

Light scattering and Fourier-transform infra-red studies on the miscibility of blends of poly(vinyl methyl ether) and styrene-containing copolymer

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The miscibility of blends containing poly(vinyl methyl ether) (PVME) and one of three different styrene/(styrene derivative) copolymers was investigated by light scattering and Fourier-transform infra-red (FTi.r.) spectroscopy. For this purpose copolymers of styrene with *o*-methyl-, *p*-methyl- or *m*-methylstyrene were synthesized by radical polymerization. The copolymer compositions were fixed at 10% and 20% (by weight) in the monomer feed ratio. The light scattering studies revealed that all the blends showed lower critical solution temperature (*LCST*) behaviour. In the FTi.r. results, the relative intensity of the 1080 cm⁻¹ peak was greater than that of the 1108 cm⁻¹ peak, due to the COCH₃ bond of PVME, in all the blends studied in this work. It is concluded that all the blends are miscible at room temperature over the entire concentration range studied, and the miscibility of the styrene/(styrene derivative) copolymers with PVME decreases in the order poly(styrene-*co*-*o*-methylstyrene) > poly(styrene-*co*-*p*-methylstyrene) > poly(styrene-*co*-*m*-methylstyrene).

(Keywords: miscibility; blends; poly(vinyl methyl ether); polystyrene; poly(styrene-*co*-*o*-methylstyrene); poly(styrene-*co*-*m*-methylstyrene); poly(styrene-*co*-*p*-methylstyrene); light scattering; Fourier-transform infra-red spectroscopy)

INTRODUCTION

Most pairs of polymers having long-chain structure are immiscible with each other because of their small entropy gain on mixing. However, some polymer blends show unusual miscibility behaviour when there is a specific interaction between the component polymers in the mixture. In most polymer mixtures that are known to be truly compatible, the degree of miscibility decreases with increasing temperature, and the phenomenon of lower critical solution temperature (*LCST*) is exhibited. Such mixtures usually owe their miscibility to the presence of some specific favourable interaction that decreases in strength on increasing the temperature, while the unfavourable effect due to the free-volume change on mixing increases, thus eventually leading to phase separation above the *LCST*^{1,2}.

Blends of polystyrene (PS) and poly(vinyl methyl ether) (PVME) have attracted much interest because

of their miscibility over a wide range of blend composition³⁻¹⁰. The miscibility of PVME with styrenic copolymers has also been extensively investigated, and the literature reports¹¹⁻¹⁴ show that the miscibility and phase separation behaviour are very much dependent on the chemical nature of the comonomer.

In this work we synthesized a series of copolymers containing styrene as the major component and a styrene derivative as the minor component. The styrene derivatives employed have the same chemical structure for the position of the methyl group, i.e. *o*-methylstyrene, *m*-methylstyrene and *p*-methylstyrene. We report here on the effects of the chemical nature of the comonomer, the composition of the copolymer and the blend concentration on the miscibility of styrene/(styrene derivative) copolymers with PVME. The blends were prepared by casting from toluene solution, and the degree of miscibility was examined by the optical clarity, light scattering and Fourier-transform infra-red (FTi.r.) spectroscopy.

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EXPERIMENTAL

Materials

Styrene (Junsei Chemical) and *p*-methylstyrene (Aldrich Chemical) were washed with 10% aqueous solution of NaOH to remove inhibitor, followed by washing with distilled water until it became neutral. After drying with CaCl₂ for two days, they were purified by distillation. *o*-Methylstyrene (Fluka Chemical) and *m*-methylstyrene (Fluka Chemical) were used without further purification. Azobisisobutyronitrile (AIBN) (Yakuri Pure Chemical) was purified by recrystallization from ethanol. The insoluble part of the saturated ethanol solution of AIBN at 50°C was filtered off. Purified AIBN was obtained by lowering the temperature of the solution to 5°C. Poly(vinyl methyl ether) (PVME) (Scientific Polymer Products) was reprecipitated twice from toluene into *n*-heptane and dried in vacuum before use.

Synthesis of polymers

PS was prepared in a polymerization tube containing 3.0 mol monomer solution in toluene with 1.0 wt% AIBN. The tube was sealed after charging with nitrogen gas and polymerization was carried out at 60°C for 4 h. Three kinds of copolymers, poly(styrene-*co*-*o*-methylstyrene) (P(S-*co*-*o*MeS)), poly(styrene-*co*-*m*-methylstyrene) (P(S-*co*-*m*MeS)) and poly(styrene-*co*-*p*-methylstyrene) (P(S-*co*-*p*MeS)), were synthesized by the same method. Purification of the polymers was accomplished by reprecipitation in methanol from the toluene solutions, followed by drying in a vacuum oven to constant weight. The characteristics of the polymers synthesized are given in Table 1.

