Determinations of Consolute Temperature of Poly[styrene-*ran*-(butyl methacrylate)] Solutions by Simultaneous Measurement of Differential Thermal Analysis and Laser Transmittance

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ABSTRACT: In order to study the phase equilibrium of copolymer solution, we constructed a differential thermal analysis instrument equipped with a laser, which allows the simultaneous measurement of thermal change via differential thermal analysis and optical property change via visible spectroscopy. With this apparatus, the consolute temperatures of poly[styrene-*ran*-(butyl methacrylate)] having various styrene contents and its homopolymer/methyl ethyl ketone solutions were measured. From the results obtained, we found that both the lower and upper critical solution temperatures exist in these systems.

Introduction

Heats of dilution of an atactic polystyrene/methyl ethyl ketone solutions were measured at 298 K by means of microcalorimetry by Fujishiro et al.[1] They reported that the heat of the interaction parameter was estimated to be negative (exothermic) for high molecular weights. The fact that the enthalpy parameter in this system is negative may be expected by the existence of the lower critical solution temperature.

Recently, the use of a polymeric stationary phase in a gas-liquid chromatographic study made it possible to obtain information on polymer-solvent interactions in highly concentrated polymer solutions. We studied the interactions between random copolymers having various chemical compositions and various kinds of solvent by means of inverse gas chromatography, and the thermodynamic quantities of these systems were estimated.[2] From the results, we predict that the consolute temperature may exist in these systems.

A few systems have been examined to confirm the presence of phase separation. Phase separation in polymeric solution has been reported for oligo(ethylene oxide) and cellulose derivatives in water via heating and cooling experiments with differential thermal analysis[3,4] and light scattering techniques.[5] No information, however, has been obtained on the phase separation of copolymers.

In this paper, in order to obtain information about the consolute temperature of homo- and copolymer solutions, we constructed a differential thermal analysis instrument equipped with laser, which allows the simultaneous measurement of thermal change via differential thermal analysis and optical property change via visible spectroscopy. With this apparatus, the consolute temperatures of poly[styrene-*ran*-(butyl methacrylate)]/methyl ethyl ketone and its homopolymer solutions were measured. We will discuss the lower and upper critical solution temperatures of these systems.

Experimental Section

Apparatus. An instrument consisting of a differential thermal analysis (DTA) system equipped with a laser possessing two glass cell ampules with a capacity of about 0.2 cm^3 was designed and constructed as shown in Figure 1. The cell holder top (A) was made of copper (diameter 30 mm and height 53 mm), and the heater block (B) was brass and was heated by a nichrome wire coil (C) (resistance 12 Ω). In order to prevent a concentration change and the evaporation of solvent with an increase of temperature, the "F" portion of the glass cell as shown in the right side of Figure 1 was sealed tightly by a small flame. Although the thermal conductivity of the glass cell is low, it is advantageous that the glass cell can be sealed easily and perfectly. A chromel-constantan thermocouple (E) was used as a sensing device for the temperature difference between the sample cell and the reference one and also between the reference cell and ice point.

The block diagram of this apparatus is shown in Figure 2. The electromotive force corresponding to the temperature difference between sample and reference cells was amplified by the dc amplifier (I) and recorded (H). The temperature was determined as the potential difference between the reference cell and the ice point (J) with the potentiometer (K). The radiation of the He-Ne gas laser (M) as a light source (wavelength 632.8 nm and 1 mW, Nihon Kagaku Engineering Co. Ltd., Japan) was applied horizontally to the side of both reference and sample cells. The intensity of the light transmitted through the solution was measured by a photodiode (P) (Hamamatsu Photonics Co. Ltd., Japan), amplified by the photosensor amplifier (Q) and then recorded (H). The heating rate of these experiments was about 1.0 K min^{-1} which was controlled by using a temperature program controller (N), and these experiments were performed over a temperature range from room temperature to 523 K.

