the maximum of photoinduced effects can be achieved is lower than that of the midpoint (pH = 5.1) of the α-helix to coil transition in Figure 4. This means that the photoinduced conformational change of the copolypeptide depends not only on the ionization degree of the neighboring acid moieties but also on the polypeptide secondary structure itself before UV irradiation. The most remarkable conformational change induced by light, therefore, can be achieved when the copolypeptide is in an α-helix structure carring adequately dissociated L-glutamic acid moieties, i.e., an unstable ordered structure.

It is also found that the opposite conformational change of azo-S-9.3-PGA from random coil to α-helix could not be induced by irradiating at $\lambda > 390$ nm or by dark adaptation in the pH range where the α-helix to coil transition induced by light occurs, thus confirming the irreversibility of the change. This result indicates that the isomerization of the azo chromophore from the cis to the trans forms does not affect the conformation of the copolypeptide in the disordered structure. We cannot find out, at present, the origin of this irreversibility of the change. However, it may be reasonable that, when the backbone is in the disordered structures, relative positional changes of the sulfonate anions resulting from the cis to trans isomerization of the azo moieties cannot induce a decrease in the local charge density of the environment around the polypeptide backbone to effectively reproduce the original ordered structure. The irreversibility of the photoinduced conformational change, including the local conformations of random coil polymer chains of the irradiated and dark-adapted samples, should be examined further.

In conclusion, α-helix to coil transitions to poly(L-glutamic acid) containing small amount of azobenzenesulfonate moieties (ca. 10 mol %) can be induced by light irradiation at adequate pH values on the basis of photoisomerization of the side-chain azobenzene chromophores from the trans to the cis forms. It is found that the photoinduced conformational transition is dependent on the azobenzenesulfonate content, ionization degree of the neighboring weak acid moieties, and polypeptide conformation itself; however, the main force of the conformational transition arises from a increase in the local charge density of the environment around the helical backborn owing to the change in the overall dimensions of the azobenzenesulfonate moieties at the fixed positions along the ordered helical axis. On the other hand, the opposite isomerization of the azo chromophores in the polypeptide in the random coil structure does not reform the original ordered structure.

The study of the photoinduced changes of the structure and functions of the azo-S-PGA membranes is in progress.

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Miscibility of Poly(vinyl methyl ether) with Styrene–Methyl Methacrylate Copolymers

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ABSTRACT: The miscibility of poly(vinyl methyl ether) (PVME) with a series of styrene–methacrylate copolymers was studied. It was found that the critical copolymer composition for achieving miscibility with PVME at room temperature was about 60 mol % styrene. The blends underwent phase separation at elevated temperatures, but the LCST passed through a maximum as the methyl methacrylate content of the copolymer was increased. The maximum value of LCST exceeded that of the PS–PVME pair. The significance of the observed miscibility window is discussed in terms of recent theories.

Introduction

The free energy of mixing of two polymers consists of three contributions:[1-3] (1) the combinatorial entropy of mixing, (2) intermolecular interaction, and (3) the "free volume" effect due to a mismatch of the equation of state parameters of the two polymers. In the context of the

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Table I
Polymer Composition, Molecular Weight, and Glass Transition Temperature

sample	molar ratio in feed, S/M	conversn, wt %	styrene in copolym,[a] mol %	GPC analysis M_n	GPC analysis M_w	GPC analysis M_w/M_n	T_g, °C
PVME				18400	35200	1.9	-28
PS		11.0		71400	116400	1.6	105
PS 200000					207700	1.06	105
PS 90000					90000	1.05	101
S-95	34.9	10.0	95	86500	137000	1.6	105
S-90	15.2	11.2	89	93100	143200	1.5	104
S-85	8.9	10.4	84	85000	131000	1.5	101
S-80	5.9	10.3	80	81800	129000	1.6	103
S-75	4.2	11.3	76	59700	101700	1.7	103
S-70	3.0	11.0	70	86800	139000	1.6	103
S-65	2.2	9.8	64	76200	119000	1.6	103
S-60	1.6	10.5	59	98000	152700	1.6	100
S-50	0.9	9.9	50	94500	145000	1.5	102
S-40	0.5	11.0	40	73400	110300	1.5	103

[a] NMR analysis.

original Flory–Huggins theory,[4] the interaction parameter χ can be interpreted to include both the interactional and the free volume contributions. Since the combinatorial entropy of mixing is small for high molecular weight polymers, a negative interaction parameter is required to achieve miscibility.

