

스티렌을 포함한 공중합체들과 폴리(비닐 메틸 에테르) 블렌드의 광산란에 의한 상용성

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Miscibility of Blends of Poly(Vinyl Methyl Ether) with Styrene-Containing Copolymers by Light Scattering

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요 약 : α -methyl styrene, *p*-methyl styrene, 1-vinyl naphthalene과 2-vinyl naphthalene을 monomer feed 비를 기준으로 10% 및 20% 포함하는 styrene공중합체들을 합성하고 이들과 poly(vinyl methyl ether) (PVME)블렌드의 상용성을 연구하였다. 이들 copolymer 및 homopolymer들은 radical공중합으로 합성하였으며 분자량은 모두 20,000이하가 되도록 반응을 조절하였다. He/Ne laser 산란 장치로 cloud point를 측정하여 블렌드의 상용성을 측정하였다. 측정결과 모든 블렌드가 저임계용액 온도(LCST) 거동을 보였으나 PVME와의 상용성은 polystyrene>poly(styrene-co- α -methyl styrene)>poly(styrene-co-*p*-methyl styrene)>poly(styrene-co-1-vinyl naphthalene)>poly(styrene-co-2-vinyl naphthalene)순으로 나빠졌으며 이러한 경향은 공중합체에 포함된 styrene 및 vinyl naphthalene 유도체들의 입체 장애 효과에 주로 기인되는 것으로 생각된다.

Abstract : Miscibility of blends of poly(vinyl methyl ether) (PVME) with several styrene containing copolymers was investigated by measuring cloud points as a function of blend compositions with He/Ne laser scattering. Copolymers of styrene and α -methyl styrene, *p*-methyl styrene, 1-vinyl naphthalene or 2-vinyl naphthalene were synthesized by radical copolymerization. All the compositions of the four styrene- or vinyl naphthalene- derivatives in the copolymers were fixed at 10% and 20% by wt. in monomer feed ratio and the molecular weights of those copolymers obtained were below 20,000. Although all the blends studied in this work showed lower critical solution temperature(LCST) behavior, miscibility of the styrene-containing copolymers with PVME was shown better in the order of polystyrene>poly(styrene-co- α -methyl styrene)>poly(styrene-co-*p*-methyl styrene)>poly(styrene-co-1-vinyl naphthalene)>poly(styrene-co-2-vinyl naphthalene). The result may be attributed in part to their steric hindrance of the styrene or vinyl naphthalene derivatives in the copolymers.

INTRODUCTION

In most of the polymer mixtures which are known to be truly miscible, the degree of their miscibility decreases with increasing temperatures and the phenomenon of lower critical solution temperature (LCST) is exhibited. Such mixtures usually owe their miscibility to the presence of some specific favorable interactions between the components. At higher temperatures the effect of the favorable interaction is reduced while the unfavorable effect of the free volume change on mixing increases, eventually leading to phase separation above LCST.^{1,2}

Recently the blends of polystyrene(PS) and poly(vinyl methyl ether) (PVME) have attracted much interests because of their miscibility over a wide range of blend concentration.^{3~6} Considerable works have been reported to investigate the nature of interaction between the two pairs using various experimental techniques.

In order to search for the accurate nature of specific interactions between PS and PVME, we synthesized a series of copolymers containing styrene as a major component in which another minor component is styrene- or vinyl naphthalene- derivatives. We have employed the following considerations: If we get informations from the effect of the composition or the molecular structure of the minor component in the copolymers synthesized on the miscibility of the blends of PVME with those styrene containing copolymers, the results may provide definite clues, even though it may be indirect approach, to interpret the accurate nature of interactions in the miscible PS/PVME blends.

In this connection, we reported on the miscibility of poly(styrene-co-1-vinyl naphthalene) with PVME in our previous work.⁷ A significant effect of the composition of styrene in the copolymers on the interaction with PVME was observed by FTIR spectroscopic and thermal studies. It appeared that the addition of 1-vinyl naphthalene decreased the miscibility of polystyrene with PVME.

