Electron beam irradiation of polystyrene–poly(vinyl methyl ether) blends

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The gelation behaviour of a series of polystyrene (PS)–poly(vinyl methyl ether) (PVME) blends that had been exposed to electron beam radiation was determined. The gel fraction produced by electron beam irradiation of this blend was determined as a function of dose, blend composition and morphology. The effect of morphology was examined by irradiating miscible blends and blends that had been phase separated by spinodal decomposition. The results indicate that PS does not offer any protection from radiation crosslinking in the miscible blends. In fact, the addition of a small amount of PVME to pure PS greatly increased the gel content, suggesting that a significant amount of grafting is occurring between the blend components. Phase separation of these blends has been shown to significantly influence the effect of blend composition on the gel content, primarily by altering the localized composition of the blend.

(Keywords: electron beam irradiation; gelation behaviour; blends)

INTRODUCTION

Polystyrene (PS) and poly(vinyl methyl ether) (PVME) are a rather unique pair of polymers in that they are chemically dissimilar and also dissimilar in their response to irradiation, yet they typically display compatibility over the entire composition range at room temperature. This combination of dissimilarity and compatibility provides the necessary prerequisites for a unique and informative radiation study, which is the focus of this work. Irradiation of a miscible polymer blend comprised of chemically different components should display some interesting behaviour since some type of intermolecular energy transfer is expected to occur. As the use of electron beam irradiation continues to grow industrially, particularly in the area of coating and packaging films, the potential of using compatible blends is of interest with respect to unique properties gained by such systems. Since PS and PVME have significantly different sensitivities to radiation-induced crosslinking, an analysis of the crosslinking behaviour of PS–PVME blends is of interest. The work presented here considers the effect of dose, blend composition and state of miscibility on the gel content produced by electron beam irradiation of PS–PVME blends. It should be stressed that the results presented here are initial findings and additional work is necessary to elucidate information concerning the specific chemistry and kinetic behaviour that is occurring in these systems. To the authors' knowledge, this is the first detailed report of the response of PS–PVME to electron beam radiation exposure. However, Briber and Bauer[1] have reported on the effects of gamma radiation crosslinking on the phase behaviour of deuterated PS–PVME blends. It was reported that a significant amount of grafting occurred between the blend components, but the main focus of their study was the effects of the presence of crosslinks on the phase separation behaviour of deuterated PS–PVME blends.

Since the state of miscibility is a consideration in this radiation study, the phase behaviour of PS–PVME blends will first be reviewed briefly. The phase behaviour of this particular blend has already been studied extensively. *Figure 1* displays a phase diagram of a PS–PVME system that was determined by Nishi *et al.*[2]. As shown, PS–PVME blends display lower critical solution temperature (*LCST*) behaviour. The blend depicted in *Figure 1* has a critical temperature and composition of about 85°C and 20 vol% PS, respectively. It should be noted, however, that the phase behaviour of PS–PVME blends is particularly dependent on the molecular weight of the components. Ubrich *et al.*[3] have reported on the effect of the molecular weight of the components on the phase behaviour of PS–PVME blends. It was shown that as the molecular weight of PS increases (at a constant PVME molecular weight) the critical point temperature and composition (in terms of wt% PS) both decrease. Conversely, as the molecular weight of PVME is increased (for a constant PS molecular weight) the critical point temperature decreases and composition (in terms of wt% PS) increases, as would be expected.

The work presented here involves the electron beam irradiation of a series of PS–PVME blends with varying composition. Both miscible and partially phase-separated morphologies were irradiated and subsequently characterized. Several different analytical techniques were employed to determine the effects of composition and morphology on the extent of gel formation as well as to determine some of the properties of the irradiated blends. This work has been carried out because it is of interest to examine the type of chemistry and gelation behaviour that result from blending a radiation-sensitive polymer (PVME) with a radiation-resistant polymer (PS). Again,

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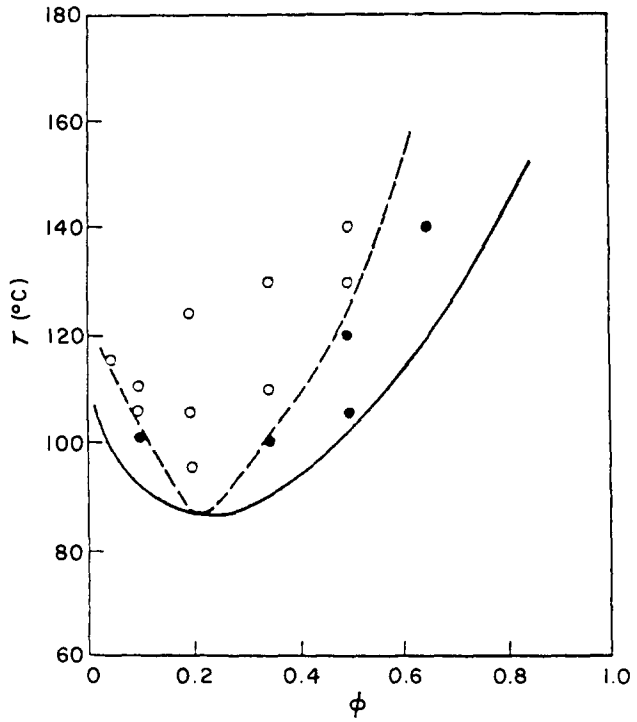

Figure 1 Phase diagram for a PS–PVME blend with PS and PVME M_ws of 210000 and 51500, respectively. Phase separation by: ●, nucleation and growth; ○, spinodal decomposition. (ϕ = PS volume fraction)[1]

since this blend is comprised of two chemically dissimilar polymers, it is expected that some intermolecular energy transfer process is likely to be displayed. This may result in the occurrence of rather interesting radiation chemistry and unique gelation behaviour, especially with regard to the influence of blend composition and morphology on these phenomena. However, at this time only information related to the effects of these variables on gel fraction has been obtained. Further analytical work would be necessary to understand the mechanisms of the radiation chemistry that is taking place.

EXPERIMENTAL

Materials and sample preparation

Both of the polymers used in this study are commercially available. The PS was obtained from Dow Chemical and has a weight average molecular weight (M_w) of 300000 and a polydispersity (M_w/M_n) of 2.5. The PVME was obtained from Dajac Labs and has $M_w = 60000$ and $M_w/M_n = 2.1$.

Films of the PS–PVME blends were formed by preparing ternary solutions of toluene, PS and PVME with various polymeric compositions (polymer wt:solvent wt = 1:9) which were subsequently cast onto Teflon sheets to form transparent films with a thickness of about 75 μm. The cast films were dried under ambient conditions for 24 h and then placed under 635 mmHg of vacuum at 80°C for at least 48 h to remove residual solvent. Blends with compositions of 95% and 100% PS were stored under vacuum at 120°C to remove residual solvent, since these films have glass transition temperatures (T_g) above 80°C.