For each monomer combination, two copolymers differing in composition were prepared by fixing the ratio of styrene/(styrene derivative) in the feed to either 90/10 and 80/20. The polymerization conversion was confined to about 15% or less in order to prevent drift in the comonomer composition in the copolymer. The actual composition of the comonomers in the polymers synthesized was determined by FT-n.m.r. spectroscopy (JEOL-FX90Q, 90 MHz) and is listed in Table 1.

Hereafter the copolymer will be designated, for brevity, by the monomer composition in the feed and not by the actual composition in the polymer. For instance, P(S9-*co*-*o*MeS1) denotes that the copolymer was obtained from a monomer feed containing 90 wt%

styrene and 10 wt% *o*-methylstyrene, even though the copolymer contains a slightly different comonomer composition.

Molecular weight

The molecular weight of the polymers was determined from g.p.c. (Waters 244) with Ultrastaygel 500 Å linear columns. The measurement was conducted using an RI detector in tetrahydrofuran (THF) at a flow rate of 1.0 ml min⁻¹ at 28°C. PS was used as the standard for calibration.

Light scattering

Weighed amounts of two polymers for a mixture (about 0.4 g total) were cast from 10 wt% solution in toluene. The films were dried slowly in a Petri dish at room temperature and then kept under vacuum to constant weight. Each sample film was put into a glass tube of about 0.6 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. A low-power 2 mW He-Ne laser was used as light source. A photodiode (EG&G HAV-1000 with a sensitivity of 7×10^6 V W⁻¹ at $R_f = 20$ MΩ for 6328 Å wavelength) was used as the detector. The sample tube was inserted in the axial position of a cylindrical aluminium block¹⁵, heated with resistance wires wound around its surface. All measurements were performed at a 90° scattering angle.

The temperature was cycled repeatedly from about 50°C below the cloud point to about 30°C above it at a constant heating and cooling rate. All measurements were performed at 2°C min⁻¹. Repeatability of the cloud point on successive temperature cycles was fairly good.

FTi.r. spectroscopy

I.r. spectra were obtained with an Analect FX-6160 FTi.r. spectrophotometer. Blends of various compositions in 3 wt% toluene solution were analysed using liquid cells. Thirty-two scans at a resolution of 2 cm⁻¹ were signal-averaged.

RESULTS AND DISCUSSION

Phase diagram

All the copolymers as well as PS formed clear films when blended with PVME. From the standpoints of

Table 1 Characteristics of polymers used in the study

Sample	Styrene (wt%)		Conversion (%)	M_n	M_w	M_w/M_n^b	Source
	In feed	In copolymer ^a					
PS	100		11.9	13 100	17 200	1.31	Synthesized ^c
PVME	0		—	46 500	99 000	2.13	SPP ^d
P(S9- <i>co</i> - <i>o</i> MeS1)	90	86.8	13.3	15 100	18 600	1.23	Synthesized
P(S8- <i>co</i> - <i>o</i> MeS2)	80	76.2	11.8	14 000	17 900	1.28	Synthesized
P(S9- <i>co</i> - <i>m</i> MeS1)	90	87.5	7.8	12 800	15 200	1.19	Synthesized
P(S8- <i>co</i> - <i>m</i> MeS2)	80	76.5	7.3	12 200	15 600	1.28	Synthesized
P(S9- <i>co</i> - <i>p</i> MeS1)	90	87.3	15.6	14 500	19 700	1.36	Synthesized
P(S8- <i>co</i> - <i>p</i> MeS2)	80	78.5	15.8	13 700	19 400	1.42	Synthesized

^aAnalysed by ¹H n.m.r.

^bG.p.c.

^cSynthesized by radical polymerization

^dScientific Polymer Products

optical clarity, the blends cast from toluene show miscibility over the whole concentration range examined in this study, regardless of the chemical nature of the styrene derivatives used as the minor comonomer component.