For the reason, in this work, we synthesized

poly(styrene-co- α -methyl styrene), poly(styrene-co- p -methyl styrene), poly(styrene-co-1-vinyl naphthalene) and poly(styrene-co-2-vinyl naphthalene) copolymers. According to the equation-of-state theory, the miscibility is significantly affected by molecular weight, molecular weight distribution, and thermal expansion coefficient, etc. of component polymers.⁸ Thus, all-out efforts were made to synthesize the copolymers of which molecular weight were not beyond 20,000 by adjusting the conversions of monomers to polymers below 20% in order to avoid any artificial effect of molecular weight and molecular weight distribution.

In this work, we evaluated the interaction parameters for polystyrene and/or styrene-containing copolymers and PVME blends from the measurements of the phase separation temperature (cloud point). The cloud points were measured by means of laser scattering. Here were presented preliminary results of the effect of the components in the copolymers on the miscibility of the blends of PVME with polystyrene and styrene containing copolymers.

EXPERIMENTAL

Styrene(Junsei Chemical), α -methyl styrene(Aldrich Chemical), p -methyl styrene(Aldrich Chemical), and 2-vinyl naphthalene(Aldrich Chemical) were purified by standard procedures. Azobisisobutyronitrile(AIBN) (Yakuri Pure Chemical) was purified by recrystallization from ethanol. Poly(vinyl methyl ether) (PVME) obtained from Scientific Polymer Products was purified according to the literature.⁴ 1-vinyl naphthalene(1VN) monomer was synthesized by dehydration of 1-naphthyl ethanol (Aldrich). Details of the synthesis of 1-VN were described elsewhere.⁷

Syntheses of Polymers and Copolymers

Polystyrene(PS), poly(α -methyl styrene) ($P\alpha$ MeS), poly(p -methyl styrene) (Pp MeS), poly(1-vinyl naphthalene) (P1VN) and poly(2-vinyl naphthalene) (P2VN) were prepared in the polymerization tubes putting a 3.0~4.5 mol monomer solu-

tion of toluene with 0.1 wt% AIBN of monomers. The tubes were sealed after charging with nitrogen gas and polymerization was carried out at 60°C for 8~18 hrs. Different reaction time was applied for each polymer so as the molecular weights and molecular weight distributions of the polymers obtained were below 20,000 and 2.0, respectively, by controlling conversions of monomers to polymers below 20% according to their reactivities.

Poly(styrene-co- α -methyl styrene) (P(S-co- α MeS)), poly(styrene-co- p -methyl styrene) (P(S-co- p MeS)), poly(styrene-co-1-vinyl naphthalene) (P(S-co-1VN)) and poly(styrene-co-2-vinyl naphthalene) (P(S-co-2VN)) were synthesized at the weight ratios(styrene/styrene- or vinyl naphthalene- derivatives) of 90/10 and 80/20 in monomer feed ratio by the same method as that of each homopolymer. Purification of the polymers was accomplished by reprecipitation in methanol from their toluene solutions, followed by drying in a vacuum oven until kept at a constant weight. The characteristics of the polymers synthesized are given in Table 1.

The composition notations described in Table 1

and in the text are based on monomer feed ratios in copolymers throughout the article, unless otherwise noted. For instance, P(S9-co- α MeS1) denotes that the composition of the copolymer is 90 wt% of styrene and 10 wt% α -methyl styrene in monomer feed ratio, even though the copolymer contains slightly different comonomer compositions.