A temperature calibration of this apparatus was carried out with standard samples such as benzyl, benzophenone, and naphthalene, and the expected results were obtained within the experimental error (accuracy ±0.5 K).

Materials. The nicotine solution used in this study was purchased from Nakarai Chemicals, Co. Ltd., Japan, and used without any purification. Water, used as a solvent, was purified according to the standard method. The atactic polystyrene, PS ($\bar{M}_n = 1.0 \times 10^5$, $\bar{M}_w/\bar{M}_n = 1.01$) samples used in this study were purchased from Toyosoda Co. Ltd., Japan. The random copolymers such as poly[styrene-*ran*-(butyl methacrylate)], P(SnBMA), containing various kinds of chemical compositions such as 40, 66, and 80 wt % styrene in the copolymer were purchased from Scientific Polymer Products, Inc., USA. The molecular weight and molecular weight distribution of these copolymer samples are listed in Table I. Poly(*n*-butyl methacrylate),

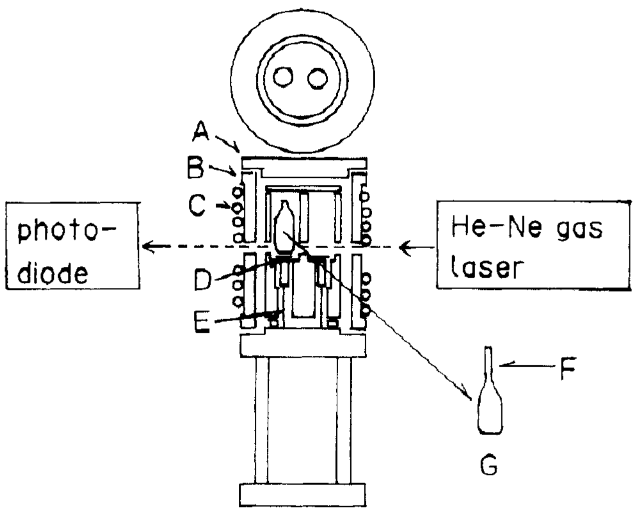

Figure 1. DTA equipped with laser and cell: A, copper cell holder; B, heater block; C, heater; D, platinum plate; E, thermocouple; F, seeled portion, G, glass cell.

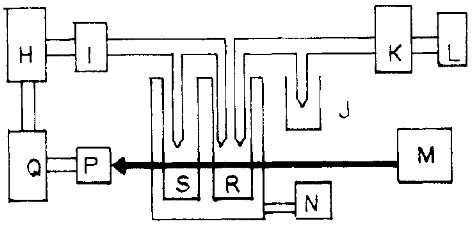

Figure 2. Block diagram of DTA equipped with laser: H, recorder; I, dc amplifier; J, 0 °C point; K, potentiometer; L, galvanometer; M, He–Ne gas laser; N, temperature program controller; P, photodiode; Q, photosensor amplifier; R, reference; S, sample.

Table I
Abbreviation and Characterization of Poly(styrene-*ran*-*n*-butyl methacrylate) Samples

sample code	styrene content, %	$10^{-5}\bar{M}_n{}^a$	$10^{-5}\bar{M}_w{}^b$	$\bar{M}_w/\bar{M}_n$
P(40SnBMA)	ca. 40	1.8	2.4	1.3
P(66SnBMA)	64.2–67.2	1.2	4.0	3.3
P(80SnBMA)	ca. 80	1.9	2.5	1.3

[a] These values are measured at 298.15 ± 0.10 K from osmotic pressure (Kuhnoel Co. Ltd., West Germany). [b] These values are measured at 298.15 ± 0.01 K by light scattering (Uniongiken Co. Ltd., Japan).

P(nBMA), was also obtained from Scientific Polymer Products, Inc., USA. The molecular weight distribution of this sample having 2 × 10^5 as the molecular weight of poly(*n*-butyl methacrylate) is relatively large. Methyl ethyl ketone, MEK, as a solvent used in this study was the reagent grade from Katayama Chemical Industries Co. Ltd., Japan, and was used without further purification.

