Dilute Solution Properties of a Polystyrene–Poly(methyl methacrylate) Graft Copolymer Studied with the Emission Probe Technique

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ABSTRACT: Transition phenomena in the aggregation processes of a graft polystyrene (PS)–poly(methyl methacrylate) (PMMA) copolymer in dilute solution were studied with the emission probe technique; 2-vinylfluorene is copolymerized at an appropriate number in the backbone PS chain and pyrene is introduced at the grafted PMMA chain endings as emission probes. The binary solvent mixtures consisting of various compositions of tetrahydrofuran (THF; a good solvent for both PS and PMMA) and acetonitrile (AN; a nonsolvent for PS) or of THF and cyclohexane (CH; a nonsolvent for PMMA) were used as solvents. The efficiency of the nonradiative energy transfer from fluorene to pyrene in a poor solvent system abruptly increased at a certain graft copolymer concentration and then leveled off with an increase in the copolymer concentration. This suggests the multimolecular micelle formation and this phenomenon took place at copolymer concentrations lower than 10^{-5} g/mL. The multimolecular micelle formation at the concentration where the efficiency of nonradiative energy transfer reached a plateau was confirmed by low-angle light scattering. A similar dependence of aggregation upon the composition of mixed solvents was observed by the emission probe technique and by the low-angle light scattering method.

Introduction

It has been known that block and graft copolymers aggregate in solvents when one polymer component is soluble and the other component is not.[1] In the case of block and graft copolymers of PS–PMMA, it has been demonstrated that they form a stable aggregate even in a dilute solution.[2-7] Light scattering is an effective tool to investigate the dilute solution properties of polymers in the aggregation process leading to the formation of higher molecular weight molecules (multimolecular micelles) from lower molecular weight molecules.[8,9] However, it is sometimes difficult to observe the changes in aggregation when transitions take place at a high dilution, since the sensitivity of light scattering measurement is limited at a high dilution. Although the emission probe technique is still qualitative, this technique is quite sensitive[10-24] and is potentially useful for examining the properties of polymers at high dilution.[25-27]

In this paper, we have studied the transition phenomena in aggregation of a PS–PMMA graft copolymer by the emission probe technique and confirmed the multimolecular micelle formation by the low-angle light scattering method. When fluorene copolymerized in the backbone PS chain is excited, nonradiative energy transfer may take place with a certain efficiency from the fluorene to pyrene introduced at the grafted PMMA chain ending. In this system, fluorene is an energy donor and pyrene is an energy acceptor; this energy transfer is Förster type[28] and its efficiency may be governed by the distance between the donor and the acceptor. It was expected that the efficiency of the energy transfer reflects the solution properties of the graft copolymer. The dependency of the energy-transfer efficiency upon the graft copolymer concentration in the binary solvent mixtures consisting of THF and CH or of THF and AN was studied; when the nonsolvent was pronounced in the binary mixted solvent, the transition phenomena shown by the change of the energy-transfer efficiency took place with an increase in the graft copolymer concentration. This suggests the formation of multimolecular micelles, which was confirmed by measuring the weight-average molecular weight by low-angle light scattering.

Experimental Section

Materials. The backbone PS is composed of a copolymer of styrene and 2-vinylfluorene (2VFl); the copolymer was made by free radical copolymerization of both the monomers in toluene with AIBN at 60 °C. The mole fraction of 2VFl contained in the backbone PS was determined by means of electronic absorption spectroscopy, assuming that the extinction coefficient of 2VFl is the same as that of fluorene; the copolymerized 2VFl unit was found to be 1 mol %, this corresponds to 4.5 units of 2VFl per backbone PS.