All phase separations were carried out isothermally at 160°C for either 30 s or 2 min. Two slightly different procedures were employed. (1) Cast films and the Teflon substrate were placed in an oven maintained at 160°C (±2°C). After phase separation for the specified time, the films were quenched by holding them directly over a liquid nitrogen bath. Samples handled by this procedure were then quickly exposed to the electron beam (see section on radiation exposure) to ensure irradiation of a phase-separated morphology. (2) Cast films were removed from the Teflon substrate and sealed in aluminium d.s.c. pans. Phase separation was carried out in a d.s.c. furnace at 160°C (±0.5°C) for the specified time. Quenching was performed by quickly submerging the sealed aluminium pans in liquid nitrogen. Samples handled by this procedure were then quickly transferred back to the d.s.c. furnace (now at ambient temperature or below) and cooled to −60°C for d.s.c. evaluation (see section on thermal analysis).

Radiation exposure

All samples were exposed to electron beam radiation with an Energy Sciences CB150 electrocurtain operating at an accelerating voltage of 175 kV and a beam current of 6 mA. Radiation exposure was carried out under a purged nitrogen atmosphere with a residual oxygen content of 250–350 ppm. However, the films were exposed to air between consecutive passes under the electron beam. Samples irradiated to 100 Mrad were passed through the electrocurtain five times at a speed of 6 m min^{-1} and received a dose of 20 Mrad/pass. Samples irradiated to 50 Mrad were passed under the electron beam at a speed of 12 m min^{-1} and received a dose of 10 Mrad/pass. All samples were irradiated at ambient temperature, but it should be noted that some sample heating does occur for a short time (~1 s) as a result of radiation exposure.

Gel content determination

Gel contents of the irradiated blends were determined by extracting weighed samples in tetrahydrofuran (THF) with a Soxhlet extractor for at least 24 h. After extraction, the insoluble fraction was dried under 635 mmHg of vacuum at 80°C (120°C for samples with high PS content) for at least 24 h. Longer extraction or drying times did not result in any further weight reduction. The gel fractions were computed by dividing the weight of the insoluble fraction by the initial weight of the film. All gel fractions reported represent an average of either two or three extractions. The error associated with the reported values does not exceed ±4 gel% for all data points.

Thermal analysis

All d.s.c. measurements were made with a Seiko DSC 210 differential scanning calorimeter at a heating rate of 10°C min^{-1}. Samples were sealed in aluminium pans and cooled in the d.s.c. furnace from room temperature (or below) to the initial scanning temperature. The reported T_gs were taken as the midpoint between the baselines established before and after the glass transition.

Cloud point determination

Cloud point temperatures of the blends were determined by isothermal experiments and visual observation of turbidity in the films. For each composition, toluene solutions of the blend were cast onto glass slides and dried under the same conditions as described previously. A Linkam PR600 hot stage was used for heating the

samples. The following procedure was implemented to determine the cloud point temperature: (1) the glass slide was placed in the hot stage for 2 min at some predetermined temperature; (2) the slide was removed from the hot stage and visually inspected for turbidity in the film; (3) the temperature of the hot stage was increased by 5°C and the glass slide was returned to the hot stage for 2 min. This procedure was repeated until the film showed signs of turbidity. At this point, a fresh sample was placed in the hot stage at the highest temperature at which turbidity was not observed. The above procedure was repeated, but with an incremental temperature increase of 2°C. The cloud point was taken as the average of the temperatures just before and after turbidity was observed. Hence, the cloud point temperatures reported have an associated experimental error of ± 1°C. Repetition showed good reproducibility and was within the stated experimental error.

FTi.r. *analysis*

*FT*i.r. analysis of the insoluble gels obtained after Soxhlet extraction was performed to determine the composition of the crosslinked gels. Analysis was carried out using an M-Tec photoacoustic cell in conjunction with a Nicolet *FT*i.r. spectrometer. Relative weight fractions of PS and PVME in the gels were determined from the ratio of the absorbance peaks at 3027 and 2820 cm^{-1}, these peaks being relatively strong and independent with the former corresponding to the PS absorption and the latter corresponding to the PVME absorption. Prior to taking ratios, the absorbances were baseline corrected since variations in baseline absorbance may affect the ratio values. In order to estimate the composition of the gels (given in terms of wt% PVME), this ratio was compared to ratios obtained by *FT*i.r. analysis of the irradiated blends prior to extraction, and hence of known composition. Values given for extracted gel compositions were calculated by simple linear interpolation of the peak ratio of the extracted gel with the peak ratios of the irradiated blends of known composition (i.e. unextracted).

RESULTS AND DISCUSSION

Characterization of the unirradiated PS–PVME blends

Figure 2 depicts the glass transition behaviour of the PS–PVME blends under consideration in this study. It is apparent from this series of d.s.c. traces that there is not a linear relationship between the composition (wt% PVME) and the T_g of the blend. Also notice that there is a significant broadening of the T_g at intermediate compositions. *Figure 3* illustrates the dependence of T_g on the blend composition. As shown, the T_g decreases sharply as the PVME content is increased in the PS-rich blends, whereas the T_g of the PVME-rich blends is much less sensitive to composition. This composition dependence of the glass transition behaviour is significant in this study because it is important to realize the physical state of each blend during radiation exposure, since this may influence the extent of radiation-induced changes in the blends.

The cloud point curve for this series of PS–PVME blends is shown in *Figure 4*. This curve covers compositions ranging from 15 to 85 wt% PVME, which is the composition range of the phase-separated blends considered in this study. Based on comparison of this

