Excimer fluorescence study on the miscibility of poly(vinyl methyl ether) and styrene–butadiene–styrene triblock copolymer

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(Received 2 September 1992; revised 5 March 1993)

The excimer fluorescence of a triblock copolymer, styrene–butadiene–styrene (SBS) containing 48 wt% polystyrene was used to investigate its miscibility with poly(vinyl methyl ether) (PVME). The excimer-to-monomer emission intensity ratio I_M/I_E can be used as a sensitive probe to determine the miscibility level in SBS/PVME blends: I_M/I_E is a function of PVME concentration, and reaches a maximum when the blend contains 60% PVME. The cloud point curve determined by light scattering shows a pseudo upper critical solution temperature diagram, which can be attributed to the effect of PB segments in SBS. The thermally induced phase separation of SBS/PVME blends can be observed by measuring I_M/I_E, and the phase dissolution process was followed by measuring I_M/I_E at different times.

(Keywords: excimer; fluorescence; copolymer)

INTRODUCTION

Polymer–polymer miscibility has aroused much interest in recent years, especially for amorphous polymer blends because of the relative ease with which material properties may be modified by physical means[1]. For homopolymer blends, it is difficult to produce blends with the desired properties by simple blending because of lack of adhesion between the component homopolymers. Therefore, corresponding block or graft copolymers are introduced to the blends to change the interface situation and achieve the desired combination of properties in the blends. Many fundamental studies have been carried out on the miscibility between homopolymers and corresponding block copolymers. In particular, there has been extensive research on ternary blends of homopolymers and block copolymers based on styrene and isoprene[2,3]. One important conclusion of this research is that the systems remain compatible in most compositions only when the molecular weights of the homopolymers are less than those of blocks of the same kind. This limits the solubilization of homopolymers with large molecular weights into the respective block copolymer microphases, which significantly affects the modification of the copolymers or the homopolymers.

Relatively few studies have paid attention to another type of blend incorporating block copolymers and homopolymers which are different chemically from all of the copolymer segments but can form miscible blends with one of the blocks in the copolymers[4,5]. For example, the homopolymer, H, could be poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), while the block, A, is polystyrene in styrene–butadiene block copolymers. In this case, miscible but unlike H and A structures are likely to involve an exothermic enthalpy of mixing that can be an important additional thermodynamic driving force for solubilization; while, for the well studied case of H = A, H is chemically identical to A, which amounts to the assumption that H and A mix athermally, for example H is polystyrene and A is polystyrene in styrene–butadiene block copolymers. On account of this, the amount of homopolymer that can be solubilized will increase greatly if H is different chemically from A.

Many methods have been used to probe blend miscibility; these include neutron[6], light and X-ray scattering[7], pulsed n.m.r. and electron microscopy[8,9]. There are different criteria for different methods to characterize polymer–polymer miscibility; each criterion has its own advantages and shortcomings. For example, the simplest is perhaps that of optical clarity, which is, however, useless if the difference of refractive index between the two phases is too small and when the phase structures are less than the order of the wavelength of the incident radiation. Differential scanning calorimetry (d.s.c.), on the other hand, only applies to pairs of polymers whose T_g values are reasonably separated. Furthermore, the sensitivity of different methods and the miscibility levels they detect are considerably different. None of the methods mentioned above provides detailed information on the segmental level or has the sensitivity to detect blend components at concentrations less than about 10%.

Owing to its intrinsic sensitivity, fluorescence spectroscopy is believed to have the sensitivity to detect small-scale phase separation and low-concentration miscibility. It has been shown that non-radiative energy transfer between fluorescent labels attached to the

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0032-3861/93/245016-04

polymers characterizes polymer miscibility on a scale of about 3 nm[10]. Another method utilizes excimer fluorescence from an aromatic vinyl polymer which is blended as a guest in a matrix of a non-fluorescent host polymer[11–14]. A critical feature of this method is the existence of 'excimer-forming sites', which are conformational structures between an excited and a ground-state fluorophore. It typically involves two aromatic rings lying approximately parallel to each other. Excimers may form either intermolecularly between rings in different chains or intramolecularly between non-adjacent rings. The fluorescence of the excimer is different from the structured vibrational progression of an isolated aromatic ring, or monomer. Experimentally, the ratio of excimer to monomer emission intensities, I_M/I_E, obtained under photostationary state conditions is used to characterize the interaction between guest and host polymers.