Procedure

Weighed amounts of two polymers for a mixture (about 0.3 g total) were casted from 3% (by weight) tetrahydrofuran(THF) solution according to their compositions in a blend. The films were dried slowly in a petri dish at room temperature and then kept under a vacuum until they reached constant weight. Each sample film was put into a glass tube of about 0.5-cm inner diameter. The tube was attached to a vacuum line and heated to about 200°C to expel volatile impurities before its top was sealed off. The sample tube was inserted in the axial position of a cylindrical aluminium block, heated with resistance wires wound around its surface. A principle of operation of the light scattering apparatus for this work was originally

Table 1. Characteristics of Polymers Used in the Study

Sample	wt.% of Styrene Conversion in Feed in Copolymer(%) ^a			\overline{M}_n	\overline{M}_w	$\overline{M}_w/\overline{M}_n^b$	Source
PS	100		17.2	13,100	17,200	1.31	synthesized ^c
PVME	0		—	46,500	99,000	2.13	Scientific Polym. Prod.
P α MeS	0		15.6	15,700	19,700	1.25	synthesized
P p MeS	0		14.8	13,700	21,000	1.53	synthesized
P1VN	0		12.9	6,900	17,600	2.55	synthesized ^d
P2VN	0		15.2	9,100	15,400	1.69	synthesized ^d
P(S9-co- α MeS1)	90	88.0	18.5	12,500	18,200	1.46	synthesized
P(S8-co- α MeS2)	80	77.5	17.1	8,600	13,500	1.57	synthesized
P(S9-co- p MeS1)	90	87.3	16.7	14,500	19,700	1.36	synthesized
P(S8-co- p MeS2)	80	78.5	16.1	11,350	19,400	1.71	synthesized
P(S8-co-1VN2)	80	80.5	17.4	11,000	13,600	1.60	synthesized
P(S8-co-2VN2)	80	78.2	19.2	11,400	15,500	1.36	synthesized

^a analyzed by NMR and/or UV. ^b GPC.

^c synthesized by the Radical Polymerization for the work.

^d synthesized in our previous work.

designed by Roe and Zin and described elsewhere.⁹ A low-power 2-mW He-Ne laser was used as the light source, and a photodiode (EG & G HAV-1000 with a sensitivity of 7×10^6 v/w at $R_f = 20 \text{ M}\Omega$ for 6328Å wavelength) was used as the detector. All measurements were performed at a 90° scattered angle.

The temperature was cycled repeatedly from about 30°C below the cloud point to about 30°C above it at a constant heating and cooling rate. The output from the detector and the monitoring thermocouple was recorded on a two-channel chart recorder. Fig. 1 shows an example of such records. The temperature at which the turbidity appeared on heating was taken as the cloud point. Two methods in the determination of the cloud temperature are described elsewhere.⁹ We applied the method to choose the temperature at which the intensity begins to deviate from the base line intensity. Since the intensity in the cloudy state (high turbidity) changed linearly on heating and

cooling in our systems, extrapolation of nearly linear portion of the intensity curve in the cloudy state to the base line was performed and the intersection was used as the cloud temperature.

All measurements were performed at $2^\circ\text{C}/\text{min}$. Repeatability of the cloud point on successive temperature cycles was fairly good.

RESULTS AND DISCUSSION

Roe suggested that the Flory-Huggins free energy of mixing, per unit volume of mixture, can be written⁹⁻¹¹ as

$$\Delta G_M = RT[(1/V_1) \phi_1 \ln \phi_1 + (1/V_2) \phi_2 \ln \phi_2] + \Lambda \phi_1 \phi_2 \quad (1)$$

Where V_1 and V_2 are the molar volumes of polymer 1 and 2, respectively and ϕ_1 , ϕ_2 are the volume fractions of the two polymers in the mixture. The last term involving Λ is considered formally to include all the free energy of mixing that is not accounted for by the combinatory entropy of mixing, represented by the first term. The quantity Λ thus defined has the dimension of energy per unit volume and can be called polymer-polymer interaction energy density. More traditionally, the Flory-Huggins free energy of mixing is written in the form

$$\Delta G'_M/RT = (1/N_1) [\phi_1 \ln \phi_1 + (1/N_2) \phi_2 \ln \phi_2] + \chi \phi_1 \phi_2 \quad (2)$$