In mixtures of a homopolymer A with a random copolymer C_yD_{1-y}, where y represents the mole fraction of C units in the copolymer, the interaction parameter χ is given by the following expressions:[5-7]

$$\chi_{blend} = y\chi_{AC} + (1-y)\chi_{AD} - y(1-y)\chi_{CD} = f(y) \quad (1)$$

Application of eq 1 to the understanding of the phase behavior of copolymer mixtures has met with great success.[5-9] We wish to report in this paper the results of our study of the miscibility of a homopolymer A, poly(vinyl methyl ether) PVME, and a copolymer of styrene (C) and methyl methacrylate (D). This pair was chosen for several reasons. First, polystyrene, PS, is miscible with PVME at room temperature. The miscibility behavior has been investigated extensively in the past[10-15] and the binary interaction parameter determined by several different methods. Second, random copolymers of styrene and methyl methacrylate can be synthesized readily by free radical polymerization. Third, χ_{AD} and χ_{CD} values should both be positive since PMMA is immiscible with PVME or PS. Furthermore, the magnitude of χ_{CD} can be estimated with reasonable confidence because the free volume and the interactional contributions can be calculated from literature values of equation of state parameters[16] and cohesive energy densities.[17] Fourth, the dependence of the phase behavior of a homopolymer–copolymer pair on the relative magnitude of χ_{AC}, χ_{AD}, and χ_{CD} has already been analyzed in ref 5 and the analysis can be used as a guide to interpret our results.

Experimental Section

Materials. Poly(vinyl methyl ether) was obtained from Polyscience Co. It was purified by precipitation twice from toluene solution into a large excess of heptane. Polystyrene and its copolymers with methyl methacrylate were synthesized in the laboratories by free radical polymerization at 70 °C, using azobis(isobutyronitrile) as initiator. Polymerization was carried out to about 10% conversion, after which the polymer was precipitated twice from toluene solution to a large excess of hexane. The compositions of the copolymers were determined by UV spectrophotometry and by proton NMR. The two methods of determination generally agree to within about 2%. The molecular weight of the polymer was measured by gel permeation chromatography, using a Waters Associates GPCI, Model 590, with a UV detector, Model 440. The sample designation, composition, and molecular weight are listed in Table I. In addition, two monodisperse PS samples were obtained from Polyscience Co., for the purpose of comparing our data with literature values.

Glass Transition Temperature. The T_g of the polymer was determined by differential scanning calorimetry, with the use of Du Pont DSC instrument, Model 9900. A heating rate of 10 °C/min was used and the midpoint of the specific heat jump was taken as the T_g.

Cloud Point Measurement. The cloud temperature was determined by monitoring the intensity of light transmission by the polymer film with the use of Nikon microscope equipped with a Mettler F82 hot stage. The heating rate was 2 °C/min.

Results

Copolymers containing 65 or higher mol % of styrene units formed transparent films when blended with PVME, and each blend showed a single glass transition temperature. The copolymer containing 60 mol % of styrene exhibited only limited miscibility with PVME. A single T_g was observed when the blend contained about 10% PVME, but films containing larger amounts of PVME were opaque and two T_g's were detected. These results are represented in Figure 1. The critical value of y for miscibility at room temperature is therefore about 0.6.