In this paper, the excimer fluorescence method is used to investigate the miscibility between poly(vinyl methyl ether) (PVME) and styrene–butadiene–styrene (SBS) triblock copolymers. Since polystyrene contains aromatic rings in its chains, it can act as the chromophore when blended as a guest in a matrix of the host polymer, PVME. It is well known that polystyrene (PS) can form miscible blends with PVME at all compositions, thus miscible but unlike segments involve an exothermic enthalpy of mixing. It is expected that the solubilization of PVME in PS domains would be much larger than that of PS homopolymer in PS domains. At the same time, light scattering is used to detect the miscible level, and the results are compared with the results of excimer fluorescence.

EXPERIMENTAL

The PVME used here is a commercial product of Polysciences Inc., the molecular weight of which, measured by gas permeation chromatography (g.p.c.), is $M_n = 37\,000$ and $M_w = 63\,000$, respectively. A special purification technique was adopted for the PVME. It was first dissolved in toluene, then activated carbon was added, the solution was shaken vigorously for several days, after which it was filtered. The filtered solution was precipitated several times from toluene into heptane in order to remove the small molecules in PVME. This technique was believed to reduce fluorescent impurities in the PVME by a factor of 10 (ref. 15).

SBS triblock copolymer was synthesized by anionic polymerization in our laboratory. It was purified by multiple precipitation from toluene into methanol. The molecular weight of SBS measured by g.p.c. is $M_n = 105\,000$ and $M_w = 128\,000$; it has been estimated to contain about 48% styrene by weight.

The PVME and SBS were weighed in the given proportions and added to toluene to produce a solution containing 3 wt% total polymer. The solutions stood for several days at room temperature and gave completely miscible clear liquids. The solid films for fluorescence study, about 10 μm thick, were prepared by casting from toluene solution onto quartz discs at room temperature in a dry atmosphere and then drying under vacuum at 333 K for at least 1 week to ensure removal of the casting solvent. Fluorescence spectra were recorded in a normal atmosphere using a Shimadzu Spectrofluorophotometer (Japan). The sample was excited at 260 nm in a front-face arrangement to minimize self-absorption; simple fluorescence intensities were measured at 280 nm (monomer) and 332 nm (excimer) where it is believed that there is no overlap of excimer and monomer bands[16]. Solid films for light scattering were prepared by casting from toluene solution at room temperature in a dry atmosphere. They were then dried under vacuum at 333 K for at least 1 week to remove the residual solvent. Light-scattering measurements were carried out using an automated laser-light-scattering photometer constructed at our laboratory, as shown in *Figure 1*. The details of the apparatus have been described elsewhere[17]. The scattering intensity of the sample was recorded with the detector at the scattering angle $2\theta = 45°$ as the sample temperature was raised at a speed of $2\ \mathrm{K\ min^{-1}}$. Below the cloud point, the films were transparent, the scattering intensity of the sample did not change as the temperature was raised. Once the temperature rose above the cloud point, the films became cloudy, and the scattered intensity increased steeply. In this way, the cloud points were determined, as shown in *Figure 2*.

RESULTS AND DISCUSSION

The fluorescence emission spectra of SBS, SBS/PVME blend (containing 5 wt% SBS), PS/PVME blend (containing 0.1 wt% PS) and PS homopolymer films are given in *Figure 3*. It can be seen that the spectrum of SBS/PVME is similar to that of PVME/PS blend. Both of them have monomer emissions with a maximum emission intensity at about 310 nm; this indicates that the block of polybutadiene does not affect the monomer

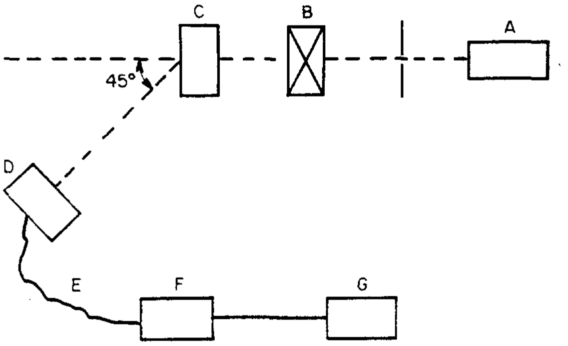

Figure 1 Schematic diagram showing optics of the automated light-scattering photometer. A: 2 mW He-Ne gas laser; B: polarization rotator; C: sample container; D: detector; E: light-transmitting fibre; F: amplifier; G: recorder