The observed cloud points of mixtures of PS with PVME are plotted in *Figure 1*. The data were fitted by a binodal curve calculated on the basis of the Flory–Huggins free energy^{9,15–20} of mixing, given below, with Λ regarded as an adjustable parameter:

$$\Delta G_M = RT \left[\left(\frac{1}{V_1} \right) \Phi_1 \ln \Phi_1 + \left(\frac{1}{V_2} \right) \Phi_2 \ln \Phi_2 \right] + \Lambda \Phi_1 \Phi_2 \quad (1)$$

where ΔG_M is per unit volume of the mixture, V_1 and V_2 are the molar volumes of polymers 1 and 2, and Φ_1 and Φ_2 are the volume fractions of the two polymers. The quantity Λ , denoting the polymer–polymer interaction energy density, may depend moderately on both the temperature and the composition of the blend. We take the simplest functional form incorporating these dependences as:

$$\Lambda = \lambda_0 + \lambda_1 \Phi_1 + \lambda_T T \quad (2)$$

The values of the constants λ_0 , λ_1 and λ_T giving the best fit to experimentally determined cloud points were evaluated by the method of non-linear least squares. The full curve drawn for PS/PVME data in *Figure 1* was calculated by equation (1) with the following Λ value:

$$\Lambda = -0.623 + 0.00012\Phi + 0.00158T \quad (3)$$

where Λ is in cal cm^{-3} , Φ is the volume fraction of PVME, and T is in kelvins. The LCST behaviour of PS/PVME blends is well known^{5,6,21,22}. The specific interaction between PS and PVME, giving rise to their compatibility, was reported to reside on the phenyl group of the styrene monomer and COCH_3 of PVME.

Figure 1 also shows the cloud points of the mixtures of P(S9-co-oMeS1) and P(S8-co-oMeS2) with PVME. The full curves drawn were calculated by using Λ values represented by:

$$\Lambda = 0.0381 - 0.000009\Phi + 0.0000252T \quad (4)$$

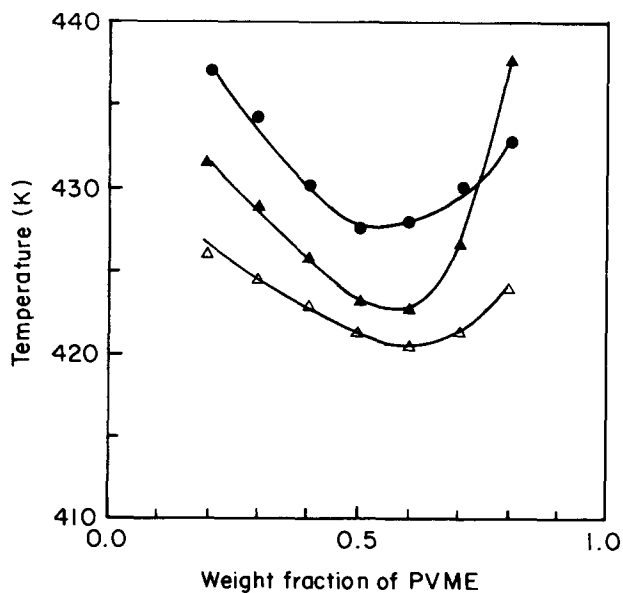


Figure 1 Cloud points of mixtures containing PVME and either PS (●), P(S9-co-oMeS1) (▲) or P(S8-co-oMeS2) (△)

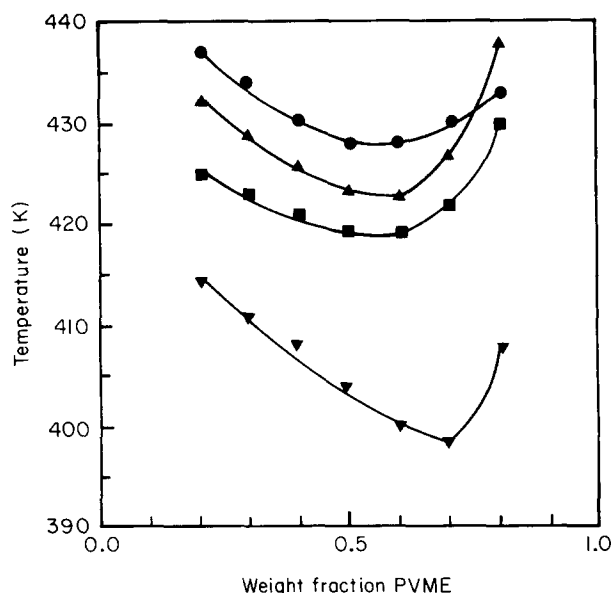


Figure 2 Cloud points of mixtures containing PVME and either PS (●), P(S9-co-oMeS1) (▲), P(S9-co-pMeS1) (■) or P(S9-co-mMeS1) (▼)