Where $\Delta G'_M$ is the free energy of mixing per lattice volume (or per segment), and N_1 and N_2 are the numbers of segments in polymer 1 and 2. If V_{ref} is the volume of a lattice (or a segment), ΔG_M is equal to $\Delta G'_M/V_{\text{ref}}$ is the volume of a lattice (or a segment), ΔG_M is equal to $\Delta G'_M/V_{\text{ref}}$ and it is seen that

$$\chi = \Lambda V_{\text{ref}}/RT \quad (3)$$

The use of χ , as a dimensionless quantity, has advantages for theoretical development, but Λ is the preferred choice for describing experimental results. There are certain advantages in using eq

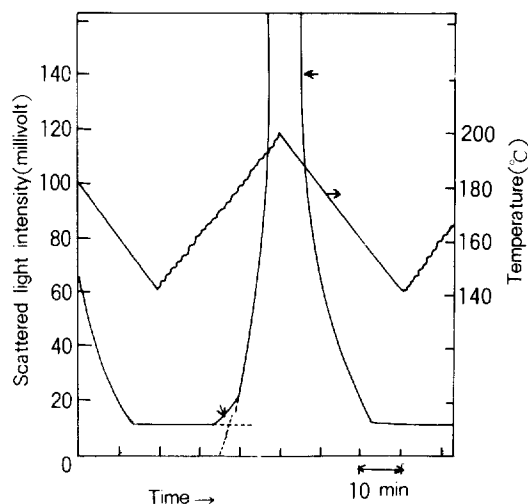


Fig. 1. Example of chart recording obtained in the cloud point measurement. The mixture containing 50 wt% PS and 50% PVME was cycled between 80° and 200°C at a constant heating/cooling rate of $2^\circ\text{C}/\text{min}$. The point (indicated by an arrow) at which the scattered light intensity on heating increases sharply from the baseline level is taken as the cloud point.

1 based on Λ rather than the more traditional expression based on χ . (see Ref. 9)

Polystyrene-Poly(vinyl methyl ether)

The observed cloud points of mixtures of PS with PVME is plotted in Fig. 2. The data were fitted to the binodal curve calculated on the basis of the Flory-Huggins eq 1, with Λ regarded as an adjustable parameter. To allow for the dependence of Λ on temperature and composition, Λ was represented by

$$\Lambda = \lambda_o + \lambda_\phi \phi + \lambda_T T \quad (4)$$

and the best-fitting values of λ_o , λ_ϕ and λ_T were determined by means of a nonlinear least-square algorithm. A single set of parameters represented by

$$\Lambda = -0.1350 + 0.019\phi + 0.000423 T \quad (5)$$

was used to fit cloud-point data set in Fig. 2. In eq 5, Λ is in calories per centimeter cubed, ϕ is the

volume fraction of poly (vinyl methyl ether) (PVME), and T is in Kelvin. The solid curves shown in the figure are the binodals calculated by means of eqs 1 and 4 by the same procedures. To analyze the data in terms of eq 1, the composition of the mixture was converted from weight fraction to volume fraction by use of the following values of specific volume. For polystyrene (above T_g)¹⁰

$$v_{sp} = 0.9217 + (5.412 \times 10^{-4}) t + (1.687 \times 10^{-7}) t^2 \quad (6)$$

for poly(vinyl methyl ether)

$$v_{sp} = 0.910 + (7.23 \times 10^{-4}) t \quad (7)$$

where t is in degree Celsius.

The LCST behavior of PS/PVME blends is well known due to specific interaction forces, even though the miscibility of the two polymer pairs was affected by several factors including solvent, temperature, molecular weight, and concentration.³⁻⁶ The specific interactions between polystyrene and PVME, giving rise their miscibility, was reported to reside on the phenyl group of the styrene monomer and COCH_3 of PVME, but the nature of this interaction should be revealed in more detail and accuracy.