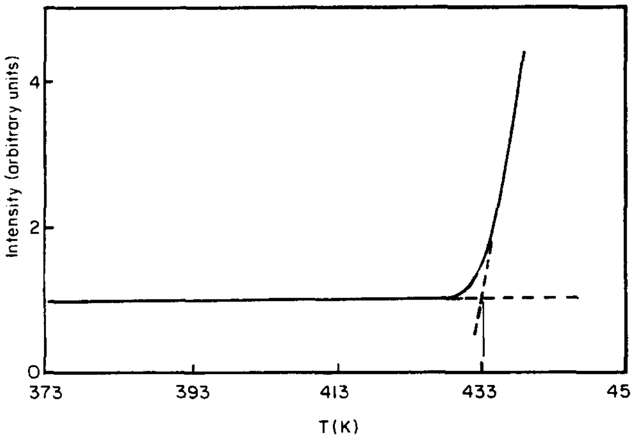

Figure 2 Cloud point temperature determined by light scattering

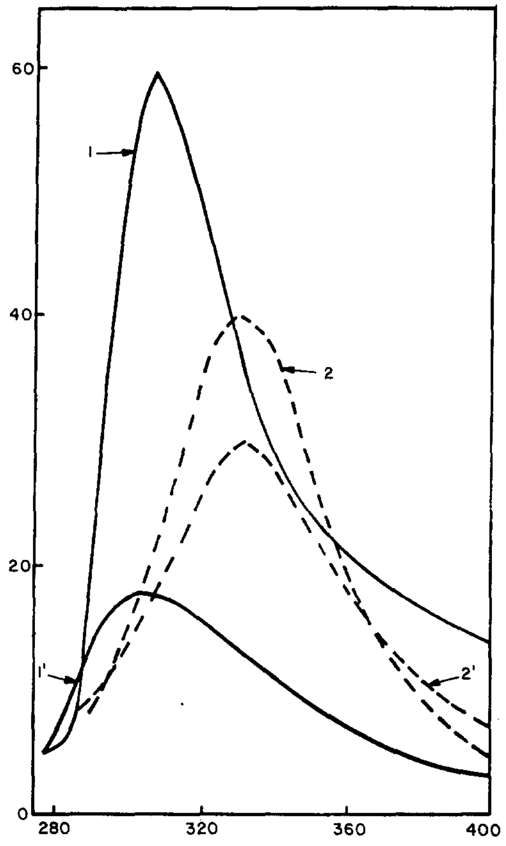

Figure 3 Emission spectra of SBS and PS in bulk and in SBS/PVME, PS/PVME blends. 1 (PS/PVME); 1' (SBS/PVME); 2 (PS); 2' (SBS)

emission properties of PS segments in SBS. On the other hand, SBS and PS films show similar emissions with a dominant excimer emission in the 330 nm region and no monomer emission was observed. This similarity indicates that the PB block does not alter the excimer emission properties of PS segments in SBS. In bulk SBS, PS domains and PB domains coexist, the packing of PS segments is just like that in PS homopolymers, the probability of excimer-forming sites existing is relatively large. The efficient energy migration from excited monomeric unit to excimer-forming sites leads to a dominant excimer emission. In contrast, for PS/PVME and SBS/PVME blends, the PS concentration is so small that the PS segments can 'sprawl' and disperse in the matrix of PVME, which favours the production of monomeric sites. Therefore, only monomeric emission is found in both cases.