The PS–PMMA graft copolymer was prepared by anionic graft copolymerization;[29-31] the 9-position of 2VFl units in the backbone PS was metalated in contact with a sodium mirror in dried THF under vacuum and then purified MMA was added to this solution and graft copolymerized at −78 °C, and finally, the living PMMA endings were terminated by the addition of 1-(bromomethyl)pyrene. The PS–PMMA graft copolymer thus formed was purified by repeated precipitations from THF solution with a mixture of methanol and AN or of methanol and CH. The weight fraction of the backbone PS was determined to be 62% by ^{1}H NMR. The number of PMMA branches in the PS–PMMA graft copolymer was determined with electronic absorption for the end-labeled pyrene unit and was found to be around 1. The molecular weight and its distribution of the backbone PS were found to be $\bar{M}_w$ = 96 000 and $\bar{M}_w/\bar{M}_n$ = 2.04, respectively, and those of the graft copolymer were found to be $\bar{M}_w$ = 152 000 and $\bar{M}_w/\bar{M}_n$ = 1.42, respectively, by gel permeation chromatography (Toyo Soda HLC-802 UR) using monodispersed polystyrene as a standard. Spectrograde THF, AN, and CH were used without further purification for fluorescence spectral measurements.

Fluorescence Measurements. Emission spectra were recorded on a differential spectrofluorimeter (Shimadzu RF-503 A) at 22 °C. The base line was confirmed prior to the measurement of the spectrum in order to check the purity of solvents at the high sensitivity where the fluorescence of the PS–PMMA graft copolymer of 10^{-8} g/mL concentration could be detected. The dependence of emission spectra upon the concentration of the PS–PMMA graft copolymer was measured as follows; several concentrated THF stock solutions of the PS–PMMA graft copolymer were prepared. By microsyringe (Gilson Pipetteman P-20), the stock solutions were added to the solution whose purity and no fluorescence were checked. This procedure was repeated many times to make more concentrated solutions. The concentration range of the PS–PMMA graft copolymer in sample solutions used for the measurement was from 10^{-8} to 10^{-3} g/mL. The most concentrated sample solutions thus prepared contained about 5 vol % THF which came from the stock solution. The compositions of the binary mixed solvents slightly changed at any concentrations of the PS–PMMA graft copolymer. The sample solutions were not deaerated. Emission spectra were obtained by exciting at 280 nm.

Light Scattering. Light scattering measurements were carried out at 24 °C by a low-angle light scattering photometer (LALS) in which a cylindrical flow-cell of 30 μL in volume is combined

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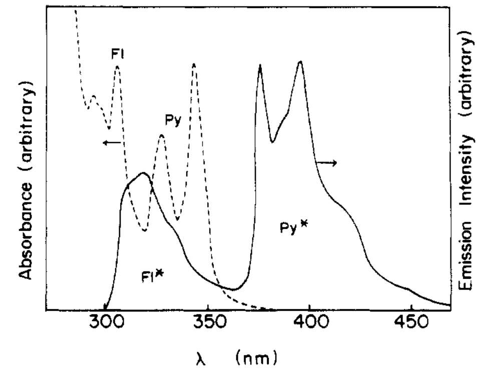

Figure 1. Absorption and typical fluorescence spectra of PS–PMMA graft copolymer in dilute solution.

with a He–Ne laser as light source (Toyo Soda LS-8). Scattering light intensity can be measured at an angle as low as 5°. The sample solution was filtered through a Teflon microfilter with a 2-μm pore size and then poured into the LALS by the pump of GPC unit. A Teflon microfilter with a 2-μm pore size was also placed between the pump and the LALS in order to remove dust. The pore size influenced the light scattering intensity for the PS–PMMA graft copolymer solutions. When the pore size was 0.45 μm, intensity of light scattering became weak. However, the influence was not observed for a homopolymer such as a standard polystyrene. For the estimation of the specific refractive index increments $\partial n/\partial c$ of the PS–PMMA graft copolymer, we used the Gladstone–Dale equation.[6,32,33] The $\partial n/\partial c$ values of LALS system for 633 nm were calculated from the values at 436 and 546 nm by use of the equation for simple Cauchy dispersion.[33]