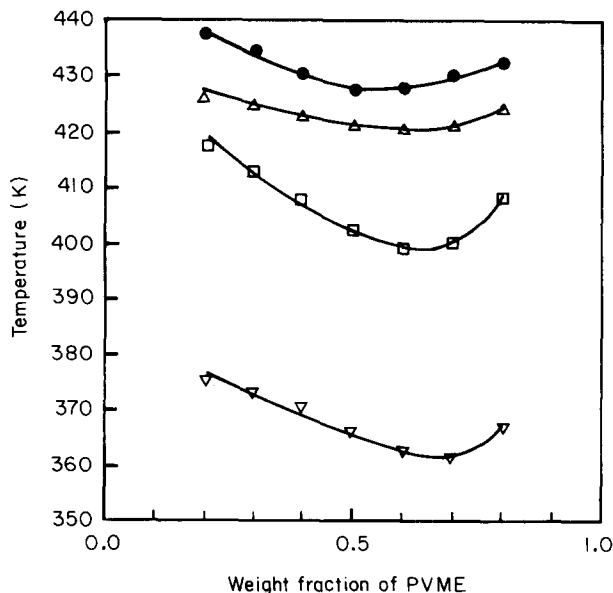


Figure 3 Cloud points of mixtures containing PVME and either PS (●), P(S8-co-oMeS2) (△), P(S8-co-pMeS2) (□) or P(S8-co-mMeS2) (▽)

for P(S9-co-oMeS1) and

$$\Lambda = -0.384 + 0.000005\Phi + 0.001039T \quad (5)$$

for P(S8-co-oMeS2). One can discern a clear indication of the effect of the addition of *o*-methylstyrene on the miscibility of PS/PVME blends. The copolymers are less compatible with PVME than is PS, and the cloud points of mixtures containing copolymers are shifted downward by 5–10°C for P(S9-co-oMeS1)/PVME and P(S9-co-oMeS2)/PVME mixtures. It shows clearly that the mixtures become less miscible as the proportion of *o*-methylstyrene in the copolymer increases.

Effect of comonomer structure

Figure 2 gives a comparison of the cloud-point data for blends of PVME with PS, P(S9-co-oMeS1),

Table 2 Best-fitting parameters for the polymer-polymer interaction energy density^a determined from fit to observed cloud points

Sample	λ_0^b	λ_1	λ_T	Λ^c	$d \ln \Lambda / dT^c$
PS/PVME	-0.623	0.00012	0.00158	0.011	0.138
P(S8-co-oMeS2)/PVME	-0.384	0.000005	0.00104	0.035	0.031
P(S8-co-pMeS2)/PVME	-0.0221	-0.000002	0.000184	0.052	0.0035
P(S8-co-mMeS2)/PVME	0.0897	-0.000010	-0.000069	0.062	-0.0011

^aIn units of cal cm⁻³^bValues based on weight-average molecular weight^cEvaluated for $\Phi = 0.5$ and $T = 130^\circ\text{C}$

P(S9-co-mMeS1) and P(S9-co-pMeS1). The full curves were calculated in the manner described above. It is to be noted that the cloud points of mixtures containing copolymers are all lower than those containing PS at all blend compositions, and the miscibility with PVME of copolymers containing styrene derivatives diminishes in the order poly(styrene-co-o-methylstyrene) > poly(styrene-co-p-methylstyrene) > poly(styrene-co-m-methylstyrene).

The same trend can be observed in the miscibility of blends of PVME with styrene derivative copolymers having the composition 80/20 (by monomer feed ratio), as can be seen in *Figure 3*. The sets of fitting parameters used to calculate the full curves are listed in *Table 2*.

Temperature dependence of Λ

The Λ values at $\Phi = 0.5$ and $T = 130^\circ\text{C}$ were calculated by means of equation (2) from the values of parameters λ_0 , λ_1 and λ_T determined against the observed cloud points, and are listed in *Table 2*. The Λ values can be utilized as a semiquantitative tool to estimate the interaction energy density between polymer pairs interacting not only through non-polar forces but also through other types of forces, such as polar or hydrogen bonding forces. As expected, the PS/PVME blend exhibits the smallest Λ value. For blends involving copolymers, the Λ values increase in the order poly(styrene-co-o-methylstyrene) < poly(styrene-co-p-methylstyrene) < poly(styrene-co-m-methylstyrene).