Poly(styrene-co- α -methyl styrene)-PVME

Fig. 2 also shows the cloud points of the mixtures of poly(styrene-co- α -methyl styrene) and PVME of two compositions of 90% and 80% styrene (P(S9-co- α MeS1) and P(S8-co- α MeS2), respectively) and PVME. The solid curves drawn there were calculated by use of the values of Λ represented by

$$\Lambda = -0.0630 + 0.023 \phi + 0.00025 T \quad (8)$$

(for P(S9-co- α MeS1))

and

$$\Lambda = -0.1260 + 0.0448 \phi + 0.000418 T \quad (9)$$

(for P(S8-co- α MeS2))

where ϕ is the volume fraction of PVME. In this case, there is a clear indication of the effect of the addition of α -methyl styrene on the miscibility of PS/PVME blends. The copolymers are evidently

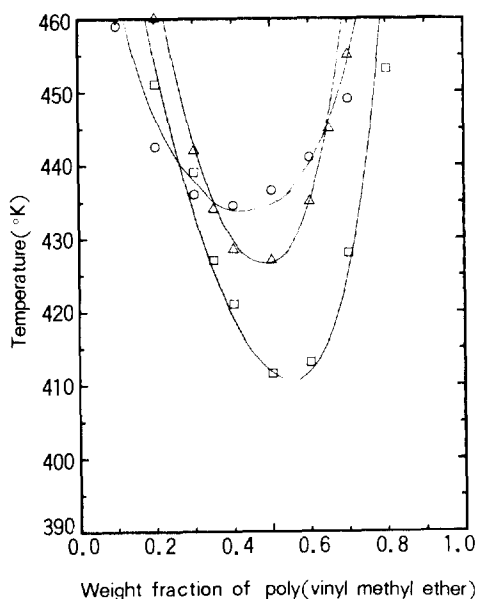


Fig. 2. Cloud points of mixtures containing poly(vinyl methyl ether) and one of the polystyrene(circles), P(S9-co- α MeS1) (triangles), and P(S8-co- α MeS2) (squares). The sample notations are same as in the text. The curves represent the least-squares fit.

less compatible with PVME, and the cloud points of mixtures containing copolymer are shifted downward by 10~20°C for P(S9-co- α MeS1)/PVME mixtures and by more than 30°C for P(S8-co- α MeS2)/PVME mixtures. It clearly shows that the mixtures become less miscible as the composition of α -methyl styrene in the copolymer increases. In Table 2, the Λ values are those evaluated by means of eqs 5,8 and 9 for $\phi=0.5$ and at 150°C. The temperature 150°C was chosen because comparison was made at the temperature in which most of our cloud point data lied. The result could present semiquantitative tool to estimate the interaction energy for polymer pairs interacting with nonpolar forces, but its applicability to polymer pairs interacting with other types of forces as well, such as polar or hydrogen bonding forces, remains to be studied. To calculate Λ values, the composition of the mixture was converted from weight to volume fraction by use of the following values of specific volume for poly(α -methyl styrene) (above T_g)¹⁴

$$v_{sp} = 0.87 + (5.08 \times 10^{-4}) t \quad (10)$$

where t is in degree Celsius. For copolymers, the general additivity rule was adapted to calculate the specific volume from that of each component.

Poly(styrene-co- p -methyl styrene)-PVME

The observed cloud points of mixtures of PVME with either p(S9-co- p MeS1) or p(S8-co- p MeS2) are plotted in Fig. 3. The binodal curves calculated with the use of eqs 11 and 12 are drawn in Fig. 3 to show the degree of fit. For p(S9-co- p MeS1),

$$\Lambda = -0.1823 + 0.0350 \phi + 0.000507 T \quad (11)$$

Table 2. Comparison of Observed Values of Λ at 150°C^a

Polymer Pairs	Values
PS-PVME	0.0536
P(S9-co- α MeS1)-PVME	0.0543
P(S8-co- α MeS2)-PVME	0.0732