Results and Discussion

Energy Transfer in the Dilute Solution of the PS–PMMA Graft Copolymer. The PS–PMMA graft polymer contains three fluorescing chromophores, which are the styrene unit (St) and fluorene unit (Fl) in the backbone PS and the pyrene unit (Py) located at the grafted PMMA end. The absorption and emission spectra of the graft copolymer in aerated THF solution are shown in Figure 1. The emission spectra of Fl and Py appeared but that of St did not. Excimer fluorescence of Py was hardly observed. The following scheme may be applied to the PS–PMMA graft copolymer system.

$$\mathrm{Fl} \xrightarrow{h\nu} \mathrm{Fl}^* \tag{1}$$

$$\mathrm{St} \xrightarrow{h\nu} \mathrm{St}^* \tag{2}$$

$$\mathrm{Py} \xrightarrow{h\nu} \mathrm{Py}^* \tag{3}$$

$$\mathrm{St}^* + \mathrm{St} \rightarrow \mathrm{St} + \mathrm{St}^* \tag{4}$$

$$\mathrm{St}^* + \mathrm{Fl} \rightarrow \mathrm{St} + \mathrm{Fl}^* \tag{5}$$

$$\mathrm{St}^* + \mathrm{Py} \rightarrow \mathrm{St} + \mathrm{Py}^* \tag{6}$$

$$\mathrm{Fl}^* + \mathrm{Py} \rightarrow \mathrm{Fl} + \mathrm{Py}^* \tag{7}$$

$$\mathrm{Fl}^* \rightarrow \mathrm{Fl} + h\nu \tag{8}$$

$$\mathrm{Py}^* \rightarrow \mathrm{Py} + h\nu \tag{9}$$

Judging from the absence of St emission as seen from Figure 1, it is most likely that the energy-transfer process of eq 5 takes place extremely rapidly. The main process which dominates in the ratio of emission intensity of Py to that of Fl must be attributable to eq 7. In Figure 1, the emission spectrum of Fl (energy donor) well overlaps the absorption spectrum of Py (acceptor) and, in such a case, nonradiative energy transfer of the so-called Förster type takes place. The efficiency E of this energy transfer depends mainly upon R, which is the distance between the donor and the acceptor groups[28,34]

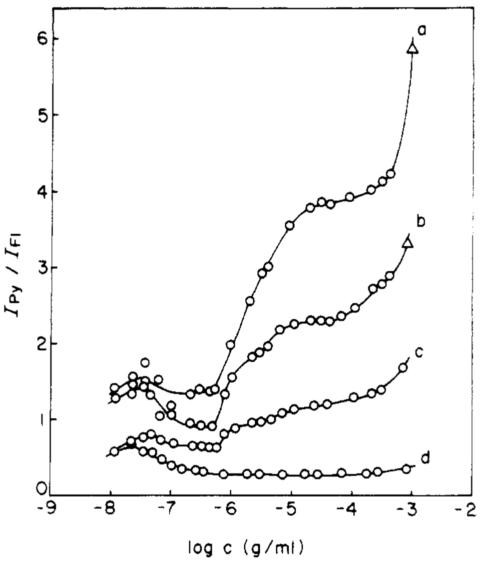

Figure 2. Dependence of $I_{\mathrm{Py}}/I_{\mathrm{Fl}}$ fluorescence ratio upon the concentration of PS–PMMA graft copolymer. Composition of the binary mixed solvents (volume ratio): (a) 100% AN; (b) AN:THF = 9:1; (c) AN:THF = 8:2; (d) AN:THF = 1:1. (△) insoluble.

$$E = R_0^6/(R_0^6 + R^6) \tag{10}$$

where R_0 is the donor–acceptor separation where 50% of energy transfer takes place.

$$R_0^6 = (8.8 \times 10^{-25})\Phi_D^0\kappa^2 n^{-4} J \tag{11}$$

Φ_D^0 is the fluorescence quantum yield of the donor in the absence of the acceptor, κ the orientation factor, n the refractive index of solvent, and J the overlap integral between the emission spectrum of the donor and the absorption spectrum of the acceptor, respectively. The R_0 between Fl and Py was about 37 Å (for the quantum yield of Fl, we assumed 0.66 which is the value of fluorene as monomer model).[35] If Gaussian chain was applied[36] to the PS–PMMA graft copolymer, the value of the end-to-end distance between Fl and Py was estimated to be 37 Å.[37]

