 1. Phase Separation Temperatures for Poly(α-methylstyrene) + Methylcyclohexane[a]

sample	prep method	mass fraction	T_p (K)
A-116 (from A-16)	A-b	0.065 ± 0.001	302.85 ± 0.08
A-16	A-c	0.100 ± 0.001	304.18 ± 0.07
A-112 (from A-12)	A-b	0.111 ± 0.001	305.5 ± 0.1
A-12 (from A-2)	A-b	0.122 ± 0.001	305.67 ± 0.01
A-13 (from A-3)	A-b	0.148 ± 0.001	305.801 ± 0.004
A-14 (from A-4)	A-b	0.180 ± 0.001	305.776 ± 0.006
A-1	***A-a***	***0.199 ± 0.001***	***305.71 ± 0.01***
A-2	A-a	0.221 ± 0.001	305.61 ± 0.03
A-3	A-a	0.252 ± 0.001	305.44 ± 0.02
A-4	A-a	0.275 ± 0.001	305.19 ± 0.01
A-115 (from A-15)	A-b	0.287 ± 0.001	302.0 ± 0.2
A-15	A-c	0.301 ± 0.001	301.78 ± 0.03
B-1	B-b	0.005 ± 0.001	<289
B-2	B-b	0.010 ± 0.001	303 ± 2
B-3	B-b	0.014 ± 0.001	307 ± 2
B-4	B-b	0.019 ± 0.001	309 ± 2
B-5	B-b*	0.023 ± 0.001	313.3 ± 0.1
B-7	B-a	0.047 ± 0.001	314.0 ± 0.1
B-8	B-a + water	0.0476 ± 0.0001	>336
B-6	B-a	0.0477 ± 0.0001	313 ± 2
B-9	B-a	0.0909 ± 0.0001	317 ± 2
B-10	B-a	0.092 ± 0.001	317.6 ± 0.1
B-11	B-a	0.1299 ± 0.0001	317 ± 2
B-13	B-b	0.130 ± 0.001	317.9 ± 0.1
B-12	B-b*	0.131 ± 0.001	317 ± 2
B-16	***B-b***	***0.166 ± 0.001***	***318.6 ± 0.1***
B-14	B-a	0.1661 ± 0.0001	317 ± 2
B-15	B-b*	0.167 ± 0.001	317 ± 2
B-19	B-b	0.197 ± 0.001	318.4 ± 0.1
B-17	B-a	0.2000 ± 0.0001	317 ± 2
B-18	B-a*	0.205 ± 0.001	317 ± 2
B-20	B-b	0.230 ± 0.001	317.5 ± 0.1
C-1	C-b	0.0059 ± 0.0001	315 ± 2
C-2	C-b	0.0105 ± 0.0001	321 ± 2
C-3	C-b	0.0147 ± 0.0001	327 ± 2
C-4	C-b	0.0195 ± 0.0001	327 ± 2
C-5	C-b	0.0243 ± 0.0001	325.9 ± 0.1
C-6	C-a	0.0481 ± 0.0001	329 ± 2
C-7	C-b	0.0505 ± 0.0001	328.5 ± 0.1
C-8	C-a	0.0907 ± 0.0001	329 ± 2
C-9	C-b	0.0918 ± 0.0001	329.2 ± 0.1
C-11	***C-b***	***0.1307 ± 0.0001***	***328.5 ± 0.1***
C-10	C-a	0.1308 ± 0.0001	328 ± 2
C-12	C-b	0.1647 ± 0.0001	327.8 ± 0.1
C-13	C-b	0.1978 ± 0.0001	326.6 ± 0.1
C-14	C-b	0.2304 ± 0.0001	325 ± 1

[a] Polymer A had a number average molecular weight M_n of 19 700 and a weight average molecular weight M_w of 20 100, giving a polydispersity index (PI = M_w/M_n) of 1.02. For polymer B, M_n = 32 300, M_w = 32 900, and PI = 1.02. For polymer C, M_n = 72 000, M_w = 75 600, and PI = 1.05. "Prep method" refers to the technique of preparation (see text); an "*" indicates that the drybox may not have been at its full specifications during the preparation. The samples made by dilution of other samples are so indicated. Sample B-8 had water added (see text). T_p is the observed phase separation temperature. The sample nearest the critical composition is in bold italics.

cooling sequences were required to refine the phase separation temperatures. The relative volumes of the two liquid phases at separation were noted by eye and used to assess the critical mass fraction, since the volumes are equal at the critical composition (as discussed in two papers by Koningsveld and Staverman on phase separations in polymer solutions (Koningsveld and Staverman, 1968a and 1968b)).