^a in cal/cm³

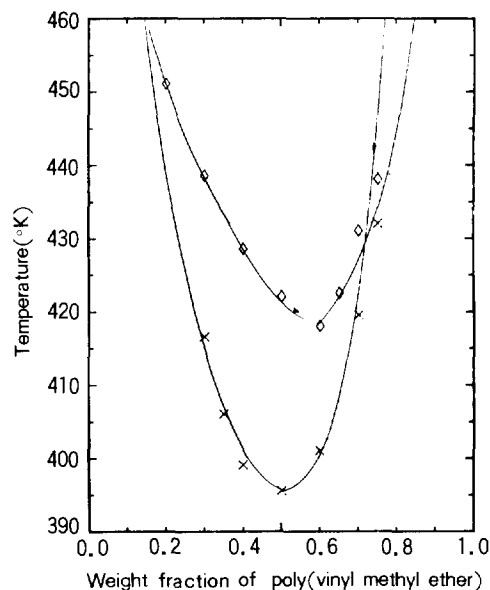


Fig. 3. Cloud points of mixtures containing PVME and one of P(S9-co- p MeS1) (diamonds) and P(S8-co- p MeS2) (crosses). The curves represent the least-squares fit.

for p(S8-co- p MeS2),

$$\Lambda = -0.06317 + 0.0231 \phi + 0.000253 T \quad (12)$$

It should be mentioned in this case, however, that there are some ambiguity to use the values of the constants λ_o , λ_ϕ and λ_T giving the best fit to experimentally determined cloud points since the specific volume data of p -methyl styrene was assumed to be equal to that of α -methyl styrene, which can induce an artificial error in calculation. Thus, the values were compared only in the means of qualitative differences. It is also shown in Fig. 3 that the copolymer with 10% of p -methyl styrene composition is more compatible with PVME than with 20% of p -methyl styrene composition.

Fig. 4 shows the cloud points of P(S9-co- α MeS1)/PVME mixtures and of P(S9-co- p MeS1)/PVME mixtures. The solid curves were explained previously. It is interesting to note that the copolymer of α -methyl styrene with styrene shows better miscibility with PVME than that of p -methyl sty-

rene with styrene. It may be assumed that these results are mainly due to the difference in steric hindrance of the component in the copolymer, even though more precise interpretation should be required to draw a conclusion.

poly(α -methyl styrene)-PVME

Fig. 5 shows that the cloud points of the mixture of poly(α -methyl styrene) and PVME. The cloud points of the mixture of polystyrene and PVME are also shown in the same figure for comparison. A single set of parameters represented by

$$\Lambda = -0.070 + 0.0340 \phi + 0.00025 T \quad (13)$$

was used to fit sets of cloud-point in the figure for P α MeS/PVME mixtures. It can be shown that the cloud points of mixtures containing P α MeS are shifted downward by more than 40°C compared to those containing PS.

Poly(styrene-co-1-vinyl naphthalene) or Poly(styrene-co-2-vinyl naphthalene)-PVME

In our previous work, we reported that the

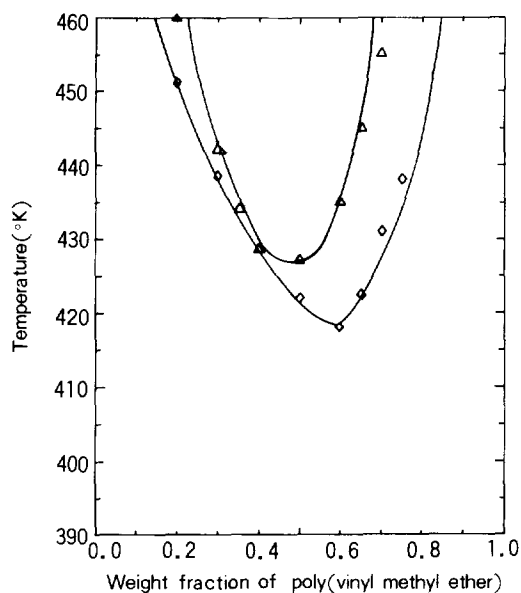


Fig. 4. Cloud points of mixtures containing PVME and one of P(S9-co- α MeS1) (triangles) and P(S9-co- p MeS1) (diamonds). The curves represent the least-squares fit.

immiscibility window becomes broader with increasing composition of 1VN in the copolymers.⁷ In this work, we did not obtain the cloud points over the entire composition range of PVME for the mixtures of 1VN or 2VN with PVME. Table 3 clearly shows that the cloud points of α -methyl styrene and p -methyl styrene copolymer with styrene are higher than those of 1VN or 2VN with PVME at 50% compositions of PVME. This must be due to the stronger effect of steric hindrance of naphthyl group rather than α - or p -