Dependence of Energy-Transfer Efficiency upon Concentration of the Graft Copolymer and Composition of Mixed Solvents. The efficiency of energy transfer from Fl to Py depends upon R. Furthermore, the efficiency must be affected significantly by a density of the acceptors Py around the donor Fl; the higher the density of the acceptors Py around the donor Fl in an active sphere with radius R_0, the more effective the energy transfer from Fl to Py. If a multimolecular micelle of the PS–PMMA graft copolymer is formed, the density of Py in the active sphere around Fl becomes higher, and then the efficiency of the energy transfer would increase. As seen from Figures 2 and 3, the efficiency of energy transfer $I_{\mathrm{Py}}/I_{\mathrm{Fl}}$ varied with an increase in concentration of the PS–PMMA graft copolymer, where I_{Py} and I_{Fl} are intensities of fluorescences of Py at 378 and Fl at 320 nm, respectively. The significant features of Figures 2 and 3 are that the efficiency increases abruptly in a range of the concentration from ca. 10^{-6} to ca. 10^{-5} g/mL, and it then reaches a plateau in a region above 10^{-5} g/mL. These phenomena appeared in the systems in which AN or CH was large excess, where AN and CH are nonsolvents for backbone PS and grafted PMMA, respectively. In contrast, significant change of $I_{\mathrm{Py}}/I_{\mathrm{Fl}}$ did not appear in the

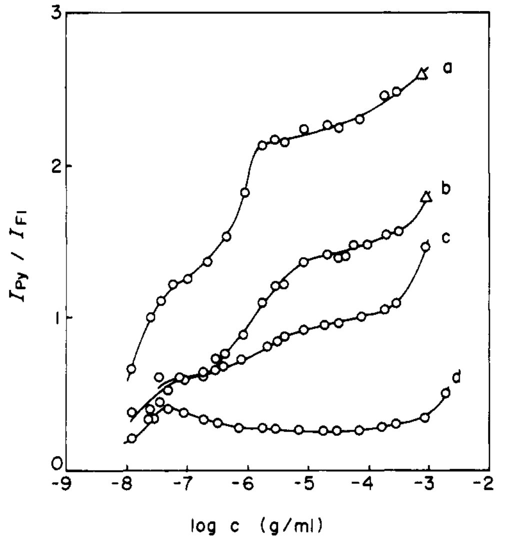

Figure 3. Dependence of I_{Py}/I_{Fl} fluorescence ratio upon the concentration of PS–PMMA graft copolymer. Composition of the binary mixed solvents (volume ratio): (a) 100% CH; (b) CH:THF = 9:1; (c) CH:THF = 8:2; (d) CH:THF = 1:1. (△) insoluble.

system of AN:THF = 1:1 ((d) in Figure 2) and of CH:THF = 1:1 ((d) in Figure 3). This suggests that the change of I_{Py}/I_{Fl} with an increase in the concentration is not caused by a simple intermolecular energy transfer observed in a homogeneous system.