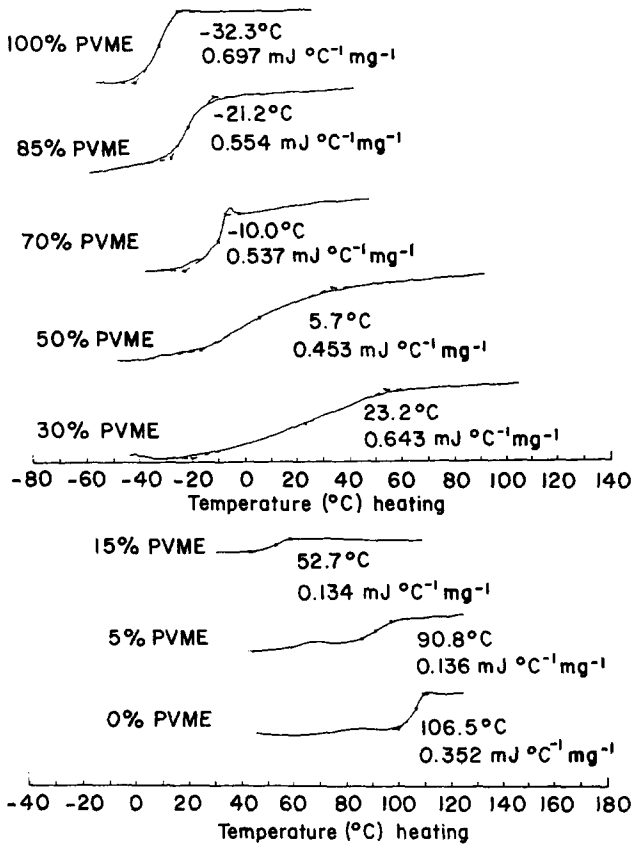

Figure 2 D.s.c. scans of the miscible PS–PVME blends

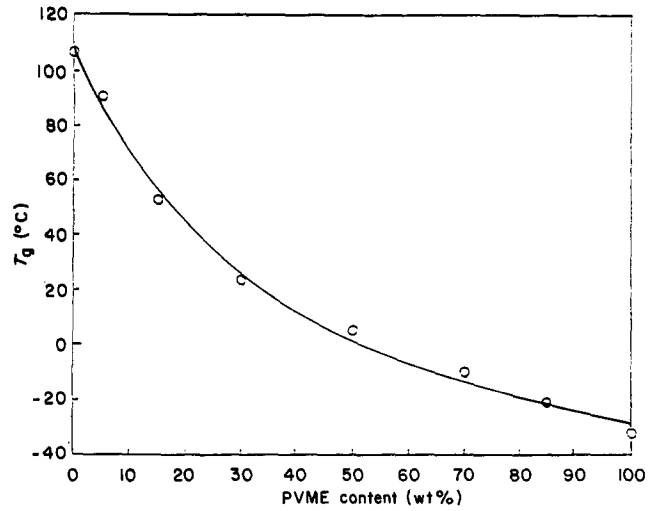

Figure 3 Plot of the glass transition temperature (T_g) of PS–PVME blends as a function of blend composition (wt%)

curve with those given in the literature (see *Figure 1*), this blend series displays *LCST* behaviour and has an apparent critical point near 115°C and at a composition in the range of 70–85 wt% PVME.

Figures 5 and *6* show the d.s.c. behaviour of the PS–PVME blends that have been isothermally phase separated at 160°C for 30 s and 2 min, respectively. As will be shown, phase separation proceeds by spinodal decomposition at 160°C for all the blends under consideration. Although two distinct T_gs are not evident in every sample, comparison of these d.s.c. scans with the d.s.c. scans of the miscible blends (see *Figure 2*) indicates that some phase separation has indeed occurred, as

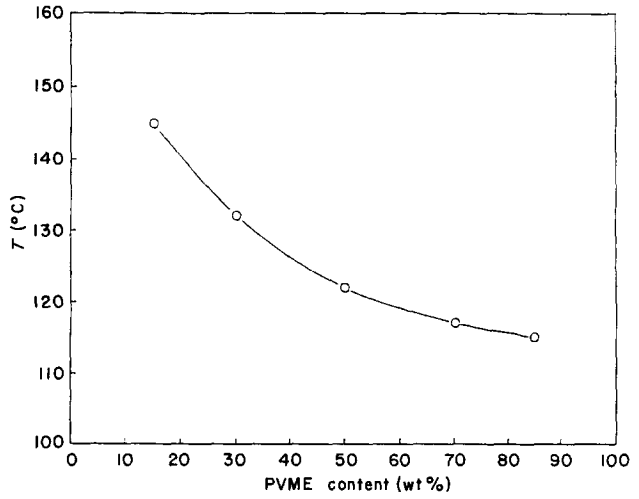

Figure 4 Cloud point curve of the PS–PVME blends

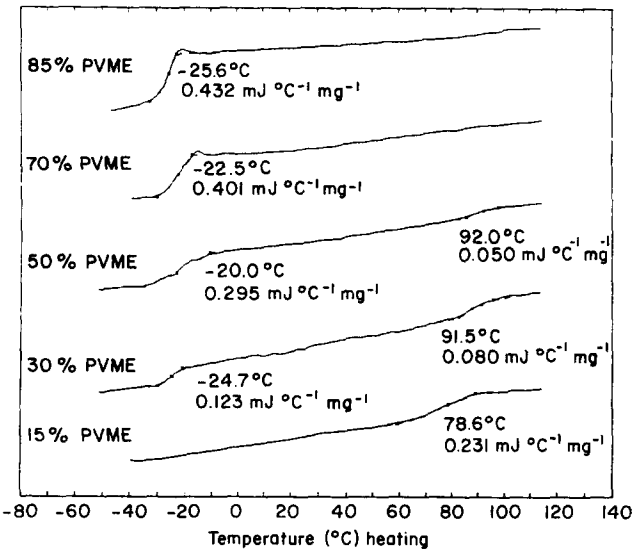

Figure 5 D.s.c. scans of PS–PVME blends that have been phase separated at 160°C for 30 s

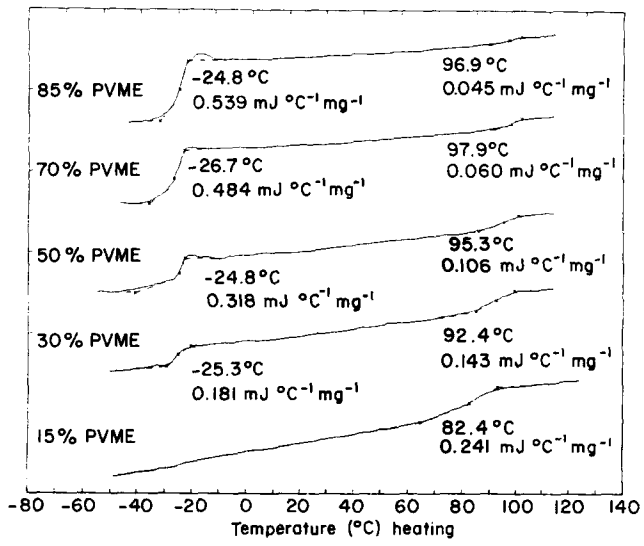

Figure 6 D.s.c. scans of PS–PVME blends that have been phase separated at 160°C for 2 min

evidenced by shifts in all the glass transitions. For example, the T_g of the 70 wt% PVME blend decreases by about 13°C after being held at 160°C for 30 s. In fact, after 30 s at 160°C, all blends except for 15 wt% PVME display a glass transition at about −23°C, indicative of the presence of a PVME-rich phase. The 15 wt% PVME blend also shows signs of phase separation; after 30 s at 160°C there is a 25°C increase in the T_g, indicative of the development of a PS-rich phase. However, comparison of *Figure 5* with *Figure 6* illustrates that phase separation is certainly not complete after 30 s at 160°C. After 2 min at 160°C, all blends except the 15 wt% PVME blend display two distinct glass transitions (see *Figure 6*); a lower T_g at about −25°C (indicating the presence of a PVME-rich phase) and a higher T_g at about 95°C (indicating the presence of a PS-rich phase). Furthermore, the glass transitions displayed in *Figure 6* at each composition are more distinct than those in *Figure 5*, as evidenced by greater ΔC_p values. It should also be noted that the ΔC_p values in both *Figures 5* and *6* are composition dependent. As the PVME content decreases, the ΔC_p of the low T_gs decreases steadily while the ΔC_p of the upper T_gs increases. This suggests that the fraction of the PVME-rich phase in the phase-separated blend decreases with decreasing PVME content while the PS-rich phase fraction increases, which is expected.