It is interesting to note that the temperature coefficient λ_T of the interaction energy density Λ is the largest and positive with the PS/PVME blend, decreases with copolymer blends in the reverse order to the above, and finally becomes negative with the poly(styrene-co-m-methylstyrene) blend. The trend is seen even more clearly with $\lambda_T/\Lambda = d \ln \Lambda / dT$ listed in the last column of *Table 2*. In general, blends exhibiting an LCST behaviour have either a negative or a small positive Λ value at low temperature, which increases rapidly with increasing temperature. On the other hand, blends exhibiting a UCST behaviour have a positive Λ value at low temperature, which in general decreases as the temperature is increased. The data presented in *Table 2* clearly demonstrate this inverse relationship between Λ and its temperature coefficient when a series of blends of systematically varying compatibility are compared.

Lin and Roe⁹ applied equation-of-state considerations, especially the one due to Flory and his coworkers^{16,23}, to analyse the value of the polymer-polymer interaction energy density and its temperature dependence obtained in their work. Starting from the Flory equation-of-state

theory, they derived the following expression for Λ :

$$\Lambda = \frac{Z_{12}}{\bar{v}^2} + \frac{3\tilde{T}p^*}{2\bar{v}(1-4\tilde{T}\bar{v})} \left(\frac{\tilde{T}_1 - \tilde{T}_2}{\tilde{T}} \right)^2 \quad (6)$$

where the quantities with asterisk and tilde have their usual meanings in equation-of-state theory and Z_{12} is a parameter denoting the change in energy density on mixing. In equation (6) the first term represents the change in the energy density on mixing due to foreign segment contacts, and the second term arises from the change in free volume on mixing. The first term is normally positive, but, in the presence of specific interactions between components of the blend, as in PS/PVME, it becomes negative and counterbalances the positive second term to render Λ very small or even negative.

When the temperature is raised, the second term always becomes more positive, arising from the fact that the free-volume difference between the two polymer components is accentuated at higher temperatures. In most cases, however, the first term is more important in determining the overall temperature dependence of Λ . Since Z_{12} is largely temperature-independent, the \bar{v}^2 factor in the denominator of the first term makes its absolute value decrease as the temperature is raised. Thus, when Z_{12} is negative, as in the case of a system having specific interactions, the first term becomes less negative as the temperature is raised, and eventually fails to counterbalance the second term, leading to a positive Λ and to the onset of phase separation. This fact was pointed out by Robard and Patterson¹ in their statement that the occurrence of LCST behaviour arises more because of weakening of the specific interactions at higher temperature and less from an increased contribution of the free-volume disparity. In the case of the systems for which Z_{12} is positive, the reduction in the magnitude of the first term with increasing temperature generally overrides the temperature dependence of the second term, and therefore the temperature coefficient of Λ becomes negative. The data presented in *Table 2* are totally consistent with the above qualitative description based on equation (6).

FTi.r. study of molecular interaction

Figure 4 shows the spectra obtained with blends containing varying weight fractions of P(S9-co-oMeS1) with PVME. The 1100 cm⁻¹ region is assigned to the COCH₃ of PVME. It is seen that the intensity of the 1080 cm⁻¹ band is greater than that of the 1108 cm⁻¹ component in all the blends. As the PVME content in