The change of I_{Py}/I_{Fl} may suggest the transition phenomena leading to the formation of a micelle. By low-angle light scattering measurement, it was confirmed that multimolecular micelle formation took place in these systems (see next section). If the formation of spherical micelles is assumed, backbone PS is a core and grafted PMMA is a fringe in an AN and THF mixture, while in a CH and THF mixture, the PS is a fringe and the PMMA is a core. The critical micelle concentrations (cmc) estimated from Figure 3 were 1.4×10^{-6} for the system of 100% CH (at final stage, about 5 vol % THF was involved, see Experimental Section), 5.0×10^{-6} for a mixture solution of CH:THF = 9:1, and 6.3×10^{-6} g/mL for CH:THF = 8:2, respectively. The higher the ratio of nonsolvent in the system, the lower the cmc became. At the plateau region, the values of I_{Py}/I_{Fl} were finally constant. This implies that these multimolecular micelles may have a monodispersed-like character in this region. In Figure 2, cmc was 1.1×10^{-5} g/mL for the system of 100% AN (finally, about 5 vol % THF was involved), however, for the systems of AN:THF = 9:1 and of 8:2, cmc could not be determined precisely and they were about 10^{-5} g/mL. At concentrations above 10^{-4} g/mL in Figures 2 and 3, a further increase in I_{Py}/I_{Fl} was shown. This increase must be attributable to insoluble states. Actually, in a film state of the PS–PMMA graft copolymer, the emission resulted almost entirely from Py, and that due to Fl was hardly observed. As another possible effect, reabsorption of Fl fluorescence by Fl in the backbone PS may be taken into consideration.

In an enormously diluted region below 10^{-6} g/mL, another transition phenomenon was suggested; below 10^{-7} g/mL the measurement was not accurate because of the virulent noise during emission spectral measurement. As seen from Figure 2, I_{Py}/I_{Fl} decreases with an increase in the concentration of the graft copolymer, while in Figure 3 it increases. There are some possible explanations for these results. One is that an impurity in the sample solutions affects I_{Py}/I_{Fl}. However, the emission base lines of solvents have been checked prior to the measurements of emission spectra. Furthermore, intramolecular energy transfer in the graft copolymer may be hardly affected by intermolecular quenching due to impurity at high dilution. Another is that the concentration change of the PS–PMMA graft copolymer affects the excitation spectra of fluorescence; the dependence of excitation spectrum upon the concentration is known in general. The emission spectra were excited by using the light of 280 nm where there are three absorption components, i.e., Fl, Py, and St in the PS–PMMA graft copolymer. If the excitation spectra of these three components at 280 nm change significantly, I_{Py}/I_{Fl} changes in a similar manner. This explanation could not be confirmed experimentally because the ratios among these excitation spectra are also changed by energy transfer. However, the above two explanations cannot make clear the difference in features between Figures 2 and 3.

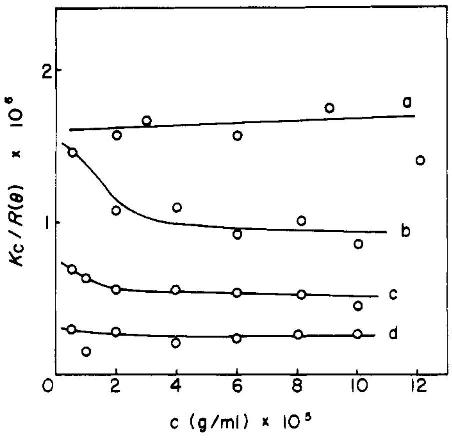

Figure 4. Plots of $Kc/R(\theta)$ vs. concentration for the PS–PMMA graft copolymer at $\theta = 5°$. Composition of the binary mixed solvents (volume ratio): (a) 100% THF; (b) CH:THF = 1:1; (c) CH:THF = 8:2; (d) CH:THF = 9:1.

There is an attractive explanation that intramolecular transition phenomena take place at such an enormous dilution prior to multimolecular micelle is formed. In the multimolecular micelle state, both PS chain and PMMA chain in the graft copolymer are significantly segregated. Such a segregation may take place within one graft copolymer chain before the micelle formation. In Figure 3, CH is a nonsolvent for PMMA component in the graft copolymer, so that the segregation is caused by the contraction of the PMMA chain. This contraction decreases the distance between Py at PMMA end and Fl in PS backbone and increases I_{Py}/I_{Fl}, as can be understood from fact that the energy-transfer efficiency between Py and Fl is expressed by eq 10. Similarly, in Figure 2, AN is a nonsolvent for PS component and the segregation is caused by the contraction of the PS chain. This does not decrease appreciably the distance between Py and Fl and the decrease of interpenetration between PS and PMMA within one graft copolymer chain may decrease I_{Py}/I_{Fl} slightly.