The cloud point temperatures of the PVME–copolymer blends are shown in Figure 2. Included in the same figure are cloud temperatures of PVME–PS as points of reference. The cloud temperature cruve of PVME–PS is in good agreement with literature data[14,15] when allowance is made for the lower molecular weight of the PVME sample used in this study. The cloud temperatures of blends consisting of copolymer S95 are higher than the corresponding values for polystyrene. The LCST continues to increase as styrene content decreases to about 84–80% but the trend is reversed for S75, S70, and S65 copolymers. The observed effect of copolymer composition on LCST cannot be attributed to molecular weight differences because the molecular weights of the copolymers and PS are nearly the same. (We are grateful to D. R. Paul for information in a pending publication in which similar LCST phenomenon is described.)

Discussion

An alternative representation of the phase diagrams depicted in Figure 2 consists of plots of cloud temperature as a function of copolymer composition[5] at different blend ratios. This is shown in Figure 3. The maximum in the miscibility window occurs at $y = 0.8 - 0.84$. The existence of a maximum in the miscibility window requires a minimum in χ_{blend}, corresponding to the condition at which

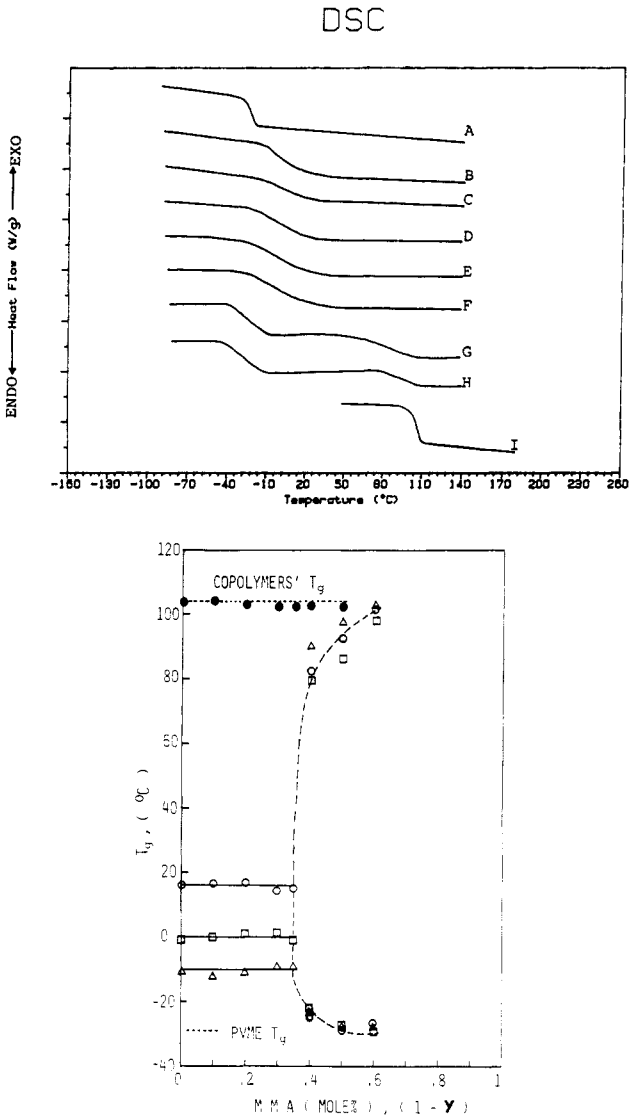

Figure 1. (Top) DSC thermograms of PVME, PS, and 50/50 wt % of PVME blends with PS and its copolymers: (A) PVME; (B) PVME–PS; (C) PVME–S90; (D) PVME–S80; (E) PVME–S70; (F) PVME–S65; (G) PVME–S60; (H) PVME–S50; (I) PS. (Bottom) Dependence of the glass transition temperature of the blend on copolymer composition. Weight percent of PVME in copolymer blends: (○) 35; (□) 50; (△) 65.