Figure 6 also illustrates that the compositions of the phases that develop upon phase separation are relatively insensitive to the overall blend composition and to the quench depth, ΔT_q (i.e. the difference between the phase separation temperature utilized and the cloud point temperature). Hence, the only significant difference among the blends depicted in *Figure 6* that has been detected by d.s.c. is the relative fraction of PVME-rich and PS-rich phases. The one exception to this is the 15 wt% PVME blend. As indicated by the cloud point curve (see *Figure 4*), this particular blend has the smallest quench depth, $\Delta T_q \approx 15$°C. Hence, the rate of phase separation will be the slowest in this blend. Given enough time, the phase separation would be expected to proceed to the point where the resulting glass transition behaviour will be similar to the other blends that have been phase separated for 2 min. This speculation is made because there is experimental evidence that all the blends considered in this study phase separate by spinodal decomposition at 160°C. More specifically, spinodal decomposition is characterized by the spontaneous formation of separate phases that undergo changes in composition with time. *Figures 2*, *5* and *6* illustrate that the observed T_g of the 15 wt% PVME blend increases steadily with phase separation time (i.e. from 53 to 83°C in 2 min), indicating changes in the composition of the dominant phase, and hence the occurrence of spinodal decomposition. Since this particular blend has the smallest ΔT_q of the blend series, all the other blends must undergo spinodal decomposition at 160°C as well. Notice that there is some change in the T_gs (and hence phase composition) of all the blends with phase separation time, but it is most evident in the 15 wt% PVME blend because the rate of phase separation is slow enough that significant changes can be observed over the time-scale between 30 s and 2 min.

The rate of phase dissolution of the blends phase separated for 2 min has also been considered because a comparison will be made with the rate of phase dissolution of these blends after irradiation. *Figure 7*

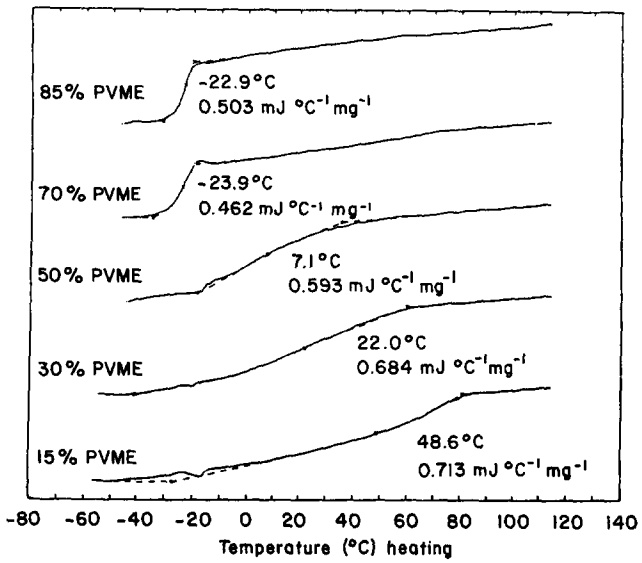

Figure 7 D.s.c. scans of PS–PVME blends that have been phase separated at 160°C for 2 min, then held at 100°C for 10 min

shows the d.s.c. behaviour of the blend series that has been phase separated for 2 min at 160°C, quenched in liquid nitrogen, and then held at 100°C for 10 min. As illustrated, the thermal behaviour of these blends is very similar (if not identical) to the thermal behaviour of the miscible blends (compare *Figure 7* with *Figure 2*), indicating that complete phase dissolution has occurred. The only exception is for the blend with 70 wt% PVME. This particular blend has a T_g of about -24°C, which is characteristic of the phase-separated state (see *Figure 5*). Nishi *et al.*[2] have reported that the rate of phase dissolution for blends with compositions very near the critical point is clearly much slower than for other blend compositions under the same dissolution conditions. This is believed to be the cause of the observed thermal behaviour of the 70 wt% PVME blend under consideration here. As mentioned previously, this composition is close to the anticipated critical point as indicated in the cloud point curve shown in *Figure 4*.

Characterization of irradiated PS–PVME miscible blends

Thermal analysis. *Figure 8* shows the glass transition behaviour of the miscible PS–PVME blends that have been irradiated to 100 Mrad. Comparison of these d.s.c. scans with those for the unirradiated blends (*Figure 2*) indicates that the thermal behaviour of this blend system is relatively unaffected by a radiation dose of 100 Mrad. There is some slight increase in the T_gs after irradiation (less than 5°C), which is likely the result of crosslinking, as will be addressed shortly.

Gel fraction analysis. *Figure 9* illustrates the effect of blend composition on the total gel fraction present in the blends after irradiation to 50 and 100 Mrad. As shown, a small increase in the PVME content of the PS-rich blends results in a drastic increase in the gel content. For instance, at a dose of 100 Mrad, the addition of only 5 wt% PVME to pure PS results in a change in gel fraction from about 1% to over 30%. This clearly indicates that a significant amount of radiation grafting is occurring between the PS and PVME. This may have technological implications in that PVME could be used as an additive in PS for increasing the crosslink density obtained by irradiation, while having relatively little effect on other properties. For instance, irradiating PS, which contains a small amount of PVME, would influence the rheological behaviour through branching, which may have practical applications in the production of oriented films, i.e. both the elongational and shear viscosity are distinctly influenced by long-chain branching.

At compositions of 50 wt% PVME and greater, there is relatively little change in the gel fraction created by exposure to 100 Mrad. This illustrates that a significant amount of grafting is occurring in the PVME-rich blends as well. This behaviour is quite surprising because PS is very resistant to radiation and is often used to afford radiation protection in polymeric materials due to the stabilizing nature of the aromatic groups[4]. It is generally thought that the presence of aromatic groups results in energy transfer to these moieties which act as energy sinks and produce a stabilizing effect. However, this is clearly not the case in this blend system. If PS were providing some radiation protection to these blends, the addition of PS to PVME would result in a significant decrease in the extent of crosslinking, which does not occur.