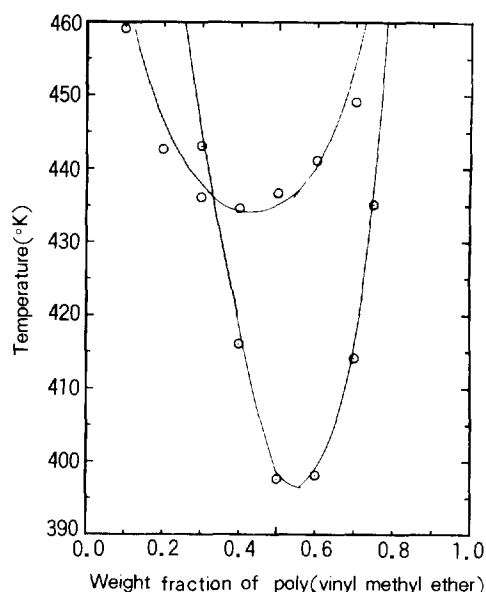


Fig. 5. Cloud points of mixtures containing PVME and one of polystyrene (circles) and poly(α -methyl styrene) (circles with points). The curves represent the least-squares fit.

Table 3. Cloud Points at the 50% of PVME Composition

Polymer Pairs	Cloud Points(°C)
PS-PVME	163.5
P(S8-co- α MeS2)-PVME	138.5
P(S8-co- p MeS2)-PVME	122.5
P(S8-co-1VN2)-PVME	53.5
P(S8-co-2VN2)-PVME	45.0

methyl substituted phenyl group.

Comparison with the Equation-of-State Theory

In recent years a number of workers have contributed to the refinement of the theories of polymer liquids and mixtures over the original Flory-Huggins treatment.¹⁵⁻¹⁹ All these theories recognize the importance of the equation-of-state contribution to the free energy of mixing or the effect on mixing arising from the difference in the free volumes of the pure components. Roe and Zin used the results of these theories, especially the one due to Flory and his co-workers,^{16,17} to analyze the value of the polymer-polymer interaction parameter obtained in their work and proposed the following equation(14)⁹

$$\Lambda = \frac{Z_{12}}{2} + \frac{3}{2} \frac{T}{\bar{v}} \frac{p^*}{1-4\bar{T}} \left(\frac{\bar{T}_1 - \bar{T}_2}{\bar{T}} \right)^2 \quad (14)$$

where Z_{12} is interpreted as a free energy density rather than an energy density and a parameter denoting the change in the energy density on mixing. Z_{12} includes the term in effect correcting for the deficiency of the Flory-Huggins expression for the combinatorial entropy mixing and varies with volume fraction of the component to some extent. The characteristic pressure p^* has the dimension of energy density(e.g., cal/cm³) and is evaluated for a given polymer liquid by means of the universal functions defined in terms of the reduced variable $\bar{p}=p/p^*$. The same universal functions can also be used to describe mixtures. \bar{T}_1 , \bar{T}_2 and \bar{T} are the reduced variables of 1 component, 2-component and mixture, respectively, according to the principle of corresponding states, \bar{v} is also reduced volume of mixture and can be evaluated from the knowledge of its thermal expansion coefficient α by means of the relation

$$\bar{v}^{1/3} - 1 = \alpha T / 3(1 + \alpha T) \quad (15)$$

In eq 14, the first term represents the change in the energy density due to the foreign segment contact and the second term arises from the change in free volume on mixing.