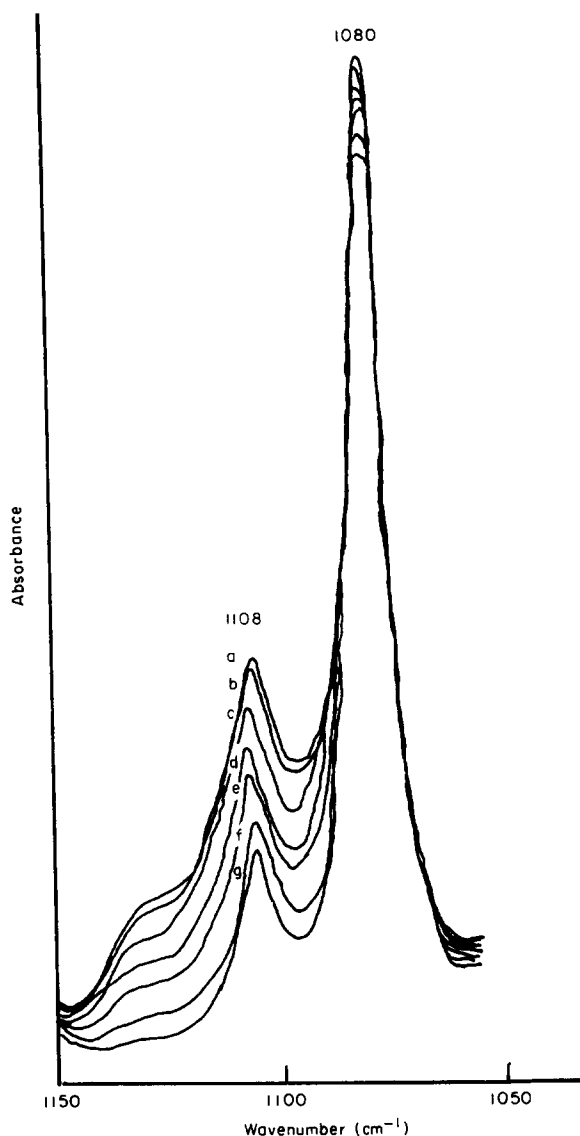


Figure 4 Relative intensities of the doublet of the 1100 cm^{-1} region for P(S9-co-oMeS1)/PVME blends: (a) 20, (b) 30, (c) 40, (d) 50, (e) 60, (f) 70 and (g) 80 wt% P(S9-co-oMeS1)

the blend increases, the 1108 cm^{-1} band becomes more prominent in comparison to the 1080 cm^{-1} band.

Hsu *et al.*⁸ and Garcia²⁴ studied miscible and immiscible blends of PS and PVME by FTi.r. spectroscopy. They independently reported that miscible PS/PVME blends showed strong evidence for molecular interaction, whereas no such interaction was detected between the two components when the blend was immiscible. Hsu *et al.*⁸ reported that PVME has a strong doublet at 1085 and 1107 cm^{-1} with a shoulder at 1132 cm^{-1} , and the relative intensity of this doublet varies considerably when the blend sample is cooled or heated. Thus, they concluded that the relative intensity of this doublet was sensitive to the miscibility of the PS/PVME blends and that the intensity of the 1085 cm^{-1} peak was greater than that of the 1107 cm^{-1} peak for the miscible blend. We will call this Hsu's criterion.

According to Hsu's criterion, the results in Figure 4 indicate that all the P(S9-co-oMeS1)/PVME blends are miscible regardless of PVME concentration, but the miscibility of the blends becomes weaker as the PVME content in the blend increases. This is in accord with the

light scattering study, indicating that all the blends exhibit LCST behaviour as well as optical clarity. The FTi.r. results, however, give more useful information about the effect of blend composition on the strength of the compatibility between the two components.

A more interesting feature is seen in the case of the blends of poly(styrene-co-*m*-methylstyrene) with PVME. The relative intensities of the doublet in the 1100 cm^{-1} region for the blends with various amounts of PVME are illustrated in Figure 5. In comparison to the results in Figure 4, there is a marked increase in the absorbance at 1108 cm^{-1} and a decrease in the absorbance at 1080 cm^{-1} .

Figure 6 gives a comparison of the relative intensities of the doublet in the 1100 cm^{-1} region among the blends containing either P(S9-co-*o*MeS1), P(S9-co-*m*MeS1) or P(S9-co-*p*MeS1). In Figures 6a, b and c, the results obtained with blends containing 30, 50 and 70 wt%, respectively, are compared. The results clearly illustrate that the intensity of the 1108 cm^{-1} component relative to that of the 1080 cm^{-1} component decreases in the order *m*-methylstyrene > *p*-methylstyrene > *o*-methyl-