Comparison of Light Scattering Data with Emission Probe Data. The values of $Kc/R(\theta)$ at $\theta = 5°$ are plotted against the concentration in Figure 4, where K is the optical constant, c the concentration, and $R(\theta)$ the difference in the Rayleigh ratios between the solution and the pure solvent. Figure 4 shows the dependence of $Kc/R(\theta)$ upon the composition of the mixed solvents and upward curve at lower concentration. These plots are analogous to a so-called open association[8] where the associates comprise all sorts of multimers (dimers, trimers, tetramers, etc.). However, it is not clear whether the systems in Figure 4 are open association or not, because we could not carry out the light scattering measurement

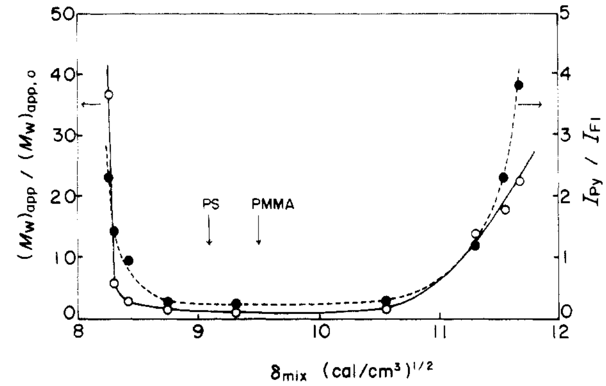

Figure 5. Plots of $(M_w)_{app}/(M_w)_{app,0}$ and I_{Py}/I_{Fl} for the PS–PMMA graft copolymer at the concentration of 2×10^{-5} g/mL against solubility parameter δ_{mix} for binary mixed solvents. $(M_w)_{app,0}$ = 635 000.

exactly below 5×10^{-6} g/mL. Judging from the data by the emission probe technique, the system of the PS–PMMA graft copolymer has the characteristic of a so-called closed association[8] where the associates comprise a unimer/multimer equilibrium.

We determined the apparent weight-average molecular weight $(M_w)_{app}$ from $1/(Kc/R(\theta))$ at $\theta = 5°$ and $c = 2 \times 10^{-5}$ g/mL. $(M_w)_{app}/(M_w)_{app,0}$, where $(M_w)_{app,0}$ is an apparent weight-average molecular weight of the PS–PMMA graft copolymer in THF ($(M_w)_{app,0}$ = 635 000),[39] reflects the degree of the association among PS–PMMA graft copolymers. The values of $(M_w)_{app}/(M_w)_{app,0}$ were plotted against the solubility parameter of binary mixed solvents (δ_{mix})[40,41] in Figure 5 and compared with the plots of I_{Py}/I_{Fl} at the concentration of 2×10^{-5} g/mL against δ_{mix}. The solubility parameters for PS and PMMA are 9.1 and 9.5, respectively.[42] When solubility parameters between solute and solvent are similar, the solubility becomes higher. In Figure 5, the same dependencies of δ_{mix} upon both $(M_w)_{app}/(M_w)_{app,0}$ and I_{Py}/I_{Fl} are seen. This suggests that the change of I_{Py}/I_{Fl} indicates the micelle formation and characteristic of micelle.

Concluding Remarks

In this paper, multimolecular micelle formation of PS–PMMA graft copolymer has been revealed by the emission probe technique using nonradiative energy transfer and by small-angle light scattering measurements. The transition phenomena in the micelle formation were confirmed in highly diluted solution below 10^{-5} g/mL. It would be expected that the properties of the isolated polymer chain are revealed at high dilution because, in such a region, interactions among polymer chains are eliminated. The present investigation has shown that the emission probe technique provides a powerful tool for the study of polymer in dilute solution because of its high sensitivity.

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Registry No. (MMA)·(styrene) (copolymer), 25034-86-0; 2-vinylfluorene, 10473-10-6; 1-(bromoethyl)pyrene, 2595-90-6.