The concentration dependence of I_M/I_E is shown in *Figure 4*, where the I_M/I_E value is plotted as a function of PVME concentration. The variation of I_M/I_E ratio with PVME concentration is rather interesting. The ratio increases significantly with PVME content if the blend contains <60 wt% PVME, and decreases slightly as PVME content increases further. When the blend contains about 60 wt% PVME, a maximum exists for the I_M/I_E ratio. It can be explained if PVME solubilizes into PS domains to form a miscible blend just like the PS/PVME blend, which strengthens the monomeric emission and weakens the excimer emission. As the amount of PVME increases in the blend, more and more PS segments sprawl and disperse in the matrix of PVME, which lowers the contact probability of benzene rings between different SBS molecules and in the same SBS molecule. Thus, the excimer-forming sites concentration decreases, and monomeric emission becomes more favourable. However, when the blend contains >60 wt% PVME, it is seen that the I_M/I_E ratio decreases with PVME content. This can only be attributed to the fact that less PVME solubilizes into PS domains than in the blend containing 60 wt% PVME. Although all the films investigated are optically transparent, the transmission electron microscopy (t.e.m.) photograph taken for a blend containing 70 wt% PVME does show some small phases of PVME[18]. Although at present we cannot assert that a unique miscible behaviour exists for blends such as SBS/PVME, solubilization of PVME in PS domains has a limit, beyond which not only does residual PVME not penetrate the PS domains, but also some PVME that can originally be solubilized into PS domains comes out. More detailed study is needed.

Figure 5 shows the cloud point curve determined by the light-scattering technique; it has the shape of an upper critical solution temperature (*UCST*) diagram, but the system is not an *UCST* system. Below the cloud point temperature the blend is clear, which designates one macroscopic phase system; just above the cloud point temperature, phase separation takes place and the films

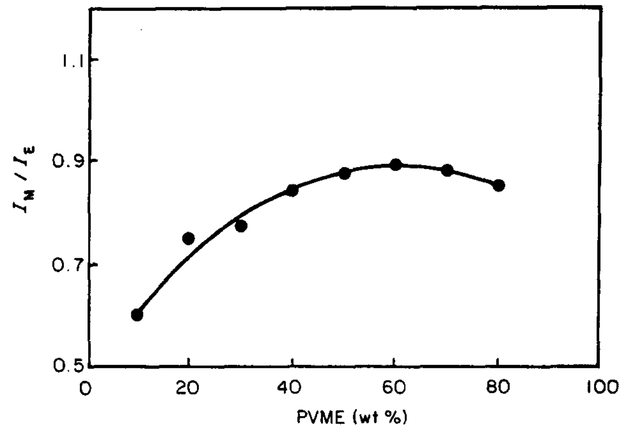

Figure 4 I_M/I_E ratio as a function of the PVME concentration in miscible SBS/PVME blend

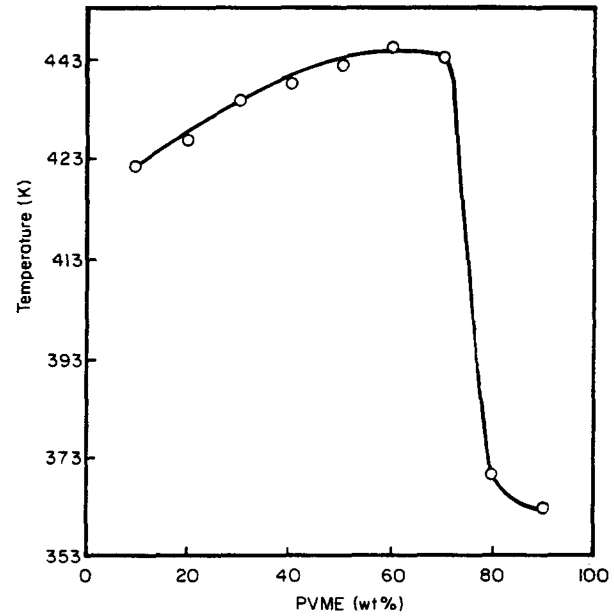

Figure 5 Phase-separation temperatures in SBS/PVME blends determined by light scattering

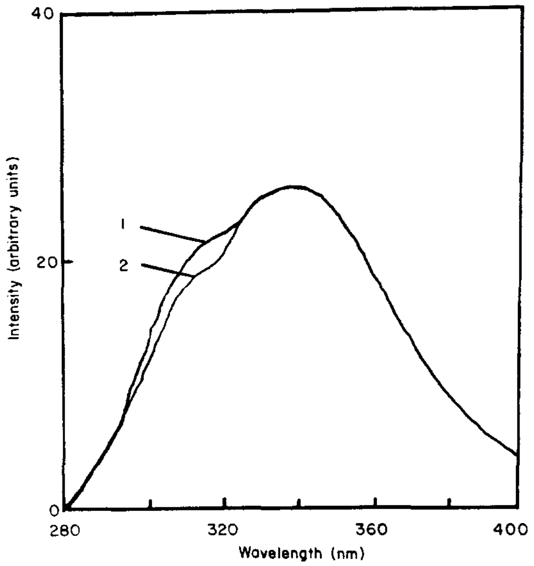

Figure 6 Emission spectra of the SBS/PVME blend containing 40/100 PVME before (1) and after (2) annealing at 443 K