In order to be able to compare eq 14 with our

experimental values of Λ , we used the values of the characteristic parameters for the two component polymers concerned according to literatures. The parameters for polystyrene, at 150°C, evaluated by Flory and co-workers,²⁰ are $T^*=8299$ °K, $\bar{v}=1.2105$ cm³, $p^*=114$ cal/cm³(extrapolated from lower temperatures), and $\alpha=5.81 \times 10^{-4}$ deg⁻¹. For PVME and poly(α -methyl styrene), \bar{v} and T^* can be evaluated using eq 15. For copolymers, the additivity rule was adapted to obtain the values. Taking the values $\alpha=5.08 \times 10^{-4}$ deg⁻¹ for poly(α -methyl styrene) and $\alpha=7.23 \times 10^{-4}$ deg⁻¹ for PVME, we obtain for 150°C $T^*=9023.3$ °K, $\bar{v}=2.1876$ cm³ for poly(α -methyl styrene) and $T^*=7320$ °K, $\bar{v}=1.2503$ cm³ for PVME. Evaluation of p^* requires knowledge of either the isothermal compressibility or the thermal pressure coefficient, but neither of which is available for PVME and poly(α -methyl styrene). For the purpose of the present discussion, however, not much error is introduced by taking the approximation $p_1^*=p_2^*=p^*$.

The relative magnitudes of the two terms on the right of eq 14 can now be estimated. Table 4 shows the characteristic parameters for the mixture at 150°C and $\phi_1=0.50$. It appears that the second term of eq 14 occupy a fairly large fraction of the observed Λ value. The effect of the free volume change on mixing becomes more significant as the composition of α -methyl styrene increases in the

Table 4. Characteristic Parameter Values Obtained from the Equation-of-State Theory²

Polymer Pairs	\bar{v} (cm ³)	T^* (°K)	Calculated ^b	Observed ^b Λ Value
			Value of Second Term of Eq14	
PS-PVME	1.2318	7810	0.1625	0.0536
P(S9-co- α MeS1)-PVME	1.2306	7846	0.1848	0.0543
P(S8-co- α MeS2)-PVME	1.2295	7882	0.2084	0.0732

^a values are obtained at 150°C and $\phi=0.5$ of PVME.

^b units are in cal/cm³.

copolymer. The importance of the free volume disparity has been stressed in the polymer pairs exhibiting a LCST behavior,^{2,8} even though Robard and Patterson¹ pointed out that the occurrence of a LCST behavior probably arises more because of weakening of the specific interaction at higher temperature and less from an increased contribution of the free volume disparity.

In summary, it can be concluded that the miscibility of polystyrene and styrene containing copolymers with PVME is in the order of polystyrene > poly(styrene-co- α -methyl styrene) > poly(styrene-co-*p*-methyl styrene) > poly(styrene-co-1-vinyl naphthalene) > poly(styrene-co-2-vinyl naphthalene). This trend may be in part due to steric hindrance difference of styrene- or vinyl naphthalene- derivatives in the copolymer which induce larger free volume change on mixing. It should be noted, however, that a very important question remains unanswered: Is the result attributed solely to the steric hindrance difference of comonomers in the copolymers? It may be assumed that another different type of inductive interactions exist due to the presence of substituent groups in styrene- or vinyl naphthalene- derivatives beside a certain interaction between PS and PVME. The inductive interactions may include dipole-dipole interaction and dispersion forces from several chemical groups in copolymers and these interactions may vary with the composition of copolymers and with the concentration of the blends. Further works are undertaking and will be reported elsewhere to reveal the nature of plausible inductive interactions using spectroscopic techniques.

In our previous publication on the study of miscibility of poly(styrene-co-1-vinyl naphthalene)/PVME blends, we suggested that a threshold energy exists to induce molecular interaction between the naphthyl ring of 1VN and the COCH₃ of PVME and to result in the miscible blends, regardless of the copolymer composition as well as the blend concentration. Further discussion relating to this kind of molecular level of interaction between the components should be made for the

other styrene containing copolymers/PVME mixtures studied in this work.

Furthermore, it should be pointed out that unless the molecular weight distribution is fairly narrow, the χ or Δ values obtained could entail an appreciable error and the error is reported to be more likely to affect the concentration or temperature dependence of the interaction parameter.²¹ Since the molecular weight distributions of the samples used in this study ranged from 1.3 to 2.0, the effect of molecular weight distribution should not be neglected.

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