the first derivative of $f(y)$ is zero and the second derivative is positive. The first derivative vanishes at

$$y_0 = 1/2 + (\chi_{AD} - \chi_{AC})/2\chi_{CD} \quad (2)$$

This condition is met if $(\chi_{AD} - \chi_{AC})/\chi_{CD}$ is less than unity. (Note that both positive and negative χ_{AC} values are, in principle, permissible.) The second derivative, $f''(y)$, is simply

$$f''(y) = 2\chi_{CD} \quad (3)$$

and is positive for positive χ_{CD} values, as in our copolymer. When $f(y)$ reaches a minimum at $y = y_0$, the parabolic function $f(y)$ is further simplified to become

$$f(y)/\chi_{CD} = y^2 - 2y_0y + \chi_{AD}/\chi_{CD} \quad (4)$$

For the special case of $\chi_{AC} = 0$ at a certain temperature T, eq 2 reduces to

$$y_0 = 1/2 + \chi_{AD}/2\chi_{CD} \quad (5)$$

Two important consequences follow eq 5. First, χ_{AD} must be smaller than χ_{CD} because y_0 cannot exceed unity. Second, if either χ_{AD} or χ_{CD} is known, the other can be

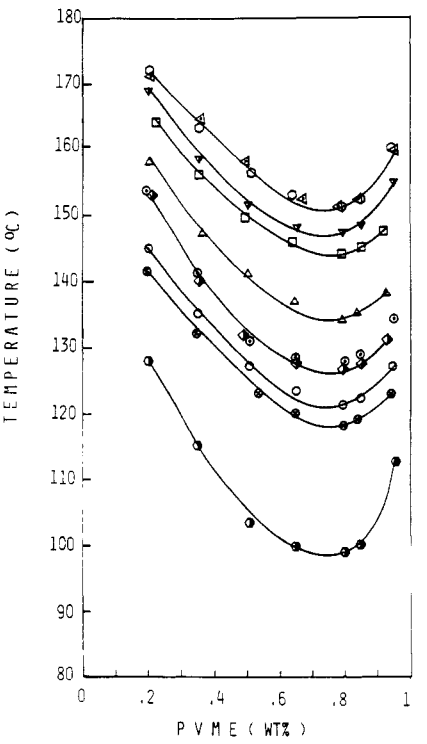

Figure 2. Phase diagrams of PVME blends with PS and its copolymers: (○) PS, (⊙) monodisperse PS-90000, (⊗) monodisperse PS-200000; (△) S95; (□) S90, (○) S85; (▲) S80; (▽) S75; (▣) S70; (◑) S65.

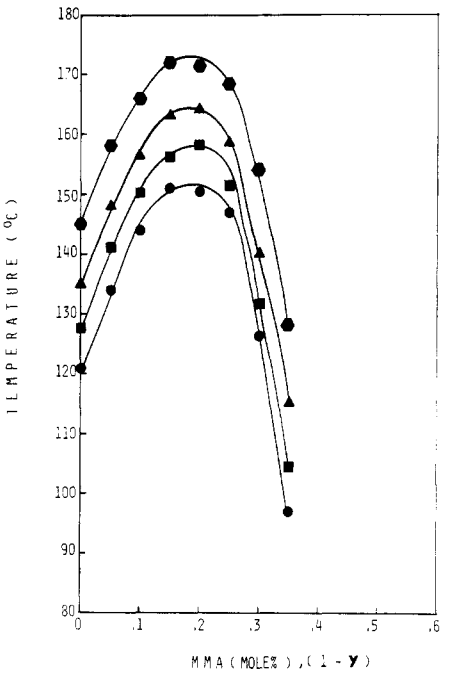

Figure 3. Miscibility Windows of PVME blends with S–MMA copolymers. Weight percent PVME in blends: (●) 80; (■) 50; (▲) 35; (◆) 20.