Results and Discussion

Table 1 lists and Figure 1 shows the phase separation curves measured for poly(α-methylstyrene) + methylcyclohexane. We note the following:

(1) The T_p values for poly(α-methylstyrene) + methylcyclohexane are not as exquisitely sensitive to water as are those of some polymer + solvent systems, including polystyrene + cyclohexane (Kuwahara et al., 1973). In the case of polystyrene + diethyl malonate, samples prepared on the bench have T_p values as much as 23 K higher than those for samples prepared under very dry conditions (Gruner and Greer, 1987). However, for poly(α-methylstyrene) + methylcyclohexane, this difference is about 1 K. Nonetheless, water does increase T_p for this system, as seen in the sample to which water was added (Table 1, sample B-8) and which then showed a very high T_p.

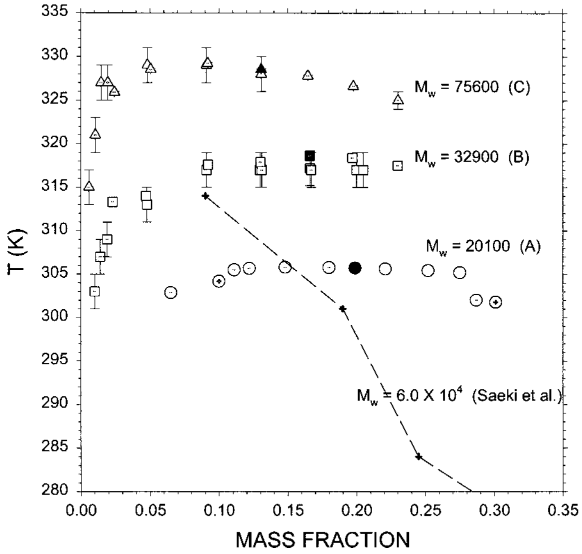

Figure 1. Phase separation temperatures for poly(α-methylstyrene) in methylcyclohexane. Symbols indicate the critical point (solid symbols) and the preparation methods (see text; A = plain symbol; B = dotted symbol; C = crossed symbol). Data of Saeki et al. (1983) are shown as crosses connected by a dashed line.

(2) Sample A (M_n = 19 700; PI = 1.02) showed equal volumes of the two phases for sample A-1 at a mass fraction $m = 0.199 \pm 0.001$ and at $T_p = (305.71 \pm 0.01)$ K. Samples A-14 and A-2 did not show equal volumes, allowing us to bracket the critical mass fraction to $m_c = 0.20 \pm 0.02$ and the critical temperature to $T_c = (305.70 \pm 0.09)$ K. The critical point is not at the apex of the phase separation curve (sample A-13, $m = 0.148$ in Table 1), which indicates that the polymer was not sufficiently monodisperse to behave as one component (Koningsveld and Staverman, 1968). This result can be compared with the report that, for polystyrene + cyclohexane, the critical point is located on the polymer-rich branch of the phase separation curve for a PI as low as 1.03 (Kuwahara et al., 1973).

(3) Sample B (M_n = 32 300; PI = 1.02) showed equal volumes of the two phases for sample B-16 at $m = 0.166 \pm 0.001$ and $T_p = (318.6 \pm 0.1)$ K. Samples B-13 and B-14 did not show equal volumes, allowing us to bracket $m_c = 0.15 \pm 0.02$ and $T_c = (318.3 \pm 0.4)$ K. Within our resolution, the critical point is at the apex of the phase separation curve.