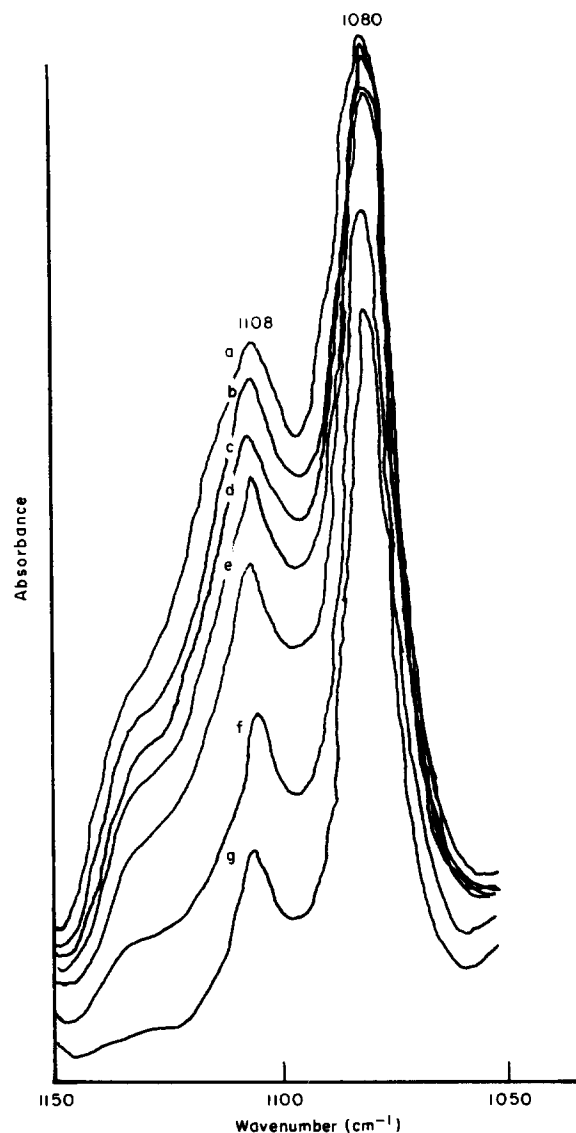


Figure 5 Relative intensities of the doublet of the 1100 cm^{-1} region for P(S8-co-*m*MeS2)/PVME blends: (a) 20, (b) 30, (c) 40, (d) 50, (e) 60, (f) 70 and (g) 80 wt% P(S8-co-*m*MeS2)

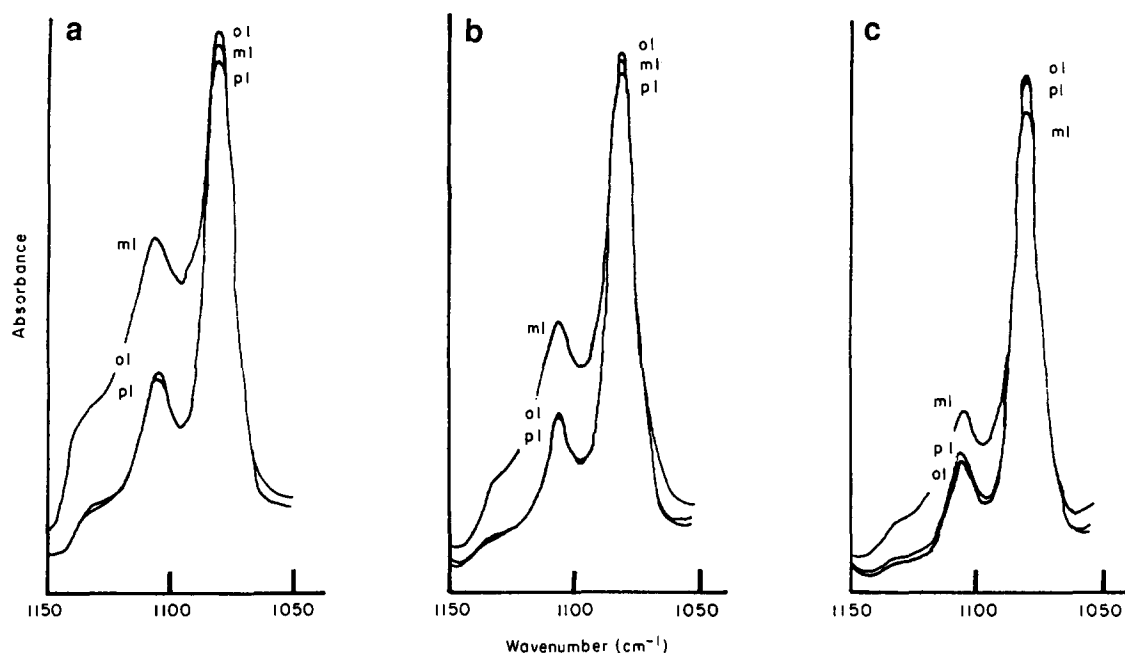


Figure 6 Relative intensities of the doublet of the 1100 cm^{-1} region for blends of PVME and either P(S9-co-oMeS1) (o1), P(S9-co-mMeS1) (m1) or P(S9-co-pMeS1) (p1). Amount of copolymer in blends: (a) 30, (b) 50 and (c) 70 wt%