Results and Discussion

The phase equilibria of the random copolymers containing various kinds of chemical compositions and its corresponding homopolymers in MEK solutions were studied by the use of a DTA instrument equipped with a laser.

The typical DTA thermogram and laser transmittance curves obtained for P(66SnBMA)/MEK solutions with various polymer concentrations are shown in Figure 3. As seen in Figure 3, the laser transmittance is divided into two parts with increasing temperature: The laser transmittance curve decreases at first and then reaches a definite value that corresponds to zero transmittance with an increase of temperature, demonstrating that the consolute temperature may exist for the copolymer solution. In the higher temperature region, the laser transmittance increases again and reaches a definite value coming back to a base line with an increase of temperature, demonstrating that the consolute temperature may also exist in the copolymer solutions at high-temperature regions. The DTA curve obtained for the concentration region less than 0.01 of the weight fraction of the polymer indicates the thermal change as endothermic, which corresponds to an increase in the intensity of the transmission at a higher temperature, but the thermal change corresponding to a decrease in the intensity of the transmission at a lower temperature was not detectable, as shown in Figure 3. However, when the weight fraction of the polymer is more than 0.01, the DTA curve obtained shows the exothermic peak which corresponds to a decrease in the intensity of the transmission at a lower temperature and shows also the change as endothermic, corresponding to an increase in the intensity of the transmission with increasing temperature.

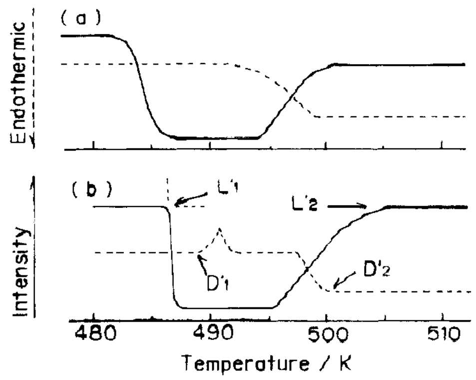

Figure 3. Typical DTA (- - -) and laser transmittance (—) curves of P(66SnBMA)/MEK system at heating rate of 1.0 K min^{-1}. Weight fraction of polymer, W_2, is (a) 0.010 and (b) 0.054.

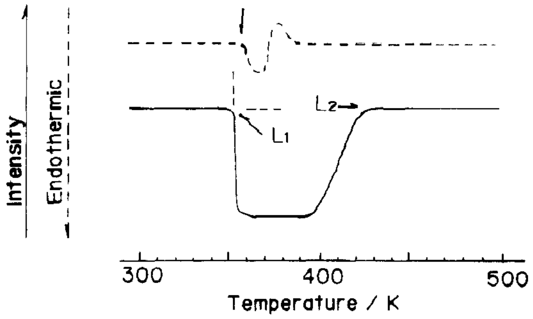

Figure 4. Typical DTA (- - -) and laser transmittance (—) curves of nicotine/water system. Weight fraction of nicotine, W_2, is 0.340.

In order to analyze the different behaviors of those curves, the phase equilibrium of known aqueous nicotine solutions was measured by using this apparatus, and the typical DTA and laser transmittance curves obtained are shown in Figure 4. As seen in Figure 4, the laser transmittance curve of aqueous nicotine solutions decreases at 360 K at first, reaches a definite value corresponding to zero transmittance, and again comes back to the vicinity of the base line of the transmittance with an increase in temperature. While, the base line of the DTA curve shifts to the endothermic direction, corresponding to the beginning of the decrease in the laser transmittance curve, and then an exothermic peak occurs at a slightly higher temperature. However, the DTA curve does not change at a higher temperature where the transmittance of the laser increases. This shift of base line in the endothermic direction may correspond to the scission of hydro-