calculated. Substitution of eq 5 into (1) results in the following expression:

$$f(y) = (1 - y)(2y_0 - y - 1)\chi_{CD} \quad (6)$$

The value of $f(y)$ becomes zero at $y = 1$ and at $y = (2y_0 - 1)$. It is positive for $y < (2y_0 - 1)$ but becomes negative when y exceeds the latter. The slope of the $f(y)$ versus y curve is

$$f'(y) = 2(y - y_0)\chi_{CD} \quad (7)$$

and is positive for $y > y_0$ and negative $y < y_0$. A schematic

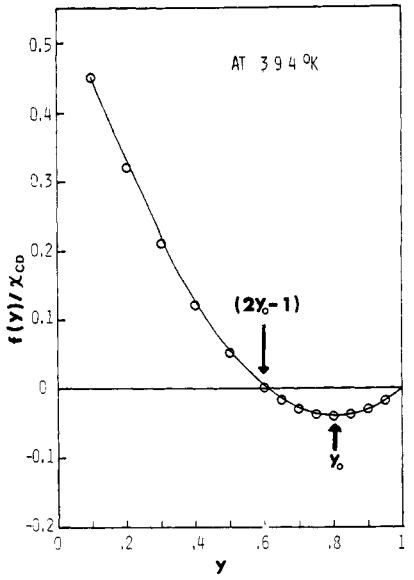

Figure 4. Functional dependence of χ blend on y for the case $\chi_{AC} = 0$, curve calculated from eq 6 with $y_0 = 0.8$.

diagram of the dependence of $f(y)$ on y is depicted in Figure 4 for this special case.

Equations 2–6 will be used in the ensuing discussion to analyze our experimental results. At the LCST of 394 K for PVME–PS, $\chi_{AC} = 0$. The experimental y_0 value of ~0.8–0.84 dictates that the ratio χ_{AD}/χ_{CD} is about 0.6–0.68 at that temperature, according to eq 5. The value of $f(y)$ is positive for $y < 0.6$–0.68 and negative for $y > 0.6$–0.68 by virtue of eq 6. The magnitude of χ_{CD} can be estimated as follows: The interactional contribution, χ_{CD}^{int}, is calculated from the solubility parameters of PS and PMMA, by using Hoy's group contribution constants,[17] to be 2.5×10^{-3}. The free volume contribution, χ_{CD}^{FV}, is calculated from Patterson's approximation[3] to be 6.1×10^{-3}. The sum of these two quantities, 8.6×10^{-2}, gives χ_{CD}. This in turn yields a χ_{AD} value of about 5.2×10^{-3} at 394 K. We note that the χ_{AD} value deduced here is almost an order of magnitude smaller than the calculated χ_{AD}^{int} value of 4.5×10^{-2}. We have no explanation for the discrepancy but it appears possible that the dipole–dipole interaction between the ether group of PVME and the carbonyl moiety of PMMA effectively cancels the dispersion force interaction. Alternatively, if the magnitude of χ_{AD}^{int} computed from solubility parameters is correct, the free volume part of the PS–PMMA interaction must have a larger value, at least ~0.1.

At temperatures below 394 K, χ_{AC} is negative and χ_{AD} is no longer related to χ_{CD} by eq 5. Nevertheless, the two interaction parameters are still expected to be comparable in magnitude provided that the temperature coefficients are not drastically different.

The critical value of y for miscibility at 300 K is about 0.6. At the critical copolymer composition, $f(y) = 0$ and eq 1 becomes

$$\chi_{AC} + (1 - y_c)/y_c\chi_{AD} - (1 - y_c)\chi_{CD} = 0 \qquad (8)$$

Since χ_{AC} is negative at 300 K, χ_{AD} must be larger than $y_c\chi_{CD}$ or $0.6\chi_{CD}$. Unfortunately, a rigorous test of eq 8 is not possible at this time due to uncertainties in the absolute values of the three interaction parameters. Only a sample calculation is given below. If χ_{AC} is chosen as -3×10^{-4}, from neutron scattering studies,[12] and χ_{CD}, 9×10^{-3}, from free volume and solubility parameter calculations, $\chi_{AD} \approx 5.8 \times 10^{-3}$. Larger values of χ_{AD} and χ_{CD} will call for a more negative value of χ_{AC}.

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