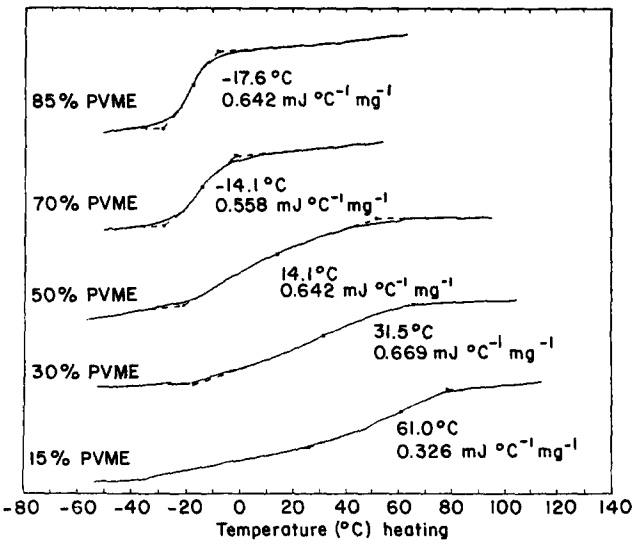

Figure 8 D.s.c. scans of miscible PS–PVME blends that have been irradiated to 100 Mrad

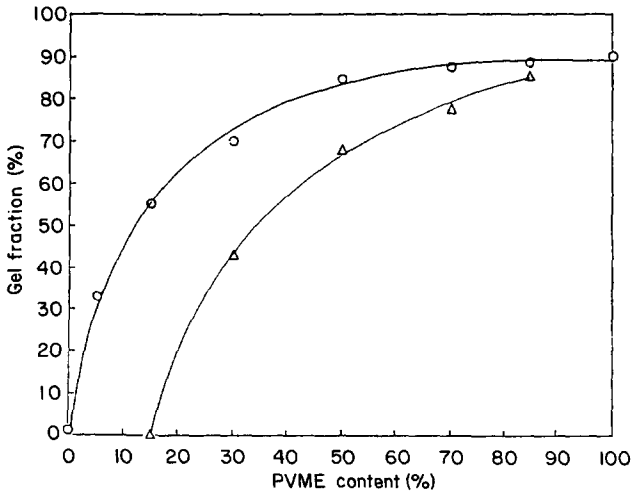

Figure 9 Plot of gel fraction *versus* composition of PS–PVME blends that have been irradiated to: △, 50 Mrad; ○, 100 Mrad

Since there are a number of different functional groups and hence a number of different excited states present in these blends after irradiation, some energy transfer is clearly occurring. The transfer of energy in irradiated systems is a downhill process; i.e. energy is transferred from excited states with high energy levels to excited states with low energy levels. Hence, it appears as though the excited state associated with the crosslinking of PVME is at a lower energy level than the excited state of the aromatic groups in PS, which would explain the behaviour displayed in *Figure 9*. Another possible explanation for this observed behaviour is that the aromatic groups in PS do act as energy traps, but then become active sites with which the PVME can react, resulting in radiation grafting between the two polymers. This is purely speculation since further experimentation and detailed chemical analysis are necessary to understand the radiation chemistry that is occurring in these systems. For example, n.m.r. spectroscopy of the irradiated blends may give information relating to the types and population of the various crosslinks present (i.e. PS–PS, PS–PVME and PVME–PVME crosslinks). However, this type of analysis has not yet been carried out for this initial study, which is focusing on key variables that affect the extent of gel formation in this specific two-component blend.

It is interesting to note that the T_g of the blend does not appear to influence strongly the extent of crosslinking. For example, a blend with 95 wt% PS has a T_g of about 90°C, which is about 15°C below the T_g of pure PS. However, after irradiation to 100 Mrad, the 95 wt% PS blend has a gel content of about 30%, as compared to 1% for pure PS. Although both blends are clearly in the glassy state, there is a significant difference in the gel content formed upon irradiation to the given dose.

Figure 9 also illustrates the effect of dose on the gel fraction formed in these miscible PS–PVME blends. Decreasing the dose from 100 to 50 Mrad appears to result in a horizontal shift in the gel–composition curve. In other words, the change in gel fraction with respect to dose is extremely composition dependent. This suggests that the *G*-values for crosslinking ($G(X)$) for this blend series are also composition dependent, which would be expected in a blend with components of very different radiation sensitivity. To illustrate this point, a Charlesby–Pinner plot was made for this blend system.

A Charlesby–Pinner plot is an analysis used for determining *G*-values for crosslinking systems that form gels in the dose range of interest. The Charlesby–Pinner plot is based on the following equation[5]:

$$S+S^{0.5}=\frac{G(S)}{2G(X)}+\frac{100N_a}{M_{w,i}G(X)mD} \quad (1)$$

where S = soluble fraction; $G(S)$ = *G*-value for chain scission; $G(X)$ = *G*-value for crosslinking; N_a = Avogadro's number; m = molecular weight of repeat unit; D = absorbed dose (Mrad); $M_{w,i}$ = initial weight average molecular weight. This relationship assumes an initially random molecular weight distribution (i.e. $M_w/M_n = 2.0$). Furthermore, it is assumed that the system under consideration is a single phase, homogeneous material. The Charlesby–Pinner plots for most compositions of the miscible PS–PVME blend under consideration are shown in *Figure 10*. It must be stressed that this is for *illustrative purposes only* as two data points were available for each plot, since only two dose levels were considered. However, as will be clear by comparison with a later figure, this approach is indeed informative. As shown in *Figure 10*, there is a steady decrease in slope with increasing PVME content in the blend. The slope in this region of the Charlesby–Pinner plot is inversely proportional to $G(X)$. Therefore, the $G(X)$ values of this blend series do indeed increase with increasing PVME content, as expected. Clearly it would be of interest to evaluate the actual $G(X)$ and $G(S)$ values as a function of blend composition for these systems. This would entail an analysis of gel content for a number of dose levels for each composition under consideration. However, for the purpose of this initial study, only two dose levels were evaluated. This is sufficient for establishing a striking contrast in relationship between $G(X)$ and blend composition for the miscible and phase-separated systems, as will be demonstrated.

Characterization of irradiated PS–PVME phase-separated blends

Gel fraction analysis. *Figure 11* illustrates the effect of dose and composition on the gel content in PS–PVME blends that have been phase separated for 2 min at 160°C

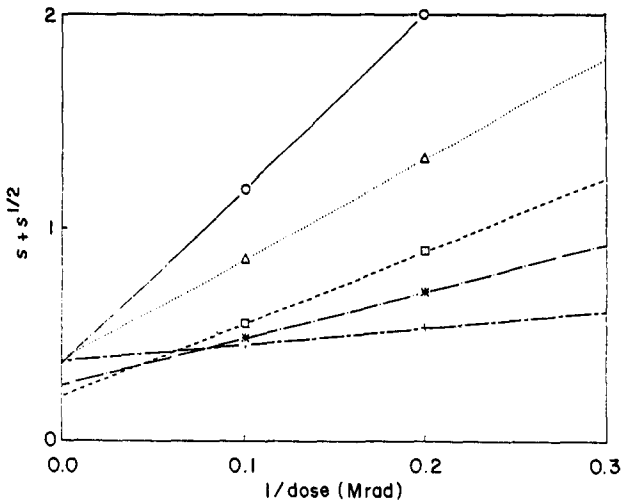

Figure 10 Charlesby–Pinner plots for the miscible PS–PVME blends: ○, 15% PVME; △, 30% PVME; □, 50% PVME; *, 70% PVME; +, 85% PVME (S = soluble fraction)