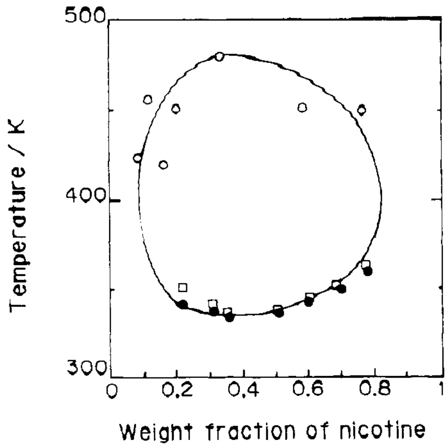

Figure 5. Phase diagrams of nicotine/water system. □, ●, and ○ are corresponding to D_1, L_1, and L_2 in Figure 4, respectively (—, literature).

gen bonding between the nicotine and water molecules in solution, and, at the same time, aggregation (exothermic) between the nicotine molecules accompanying the phase separation may account for the observed exothermic peak.

Thus, the existence of both the upper and lower critical solution temperatures can be shown by the simultaneous measurement of DTA and laser transmittance data obtained with this instrument.

In order to match the literature of the consolute temperature of the solutions, the determination of the consolute temperature of the estimated DTA and laser transmittance curves is done as follows: The cloud points at each concentration of the aqueous nicotine solution were determined as D_1 which is where the thermal change in the DTA curve began, as L_1 which is where the phase separation began, and as L_2 which is the end point for forming the homogeneous phase as shown in Figure 4. The cloud points determined by such a way are plotted against the weight fraction of the nicotine solution and shown in Figure 5 together with the literature data[6] indicated by a solid line for nicotine solutions. As seen in Figure 5, the results obtained are in good agreement with those of the literature which are shown as a solid line.

Using the data analysis techniques developed for the consolute temperature of the nicotine solution, the phase equilibrium of the poly[styrene-*ran*-(butyl methacrylate)] (SnBMA)/methyl ethyl ketone (MEK) solutions was analyzed. The typical DTA and laser transmittance curves obtained for the P(SnBMA)/MEK systems are shown in Figure 3. Figure 3 shows the typical DTA and transmittance curves of P(66SnBMA)/MEK systems, and the behaviors of DTA and transmittance curves are similar to those of the other copolymer systems: P(40SnBMA) and P(80SnBMA). As seen in Figure 3, with increasing temperature, the laser transmittance decreases at first and then reaches a definite value that corresponds to zero transmittance, suggesting that copolymer solutions may exist at a lower critical solution temperature (LCST). Further, with an increase in temperature, the laser transmittance increases again and reaches a definite value coming back to the vicinity of the base line of the transmittance curve, suggesting that the copolymer solutions at high-temperature regions may have an upper critical solution temperature (UCST).

While, in the DTA curve obtained for the concentration region less than 0.01 of the weight fraction of the polymer, the base line of DTA curve shifts in an endothermic direction, corresponding to an increase in the intensity of the transmission at a higher temperature, but a thermal change corresponding to a decrease in the intensity of the transmission at a lower temperature could not be observed. At a concentration of ≤ 0.01 of the weight fraction of the polymer, it appears that the DTA apparatus equipped with a laser could not resolve minute thermal changes because the polymer solution was too dilute. However, when the weight fraction of the polymer is more than 0.01, the obtained DTA curve exhibits an exothermic peak that is related to a decrease in the intensity of the transmission at a lower temperature. Thermal change at a higher temperature indicates the same behavior as the concentration region less than 0.01 of the weight fraction of the polymer, demonstrating that this system may exhibit both the lower and upper critical solution temperatures. The exothermic peak at a lower temperature obtained by the DTA curve may explain the heat change by precipitation of the polymer accompanying the phase separation, suggesting that the energy of the cohesive force between polymer molecules is stronger than that of the separation between the polymer and the solvent. But it is presently unclear why the exothermic peak in dilute polymer solutions (<0.01) is not observable. The shift in the base line of the DTA curve in the endothermic direction may mean that the phase condition at the lower temperature is different from that at the higher temperature.