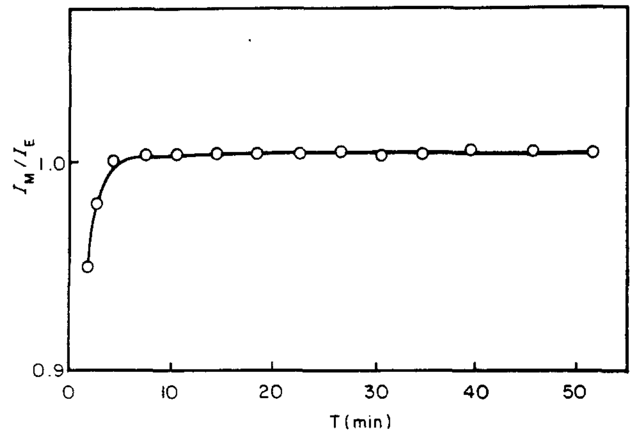

Figure 7 I_M/I_E ratio during phase dissolution for the SBS/PVME blend containing 80/100 PVME at 338 K

become cloudy showing a two-phase system. The unique cloud point curve can only be attributed to the effect of PB segments in SBS block copolymer, but how the PB segments affect the phase behaviour is still unknown; further studies on this point are in progress.

Figure 6 shows the emission spectra of a PVME/SBS blend containing 40 wt% PVME before and after annealing at 443 K; the spectra have been reconstructed in a computer, keeping the ratio I_M/I_E constant in order to make them clear. It can be seen that before annealing the sample exhibits a higher monomer emission than after annealing. This phenomenon indicates that a phase separation has taken place for this miscible blend during annealing. As phase separation proceeds, PVME is extruded from PS domains to form another phase in the blend and PS segments aggregate. This leads to a high concentration of excimer-forming sites. Thus, a dominant excimer emission appears.

Figure 7 shows the emission intensity ratio of monomer to excimer during the phase dissolution process. The film containing 80% PVME was first annealed at 413 K for 1 min, then it was put into a copper slit whose temperature was maintained at 338 K by a TB-85 Thermal Bath (Shimadzu). Gelles and Frank[19] used this method to study the kinetics of phase separation. As shown in *Figure 7*, I_M/I_E increases rapidly over a period of about 5 min, becoming constant after 10 min. Detailed results of the investigation of phase-dissolution kinetics will be presented elsewhere.

CONCLUSION

It is shown that excimer fluorescence is a sensitive technique to characterize the interaction between guest and host polymer. The intrinsic ratio I_M/I_E is related to the blend miscibility, because the excimer-forming site concentration depends on the extent of the guest polymer aggregation. If the blend is miscible, the guest polymer sprawls in the matrix of the host polymer, which lowers the excimer-forming site concentration, thereby leading to a decreased intensity of excimer emission. The technique shows that the blend is miscible at all compositions studied; the solubility of PVME in PS domains is much more than of PS homopolymer in PS domains, which indicates that the exothermal mixing enthalpy has an effect on the blend miscibility. A unique cloud point curve determined by light scattering is different from that for the PS/PVME blend and shows unusual phase behaviour of the SBS/PVME blend; this behaviour may be attributed to the effect of PB segments in SBS.

It is convenient to use intrinsic fluorescence to investigate blend miscibility since there is no need to attach fluorescent labels to the polymer, and therefore polymers containing aromatic rings in the main chain which exhibit intermolecular excimer emission are suitable for this kind of investigation. Because of its sensitivity, fluorescence is useful to detect blend properties that cannot be observed by other techniques. Some results about this aspect will be presented in another paper.

ACKNOWLEDGEMENT

This work was supported by the National Natural Science Foundation, China.

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