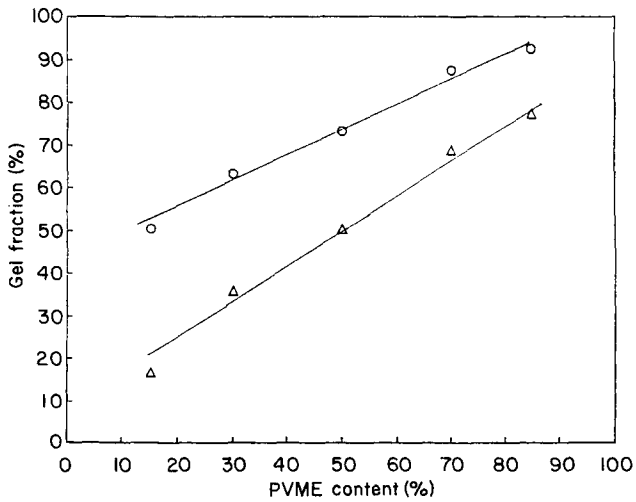

Figure 11 Plot of gel fraction *versus* composition of PS–PVME blends that have been phase separated for 2 min at 160°C prior to radiation exposure at: △, 50 Mrad; ○, 100 Mrad

prior to radiation exposure. As shown, these blends display a linear dependence of gel content on composition over the range of compositions under consideration. This is in striking contrast to the behaviour displayed by the miscible blends. It should be realized, however, that this linear behaviour cannot be extrapolated to compositions outside of the range under consideration, as will be explained. This linear dependence shows that there is a strictly additive effect of composition on the gel content formed. The reason for this behaviour can be related to the morphology that develops in these blends as a result of phase separation. Recall that the thermal behaviour of this blend series prior to irradiation suggested that phase separation resulted in the formation of a PVME-rich and a PS-rich phase. Furthermore, the composition of these phases was relatively independent of the overall blend composition and only the relative fractions of these phases varied over the composition range under consideration. In fact, there is a linear dependence of the ΔC_p values at the low-temperature glass transitions displayed in *Figure 6* on the PVME content, as shown in *Figure 12*. This suggests a linear dependence of the PVME-rich phase fraction on the overall blend composition. Hence, the linear increase in gel content with increasing wt% PVME is due to a linear increase in the PVME-rich phase fraction, which will govern gel formation since it is readily crosslinked as compared to the PS-rich phase. It should be stressed again that this is valid only within the composition range under consideration. At PVME contents below the stated range, one would expect to see the gel fraction drop to 0% as the wt% PVME decreases to 0%. On the other hand, at PVME concentrations above the stated range, one would expect the gel fraction to level off at some value as the wt% PVME is increased.

Recalling *Figure 11*, this also shows the effect of dose on gel content in these phase-separated blends. Increasing the dose from 50 to 100 Mrad results in an upward shift in the gel content–composition curve, as opposed to the horizontal shift that was observed in the miscible blends. Furthermore, the relative change in gel content with dose is relatively independent of composition. This suggests that the rate of crosslinking (i.e. $G(X)$) is independent of composition as well. To illustrate this point, a second Charlesby–Pinner plot was constructed for each composition in the same fashion as was done for the miscible blends described earlier. Again, this is for *illustrative purposes only*, especially in this case since the Charlesby–Pinner analysis was developed for homogeneous, single-phase materials. However, the sloping region in the Charlesby–Pinner plot should still give an indication of the relative overall $G(X)$ values in these blends, which is sufficient for comparative purposes. The Charlesby–Pinner plots for this series of phase-separated blends are shown in *Figure 13*. As shown, the slopes in this series of plots are relatively constant over the composition range under consideration, indicating that $G(X)$ is indeed independent of composition. Again, this contrasts with the behaviour of the miscible blends. Since the composition of the highly crosslinkable phase (PVME-rich phase) is independent of overall blend composition, a constant $G(X)$ value for this series should not be surprising and indeed is expected.

Figure 14 illustrates the effect of phase separation time on the gel content–composition curve for a dose of

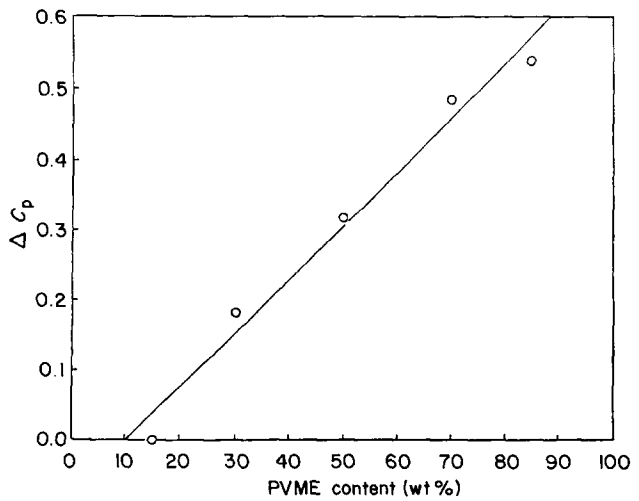

Figure 12 Plot of the ΔC_p values *versus* blend composition for the glass transitions of the PVME-rich phase displayed by the phase-separated blends in *Figure 6*

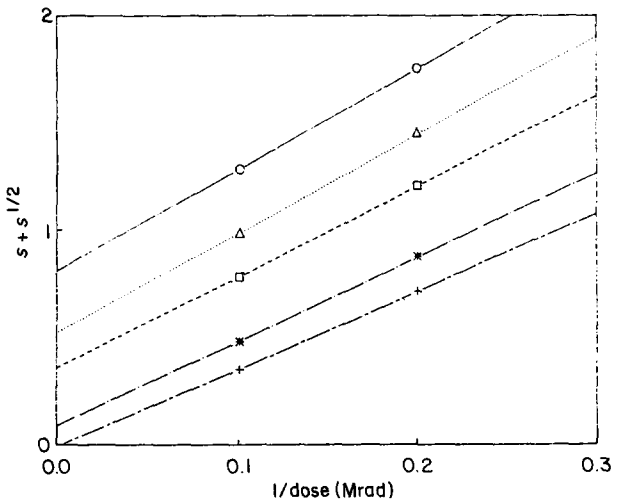

Figure 13 Charlesby–Pinner plots of the PS–PVME blends that have been phase separated at 160°C for 2 min: ○, 15% PVME; △, 30% PVME; □, 50% PVME; *, 70% PVME; +, 85% PVME (S = soluble fraction)