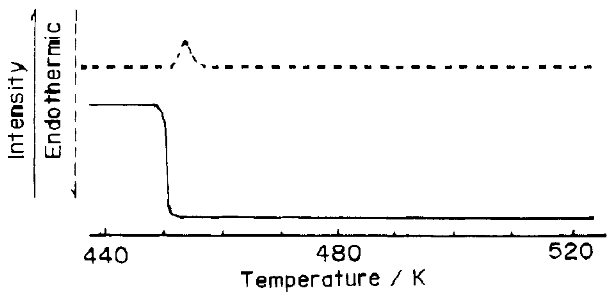

Figure 6. Typical DTA (- - -) and laser transmittance (—) curves of PS/MEK system. Weight fraction of polymer, W_2, is 0.047.

The phase equilibria of poly(*n*-butyl methacrylate) P(nBMA) and poly(styrene) (PS) in MEK solutions were also studied by use of DTA equipped with a laser. The laser transmittance and DTA curves for P(nBMA)/MEK solutions are similar to those for P(66nBMA)/MEK solutions as shown in Figure 3 but are different from those of the PS/MEK solution as shown in Figure 6, suggesting that the PS/MEK solution may show only a LCST although P(nBMA), P(40SnBMA), P(66SnBMA), and P(80SnBMA)/MEK solutions may show both the LCST and the UCST. The UCST of the PS/MEK solution may exist at a higher temperature, but the measurement of a UCST at a higher temperature of the PS/MEK solution by the present apparatus is impossible.

In order to obtain the temperature–composition phase diagram from the transmittance and DTA measurements for homo- and copolymer/MEK solutions, the determination of the consolute temperature accompanying the phase change of the LCST and the UCST was done according to the same method of determination for the consolute temperature of the nicotine solution as described above: The cloud point at each concentration was determined as D_1' and D_2' in the DTA curve and as L_1' and L_2' in the laser transmittance curve, respectively, as shown in Figure 3. The plots of these cloud points against the weight fractions of poly[styrene-*ran*-(butyl methacrylate)] and its corresponding homopolymer solutions are shown in parts a and b of Figure 7, respectively. The

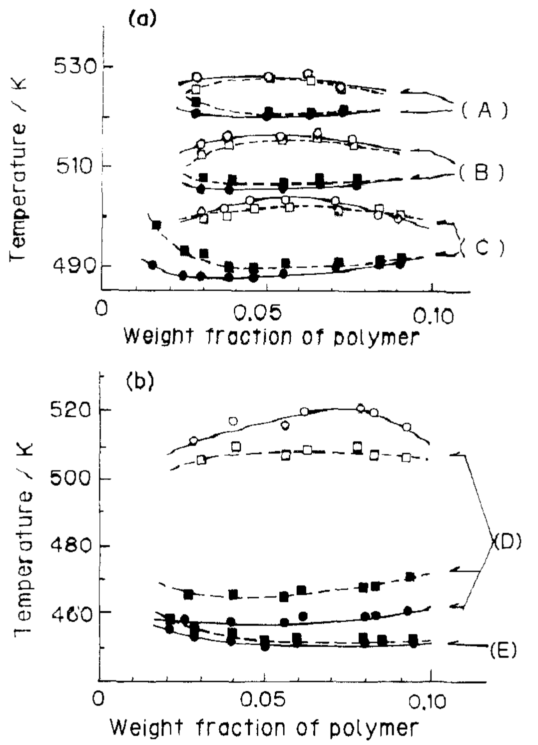

Figure 7. Phase diagrams of (a) P(nBMA) (A), P(40SnBMA) (B), and P66SnBMA) (C) and (b) P(80SnBMA) (D) and PS (E) in MEK solutions. ■, □, ●, and ○ are corresponding to D_1', D_2', L_1', and L_2' in Figure 3, respectively.