(4) Sample C (M_n = 72 000; PI = 1.05) showed equal volumes of the two phases for sample C-11 at $m = 0.1307 \pm 0.0001$ and $T_p = (328.5 \pm 0.1)$ K. Samples C-9 and C-10 did not show equal volumes, allowing us to bracket $m_c = 0.11 \pm 0.02$ and $T_c = (328.9 \pm 0.4)$ K. The critical point is not at the apex of the phase separation curve (sample C-9, $m = 0.0918$).

(5) Our measurements are *not* consistent with those of Saeki et al. (1983), as is clear from Figure 1. The polymer sample used by Saeki et al. was characterized only by $M_w = 6.0 \times 10^4$. The phase transitions were detected by

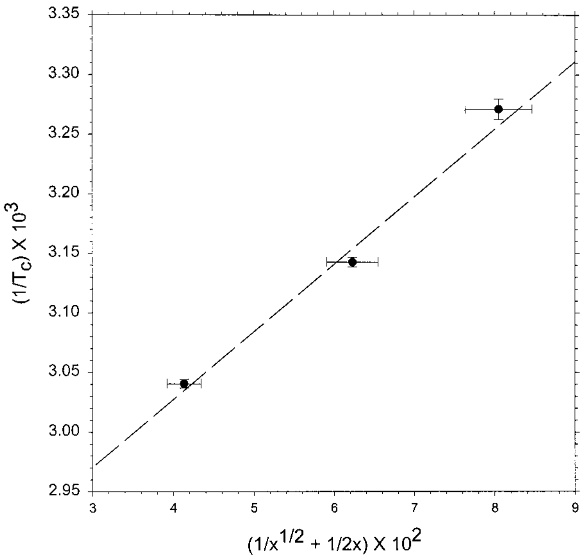

Figure 2. $(1/T_c)$ as a function of $(1/x^{0.5} + 1/2x)$, where x is the degree of polymerization for each sample. Error bars show one standard deviation. A straight line fitted to these data (dashed line) yields values for the theta temperature, the entropy of dilution parameter, and the polymer/solvent interaction parameter (see text).

measuring the increased light scattering on phase separation. The samples were cooled at 0.3 to 1.1 K/min and then heated to confirm the transition temperatures to 1 K. We can hypothesize two possible reasons for the discrepancy with our data: (1) The sample of Saeki et al. was very polydisperse; (2) the method of detection did not sense the actual transition temperature.

(6) Figure 2 shows $(1/T_c)$ as a function of $(1/x^{0.5} + 1/2x)$, where x is the degree of polymerization for each sample (Flory, 1953). A fit of $(1/T_c) = a_1 + a_2(1/x^{0.5} + 1/2x)$ by weighted least squares analysis yields $a_1 = 1/\Theta$ and $a_2 = 1/(\Theta\psi_1)$, where Θ is the theta temperature and ψ_1 is the entropy of dilution parameter. We obtain $\Theta = (357 \pm 5)$ K and $\psi_1 = 0.49 \pm 0.06$ for poly(α-methylstyrene) + methylcyclohexane. The polymer/solvent interaction parameter $\chi_1 = 0.5 - \psi_1(1 - \Theta/T_c)$ can then be calculated for each sample: (A) 0.54 ± 0.01; (B) 0.56 ± 0.01; (C) 0.58 ± 0.01. Uncertainties of these fitted parameters are given as one standard deviation. We are aware of no other measurements of these parameters for this system. Our Θ value for poly(α-methylstyrene) + methylcyclohexane can be compared to those for PαMS + cyclohexane (Brandrup and Immergut, 1989) ($\Theta = 305-312$ K) and for polystyrene + cyclohexane (Imre and Hook, 1996) ($\Theta = 307$ K) and polystyrene + methylcyclohexane (Imre and Hook, 1996) ($\Theta = 345$ K).

(7) The system is very sensitive to the polydispersity. Even a polydispersity index of 1.02 does not guarantee that the critical point will be at the apex of the phase separation curve.

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