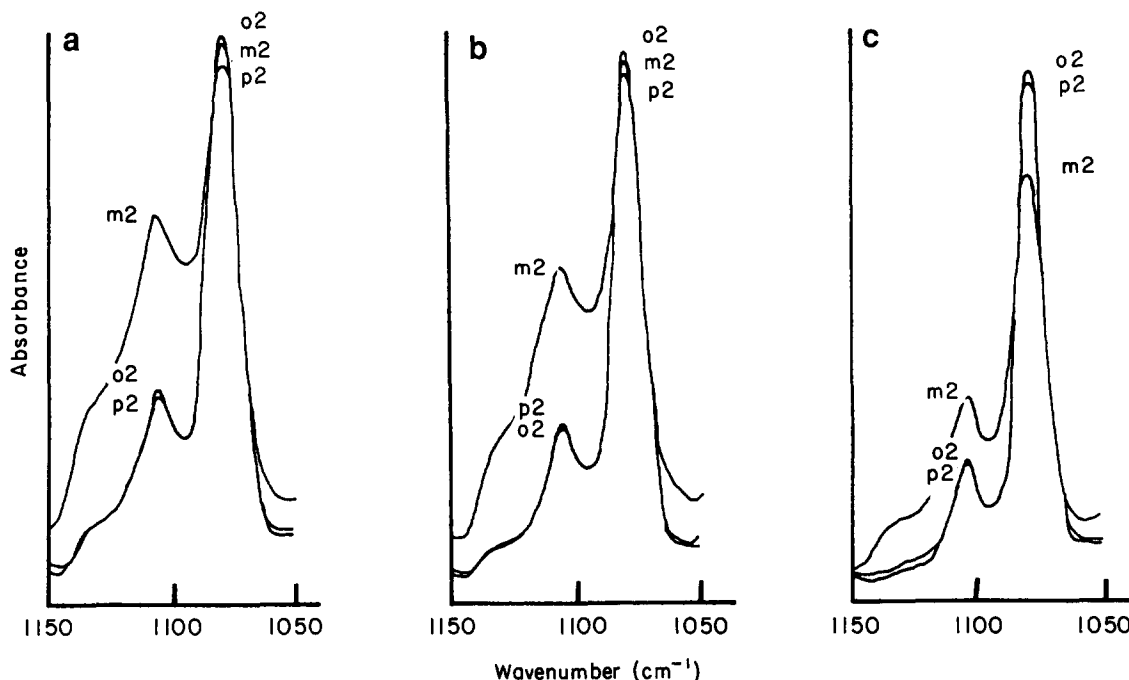


Figure 7 Relative intensities of the doublet of the 1100 cm^{-1} region for blends of PVME and either P(S8-co-oMeS2) (o2), P(S8-co-mMeS2) (m2) or P(S8-co-pMeS2) (p2). Amount of copolymer in blends: (a) 30, (b) 50 and (c) 70 wt%

styrene irrespective of the copolymer content in the blends. One can also note that the relative intensity of the 1108 cm^{-1} component increases as the copolymer content decreases (i.e. PVME content is increased) regardless of the type of copolymer involved. Figure 7 shows similar plots obtained with blends containing copolymers having 20 wt% styrene derivatives, and exactly the same trend can also be noted here.

These results can be interpreted on the basis of Hsu's criterion that the compatibility of PVME with a copolymer containing a styrene derivative decreases in the order polystyrene > poly(styrene-co-o-methylstyrene) > poly(styrene-co-p-methylstyrene) > poly(styrene-co-

m-methylstyrene). It implies that the miscibility is affected very sensitively by subtle changes in the chemical nature of the styrene derivative in the copolymers. The m-methylstyrene unit exerts a stronger influence in reducing the miscibility of polystyrene with PVME than do p-methylstyrene or o-methylstyrene units.

CONCLUDING REMARKS

Both the light scattering and FTi.r. studies indicate that all the blends prepared in this work are miscible at low temperatures over all the composition ranges investigated, and that the miscibility of styrene/(styrene derivative)

copolymers with PVME decreases in the order poly(styrene-*co-o*-methylstyrene) > poly(styrene-*co-p*-methylstyrene) > poly(styrene-*co-m*-methylstyrene).

Since the details of the miscibility behaviour are affected by molecular weight and molecular-weight distribution, an effort has been made in this work to synthesize polymers for the study under closely comparable conditions. To limit the composition drift of prepared copolymers, the polymerization conversion was kept to below 20%. In comparing the results obtained with different copolymers, any artifacts due to differences in molecular weight and its distribution were in this way minimized. When the polymer sample employed is not strictly monodisperse, the Λ values evaluated from cloud-point measurements could entail some error. It has been shown²⁵ that the error is more likely to affect the concentration dependence and temperature dependence of the interaction energy density. However, in this work, the polydispersities of the copolymers used are moderate, ranging from 1.2 to 1.5, and also comparable among the several copolymers studied. In comparing the relative miscibility of various styrene derivative copolymers with PVME, the conclusions drawn should be unaffected by any minor errors due to the differences in the molecular-weight distributions.

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