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(37) If a Gaussian chain is applied, the mean square end-to-end distance $\langle r^2 \rangle$ is expressed by $\langle r^2 \rangle = nl^2$, where n and l stand for the number of bonds and bond length, respectively. The value of the end-to-end distance between Py and Fl (37 Å) was estimated by using $n = 287 \times 2$ and l = 1.53 Å. (The n was calculated by using the values of $\bar{M}_n$ for the PS backbone and fraction of PMMA (0.38). When it is calculated by using the value of $\bar{M}_n$ for the graft copolymer, the distance is estimated to be 44 Å.) In a good solvent for PMMA such as THF or AN, the PMMA chain would form an extended chain more than the Gaussian chain, and this is represented by an expansion factor α $(= \langle r^2 \rangle^{1/2} / \langle r^2 \rangle_0^{1/2})$, where $\langle r^2 \rangle$ is the mean square end-to-end distance for a real chain and $\langle r^2 \rangle_0$ is that for a Gaussian chain (ideal chain): α is determined to be ca. 2 for PMMA in good solvents[38] and the end-to-end distance is calculated to be ca. 73 Å. In such a case, energy-transfer efficiency E calculated with eq 10 is ca. 2%. However, the efficiency E may be larger, since the PS–PMMA graft copolymer sample used is a polydispersed copolymer having a considerably shorter PMMA branch, and chain dynamics may increase the efficiency. When the PS–PMMA copolymer is aggregated and the density of Py around Fl becomes higher, the nearest energy acceptor Py governs the energy-transfer efficiency E, and thus I_{Py}/I_{Fl} may be increased.
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(39) The value of $\bar{M}_w$ for the PS–PMMA graft copolymer determined in THF are significantly different by the measurement methods; $\bar{M}_w$ by means of light scattering (635 000) is about 4 times larger than that by GPC (152 000). Judging from $\bar{M}_w$ for backbone PS (96 000) and the copolymer composition of PS and PMMA (0.62:0.38) determined by ^{1}H NMR, the value of $\bar{M}_w$ determined by GPC is the more reasonable one. The discrepancy may be caused by following reason: as described in the Experimental Section, there is a dependency of the intensity of the light scattering upon the pore size of the Teflon filter used for the purification of sample solutions. This may

imply that the aggregate states consisting of a large size were removed by filtration. The intensity of light scattering can be affected significantly by a small amount of large aggregates. At the light scattering measurement for micelle formation in polydispersed copolymer, this effect may become nonnegligible.

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Glass Temperature Mixing Relations and Thermodynamics

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ABSTRACT: The view of Couchman that the following equation for the glass temperature of a mixture of polymers

$$\ln T_{gm} = \frac{X_1 \Delta C_{p1} \ln T_{g1} + X_2 \Delta C_{p2} \ln T_{g2}}{X_1 \Delta C_{p1} + X_2 \Delta C_{p2}}$$

can be justified from a purely thermodynamic standpoint is disputed. The reasoning behind this claim is shown to be based on an inappropriate definition of the entropy of mixing when either or both pure polymers are in their glassy states. An alternative definition of ΔS_{mix} having a sounder physical basis does not lead to any prediction of T_{gm}. The above equation has also been derived from the standpoint of the Gibbs–DiMarzio *molecular* theory of the transition, and to the extent that it successfully predicts T_{gm} it supports molecular theories that attribute a special importance to the configurational entropy.

Introduction

In a series of papers in this Journal[1-3] and elsewhere[4-7] Couchman has developed a thermodynamic approach for predicting the glass temperatures of various polymer mixtures, based on a thermodynamic discussion of the effect of composition on the glass transition by him and Karasz.[8] This approach bypasses any consideration of molecular theories of the transition (such as the Gibbs–DiMarzio entropy theory[9] or free volume theories,[10-12] although molecular considerations are used to estimate the values of certain thermodynamic quantities.