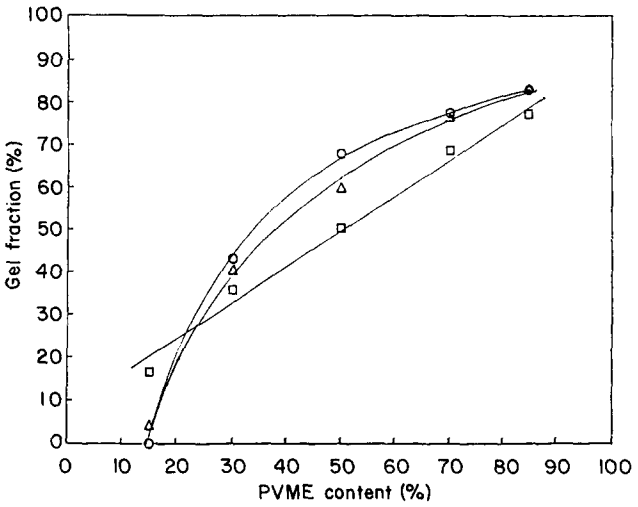

Figure 14 Plots of gel fraction *versus* composition of PS–PVME blends that have been irradiated to 50 Mrad after phase separation at 160°C for: ○, 0 min; △, 0.5 min; □, 2 min

50 Mrad. As shown, the gel content–composition curve is transformed from a non-linear to a linear curve as the phase separation time is increased. Furthermore, the change in gel content with phase separation time is composition dependent. At all compositions (except 15 wt% PVME), increasing the phase separation time results in a decrease in gel content, and this decrease is greatest at a blend composition of 50 wt% PVME. This behaviour must clearly be related to the relative $G(X)$ values of the miscible blend, the PVME-rich phase, the PS-rich phase and the relative concentrations of the latter two phases in the phase-separated blend. For instance, at a composition of 85 wt% PVME, phase separation results in the formation of one phase with a $G(X)$ value similar to that of the miscible blend and another phase with a relatively small $G(X)$ value. However, the fraction of the low $G(X)$ phase is fairly small, so there is only a small decrease in the gel content relative to the miscible blend. As the PVME content is decreased, the fraction of this low $G(X)$ phase increases, resulting in a larger decrease in gel content as a function of phase-separation time. This trend reverses at low PVME concentrations because the $G(X)$ of the miscible blend becomes sufficiently small that phase separation results in the development of a phase with a comparatively high $G(X)$, causing an increase in gel content with phase-separation time. This behaviour is displayed by the 15 wt% PVME blend, where phase separation results in an increase in gel content from 0 to about 15%.

Thermal analysis. *Figure 15* shows the d.s.c. behaviour of the phase-separated blends (for 2 min at 160°C) that have been exposed to a 100 Mrad dose. Comparison of these d.s.c. scans with those for the unirradiated blends indicates very similar thermal behaviour between these two blend series at low temperatures. However, it is evident that the upper glass transition of the irradiated blends is very broad and not as distinct as the corresponding glass transition of the unirradiated blends. It should be noted that these two blend series have slightly different thermal histories. The unirradiated blends were quenched from 160°C and placed immediately in the d.s.c. furnace for analysis. The irradiated blends were quenched

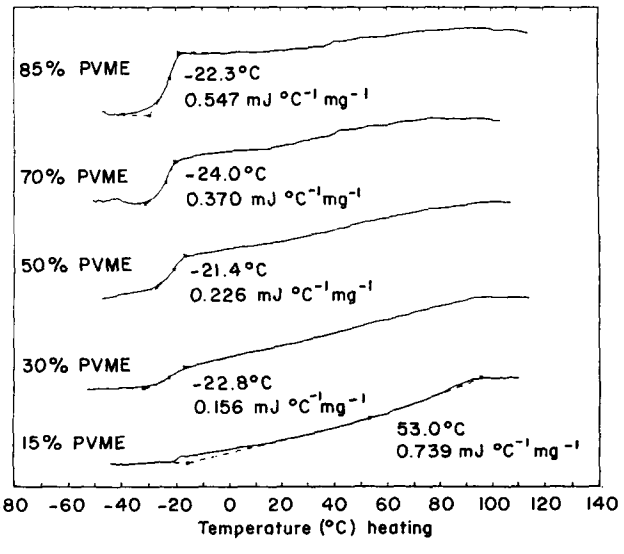

Figure 15 D.s.c. scans of PS–PVME blends that have been phase separated at 160°C for 2 min followed by irradiation to 100 Mrad

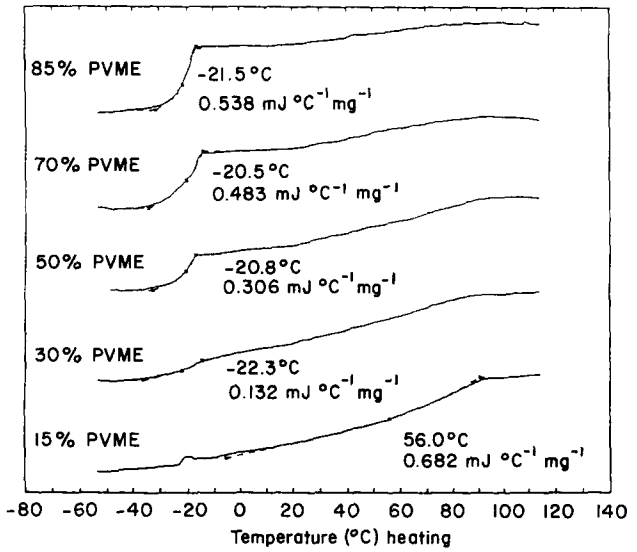

Figure 16 D.s.c. scans of PS–PVME blends that have been phase separated at 160°C for 2 min, irradiated to 100 Mrad, and then held at 100°C for 10 min

from 160°C, prepared for radiation exposure at room temperature, which took about 5 min, exposed to the electron beam and then analysed by d.s.c. Hence, the smearing of the upper glass transition could be the result of exposure to room temperature for a period of time or a result of radiation exposure. D.s.c. analysis of the 50 wt% PVME blend just before radiation exposure confirmed the former possibility, as it displayed exactly the same thermal behaviour after irradiation. This is of little consequence, however, since these blends were still phase separated during irradiation, as evidenced by film turbidity and the presence of a low T_g, even though the presence of a distinct PS-rich phase is not clearly displayed by d.s.c.

The phase stability of these irradiated, phase-separated blends was analysed by the same method as described for the unirradiated blends. Recall that this involved holding the blends at 100°C for 10 min and then performing the d.s.c. analysis. The results of this experiment for the irradiated blends are shown in *Figure 16*. Comparison of this figure with *Figure 15* shows no significant differences in the thermal behaviour of this blend series, indicating that no phase dissolution occurred in 10 min at 100°C. Recall that most of the unirradiated blends became completely miscible under these same conditions. Hence, radiation crosslinking of phase-separated PS–PVME blends by a 100 Mrad dose greatly enhances the phase stability of this system, which is certainly of significance with respect to thermal utility.