P(nBMA) and copolymers/MEK solutions seem to show both the LCST and the UCST similar to those of the aqueous nicotine solutions. However, the PS/MEK solution shows only a LCST. The consolute temperature from the homogeneous phase to the binary one at lower temperatures estimated from the transmittance curve is slightly lower than that from the DTA curve. However, these temperature differences for P(nBMA) and PS are very small. The temperature difference for copolymers seems to increase with increasing styrene content in the copolymer. The differences are about 0.2–1.0 K for P(40SnBMA) and 9–10 K for P(80SnBMA) systems, respectively. The dependence of the temperature difference between consolute temperatures estimated from the laser transmittance and DTA curves on the styrene content in the copolymer may relate to the interaction between styrene and *n*-butyl methacrylate sequences in the copolymer with a delay in the nucleation and growth of the domains produced by precipitation of polymer. However, it is very difficult to explain this behavior at the present time because of a lack of information about the behavior of copolymer chains in solution.

The temperature of the phase change from the binary phase to a single phase estimated from the transmittance curve for P(nBMA), P(40SnBMA), and P(66SnBMA) at higher temperatures is almost in good agreement with that from DTA curve except for P(80SnBMA).

The LCST and the UCST for the copolymers and their corresponding homopolymers are plotted against the styrene content in the copolymer, and the results obtained are shown in Figure 8. As seen in Figure 8, the LCST decreases and, at 80 wt % styrene content, shows drastic behavior with an increase in the styrene content in the copolymer molecule.

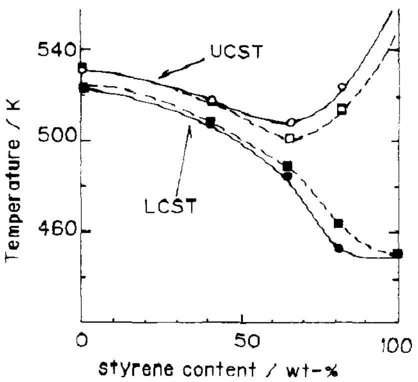

Figure 8. Plots of LCST and UCST against styrene content in copolymer for homo- and copolymer in MEK solutions. ■, □, ●, and ○ are presented as the LCST and the UCST estimated from the curve in Figure 7, respectively.

While the UCST decreases at first and, at 80 wt % styrene content, shows a drastic increase, the UCST of polystyrene solution is not obtained under the present experimental conditions. The behaviors of a drastic increase of the UCST at 80 wt % styrene content in the copolymer molecule are comparable to those for the Θ temperature of the poly(styrene–methacrylate)/cyclohexanol solution reported by Kotaka et al.[7] And also the behaviors at 80 wt % styrene content in the copolymer molecule are similar to the relationship of the interaction parameter between the styrene sequence and the *n*-butyl methacrylate one in a copolymer chain estimated by calorimetry and radius of gyration determined by light scattering in a previous paper.[8]

As seen in Figure 8, the region of two-phase behaviors between the UCST and the LCST of P(SnBMA)/MEK becomes narrow for a *n*-butyl methacrylate sequence rich region in the copolymer chain, suggesting that those results may be due to a favorable entropy of the increase accompanying the compatible interaction between styrene and *n*-butyl methacrylate units of the copolymer although the miscibility between the *n*-butyl methacrylate sequence in the copolymer chain and MEK is wrong from the enthalpy viewpoint as pointed out previously.[8] With increasing styrene content in the copolymer chain, a region of two phases between the UCST and the LCST becomes wider. A possible explanation of these results is that the insertion of *n*-butyl methacrylate in the styrene sequence rich region decreases the solubility of the interaction with the solvent. However, a better estimation of the thermodynamic parameters for copolymer solutions will be needed to further understand the dependence of the LCST and the UCST on the styrene content in these copolymers.

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Registry No. PS, 9003-53-6; P(SnBMA), 25213-39-2; P(*n*BMA), 9003-63-8; nicotine, 54-11-5.