Additional developments depend on what is assumed about the continuity of the changes of first-derivative thermodynamic properties on mixing. If it is assumed that ΔS_{mix}, ΔH_{mix}, and ΔV_{mix} are continuous through the transition, three separate equations for T_{gm}, the glass temperature of a mixture, are obtained (for simplicity, ΔC_p and $\Delta\alpha$ are taken to be temperature independent):

Entropy S:

$$\ln T_{gm} = \frac{X_1 \Delta C_{p1} \ln T_{g1} + X_2 \Delta C_{p2} \ln T_{g2}}{X_1 \Delta C_{p1} + X_2 \Delta C_{p2}} \tag{1a}$$

Volume V:

$$T_{gm} = \frac{X_1 V_1{}^\circ \Delta\alpha_1 T_{g1} + X_2 V_2{}^\circ \Delta\alpha_2 T_{g2}}{X_1 V_1{}^\circ \Delta\alpha_1 + X_2 V_2{}^\circ \Delta\alpha_2} \tag{1b}$$

Enthalpy H:

$$T_{gm} = \frac{X_1 \Delta C_{p1} T_{g1} + X_2 \Delta C_{p2} T_{g2}}{X_1 \Delta C_{p1} + X_2 \Delta C_{p2}} \tag{1c}$$

In the above equations, subscripts 1 and 2 denote properties of the pure polymers, and the subscript m properties of the mixture. T_g is the glass transition temperature, X is the mole fraction, $V°$ is the volume of the pure polymer, and ΔC_p and $\Delta\alpha$ are the discontinuities in the specific heat and thermal expansivity at the respective T_g's.

As Couchman has noted, each of the above equations has been previously given by others on the basis of specific *molecular* theories,[13-16] but Couchman's claim that they follow from purely thermodynamic arguments[19] based on the continuity of ΔS_{mix}, ΔH_{mix}, and ΔV_{mix} at T_g would seem to make molecular considerations irrelevant.

Problems with the Thermodynamic Approach

Couchman has recognized problems with these equations and discussed them in a number of papers.[28] He has noted for example that if both (1b) and (1c) are *simultaneously* true, it would follow that the following relation must hold for any two compatible polymers:

$$\frac{\Delta C_{p1}}{T_{g1} V_1{}^\circ \Delta\alpha_1} = \frac{\Delta C_{p2}}{T_{g2} V_2{}^\circ \Delta\alpha_2} \tag{2}$$

This seems to imply a universal value of $\Delta C_p / T_g V^\circ \Delta\alpha$ for *all* polymers, a possibility contradicted by experiment: The quantity in question is a good predictor of $\mathrm{d}T_g/\mathrm{d}P$ and has been frequently calculated. Observed values range over a factor of 3.[17,18]

An even more serious difficulty would arise if (1a) and (1c) were simultaneously true. For simplicity, if we consider mole fractions X_1 and $X_2 = {}^1/_2$ and further consider a case in which $\Delta C_{p1} = \Delta C_{p2}$, we obtain

$$\ln T_{gm} = \tfrac{1}{2} \ln T_{g1} + \tfrac{1}{2} \ln T_{g2} \tag{1a$'$}$$

$$T_{gm} = \tfrac{1}{2} T_{g1} + \tfrac{1}{2} T_{g2} \tag{1c$'$}$$

In other words eq 1a gives T_{gm} as the geometric mean of T_{g1} and T_{g2}, while eq 1c gives it as the arithmetic mean. This can never occur unless $T_{g1} = T_{g2}$. In short, (1a) and (1c) are actually mathematically incompatible.

Couchman notes that when experimental values of ΔC_p and $\Delta\alpha$ are used in eq 1a–c the predicted T_g's differ. He finds eq 1a the most successful and applies it to many kinds of systems. He suggests that the assumption of continuity for ΔV_{mix} and ΔH_{mix} at T_{gm} will not generally be satisfied, but that for ΔS_{mix} is, on molecular grounds, less likely to be violated, and in polymer systems at least is sufficiently small so that any discontinuity in its value may be neglected even if it were to have a discontinuity at T_{gm}.[1]

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