FT*i.r. analysis of gel fractions.* In addition to the analysis of the blends that has been described, an analysis of the insoluble gel fractions was undertaken to obtain more information on the gelation behaviour of electron beam irradiated PS–PVME blends. Specifically, *FT*i.r. analysis of the insoluble fractions obtained after Soxhlet extraction was performed to estimate their composition (in terms of wt% PVME) as a function of initial blend composition and morphology (i.e. homogeneous *versus* phase-separated states). This analysis entailed measuring two absorbance peaks of the gel which were characteristic of PS and PVME respectively, and then calculating the

Table 1 Summary of *FT*i.r. analysis of the irradiated blends and corresponding extracted gels

Blend composition (wt% PS–wt% PVME)	Peak ratio[a]	Peak ratio[b]	Peak ratio[c]
85–15	0.24	0.45	0.54
70–30	0.80	0.73	0.90
50–50	2.04	1.25	1.50
30–70	2.68	2.63	2.17
15–85	4.03	3.85	3.53

[a] 2820 cm^{-1}/3027 cm^{-1} ratio of unextracted blend
[b] 2820 cm^{-1}/3027 cm^{-1} ratio of extracted blend
[c] 2820 cm^{-1}/3027 cm^{-1} ratio of extracted blend that has been phase separated for 2 min at 160°C prior to irradiation

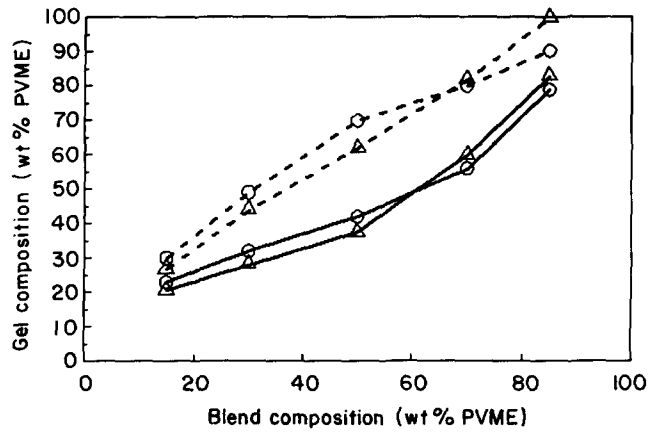

Figure 17 Plots of actual (——) and maximum possible (– – –) gel composition *versus* blend composition for homogeneous (△) and phase-separated blends (2 min at 160°C) (○) as determined by *FT*i.r. analysis

ratio of the two absorbances. This ratio was then compared to the ratio of the same absorbance peaks in the blend prior to extraction, through which a composition for the gel fraction was obtained (see Experimental section for details). A summary of the calculated ratios is given in *Table 1*. As calculated, the ratio is proportional to the weight fraction of PVME in the sample. The extracted gel compositions calculated from the ratios given in *Table 1* are plotted as a function of the original blend composition in *Figure 17*. The gel composition that would result if all of the PVME originally present in the blend were incorporated into the gel is also plotted in *Figure 17* as a function of blend composition. These values were obtained by simply dividing the wt% PVME of the original blend by the wt% gel determined by extraction after irradiation. Notice that this plot is linear for the miscible blends over the entire blend composition range under consideration. On the other hand, the phase-separated blends display two linear regions with a slope change occurring at 50 wt% PVME. Comparison of these maximum gel compositions (in terms of wt% PVME) with the actual gel compositions gives an indication of the fraction of PVME present in the blend that is incorporated into the crosslinked gel. Notice that for the miscible blends the greatest extent of PVME incorporation in the gel occurs at the lowest blend composition and decreases as the blend composition is increased to 50 wt% PVME. Above this value, the fraction of PVME incorporated into the gel becomes relatively constant (as evidenced by the nearly parallel lines in *Figure 17*). In contrast, the fraction of PVME incorporated into the gel in the phase-separated blends is greatest at both low and high wt% PVME blend compositions and decreases as intermediate blend compositions are approached.

Several other observations should be noted from *Figure 17*. Initially, there is a linear increase in the wt% PVME in the gel fraction with increasing wt% PVME in the blend, with a discontinuity in this linear relationship occurring at a blend composition of about 50 wt% PVME in the homogeneous blend. Hence, this linear relationship between PVME content in the gel and PVME content in the blend is dependent on which component is predominating in the blend. Notice that the discontinuity occurs at about 70 wt% PVME for the phase-separated blend. The reasons for this are not entirely clear, as one may expect no discontinuity for the phase-separated blend since it has been established that the localized compositions in these blends are independent of the overall blend composition. Second, for any blend composition, there is less than a 5 wt% PVME difference in gel compositions between the homogeneous and phase-separated blends. This seems a little surprising, as one might expect that phase separation would have a significant effect on the gel composition and its dependence on blend composition, since it has been established that phase separation influences the relationship between gel fraction and overall blend composition (see *Figure 14*). Clearly, to understand the cause for this similarity in behaviour would require a more detailed study regarding the mechanisms of localized radiation chemistry. For example, a determination of the relative $G(X)$ values for crosslinking PS–PS, PVME–PVME and PS–PVME in both the homogeneous and phase-separated blends would be extremely useful in understanding the phenomenon that has just been described. However, this would require considerably more analytical work and is beyond the scope of these initial findings. Such studies on this blend, or other miscible blends having variations in their response to irradiation, will be of future interest as the technology of electron beam processing grows in importance.

CONCLUSIONS

This study has illustrated the effects of dose, blend composition and morphology on the gel content and thermal behaviour of a series of PS–PVME blends exposed to electron beam radiation. It was shown that the addition of small amounts of PVME to pure PS significantly increases the gel fraction obtained after irradiation, which could have technological implications. On the other hand, relatively large amounts of PS must be added to pure PVME in order to influence the gel content. The extent of phase separation was shown to have a striking effect on the response of this blend system to radiation exposure, as determined by gel fraction measurements. It was suggested that the extent of phase separation influenced the composition and dose dependence of gel formation through changes in localized composition of the blends, although phase separation seemed to have little effect on the gel composition. Although exact values were not determined, changes in localized composition obviously affected the $G(X)$ in these systems since PVME was shown to crosslink readily while PS was quite resistant to radiation crosslinking under

the conditions employed. It was also shown that irradiation of the phase-separated blends drastically slowed the rate of phase dissolution at 100°C, while having little effect on the glass transition behaviour of this system. Clearly, extensive analytical work focusing on the specific radiation chemistry occurring in these systems is necessary to fully understand the phenomenon that has been described here. However, these initial findings have demonstrated the potential technological importance of electron beam processing of PS–PVME blends and will hopefully provide a basis for future work on the irradiation of polymer blends in general.

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