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Electronic energy transfer in compatible blends of poly(di-*n*-hexylsilane) and poly(methyl-*n*-propylsilane)

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Abstract

Blends of poly(methyl-*n*-propylsilane) (PMPrS) and poly(di-*n*-hexylsilane) (PDHS) were prepared in various compositions by solution mixing method. The blends were studied using differential scanning calorimetry, optical microscopy, fluorescence and UV spectroscopy. The blend samples were isothermally crystallized at temperatures in which only the PMPrS crystallized. The equilibrium melting point of PMPrS was estimated from the Hoffman–Weeks plots. Depression of equilibrium melting point of PMPrS with increasing PDHS content indicated some degree of miscibility. Fluorescence spectroscopic studies indicated that energy transfer occurs form PMPrS to PDHS. Comparison with an immiscible blend showed that energy transfer occurs only in miscible blends. Optical microscopy studies using crossed polarizers showed liquid crystalline mesophase in all the blends with PMPrS/PDHS = 90/10–0/100.

Keywords: Electronic energy transfer; PMPrS; PDHS

1. Introduction

Polysilanes have attracted considerable research and commercial interest in recent years owing to their useful electronic and optical properties [1–6] resulting from the conformation-dependent σ electron delocalization along the polymer backbone [7–9]. Several studies have been reported [1–3,10–23] on the spectroscopic investigations of various polysilanes with different lengths of alkyl or aryl side chains. Poly(di-*n*-hexylsilane) (PDHS) is one of the most extensively studied polysilanes. In the case of PDHS, which has an all-trans planar zig-zag conformation, a dramatic change in its u.v. absorption has been observed above the phase transition temperature [3,18]. PDHS exhibits strong fluorescence and energy transfer between chromophores [16,24]. It has been pointed out that most of the emission comes from the low energy chromophores even when the crystallinity is low and this is an indication of the occurrence of energy transfer from the disordered phase to the crystalline phase. It was suggested that the extended all-trans segments of the polymer backbone, which are associated with the crystallites, would effectively act as traps for the excitation energy of the polymer [16]. Poly(methyl-*n*-propylsilane) (PMPrS) is an asymmetric polysilane showing ordered all-trans planar zig-zag conformation in the crystalline phase [25,26].

There are few reports [27,28] on the blend of polysilanes with other conventional engineering polymers. It has been shown that a blend of a polysilane copolymer, polysilastyrene with polystyrene and polypropylene decreased surface resistance, increased hardness and provided some protection from sunlight to a significant extent to polystyrene and to a smaller extent to polypropylene [27]. Blending of poly(di-*n*-pentylsilane) with drawable UHMW-PE has shown that poly(di-*n*-pentylsilane) could be dispersed as nanometer-sized domains in the UHMW-PE matrix and afterwards cooriented by ultradrawing [28]. Blends of two polysilanes have not been reported.

On the other hand, intermolecular fluorescence energy transfer has successfully been used to study the miscibility of polymer blends. Polymers were labeled with fluorescence donor and acceptor and the mutual interpenetration in their blends was characterized by the non-radiative energy transfer between the fluorescent chromophores [29–33]. As the silicone main chains of polysilane give rise to strong fluorescence in the ultraviolet and visible region, polysilanes with different spectroscopic characteristics are capable of acting as fluorescence donor and acceptor in the miscible polysilane blends.

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In the present paper, we studied the compatibility of PDHS and PMPrS by differential scanning calorimetry (d.s.c.), u.v. and fluorescence spectroscopy. The thermal studies were used to evaluate the compatibility by analyzing the equilibrium melting points of the component polymers. Fluorescence spectroscopy was used to probe energy transfer from one component to the other resulting from the miscibility of the polysilane blends. The liquid crystalline nature of the blend samples was also investigated by observing the sample film under crossed polarizers.

2. Experimental

2.1. Materials and blend preparation

Polysilanes were prepared by Wurtz coupling of the corresponding dichlorosilane monomer with molten sodium in refluxing toluene for 2 h. Excess sodium was treated with 2-propanol. The mixture was washed many times with deionized water and the polymer was precipitated using 2-propanol. The polymer was dried in vacuum at 45°C. Different molecular weight fractions were separated by reprecipitation using toluene and 2-propanol as solvent and non-solvent respectively. The molecular weights of the polymers were determined by g.p.c. using polystyrene standards. The molecular weight of PMPrS used for the study was $M_w = 2.7 \times 10^4$ and those of PDHS and poly(-methyloctadecylsilane) (PMOdS) were 6.4×10^5 and 4.0×10^5 respectively. Polymers were dissolved in hexane and mixed in different predetermined weight proportions. The mixtures were then stirred well and the solvent was evaporated to get a well mixed blend sample.

2.2. D.s.c.

A Perkin Elmer model DSC7 differential scanning calorimeter was used for the thermal studies. The temperatures were calibrated with indium (m.p. = 156.6°C) and cyclohexane (m.p. = 6.54°C). Samples were isothermally crystallized at various crystallization temperatures under a nitrogen atmosphere. The isothermally crystallized samples were heated to 100°C at a rate of 5°C min^{-1}. They were held at 100°C for at least 10 min to ensure complete melting before cooling to the crystallization temperature.

2.3. U.v. and fluorescence spectroscopy

U.v. absorption spectra were obtained using a Shimadzu UV-2500PC u.v.–vis spectrophotometer. Fluorescence spectra were recorded on a Jasco FP777 spectrophotometer. Thin films of the samples were prepared by spin coating the solution on a quartz substrate. Measurements were done not only on the samples crystallized at 8°C for several minutes, but also on the samples heated to 80°C.

2.4. Optical microscopy

Preliminary investigations were carried out to study the compatibility of the blends by observing a thin film of the blend under an optical microscope. The blends of PMPrS and PDHS of various compositions were observed under crossed polarizers at various temperatures in order to study the liquid crystalline nature of the blend.

3. Results and discussion

Blends of many polysilanes such as PDHS, PMOdS, poly(di-*n*-butylsilane) (PDBS) and PMPrS were examined by observing a film of the blend under an optical microscope at various temperatures and compositions. Blends of PDHS/PMOdS PDBS/PMOdS, PMPrS/PMOdS showed distinct phase separation. Photomicrograph of blend of PDHS/PMOdS = 50/50 at room temperature is given as an example of a phase separated blend in Fig. 1a. As can be seen, there is a clear phase separation of the component polymers in the blend. Blends of PDHS/PDBS, PMPrS/PDBS and PMPrS/PDHS appeared to be compatible (although it is difficult to draw any conclusion from this observation, relative compatibility can be deduced). A photomicrograph of the blend of the PMPrS/PDHS = 50/50 combination is given in Fig. 1b. As can be seen from the figure, the blend of PMPrS and PDHS shows

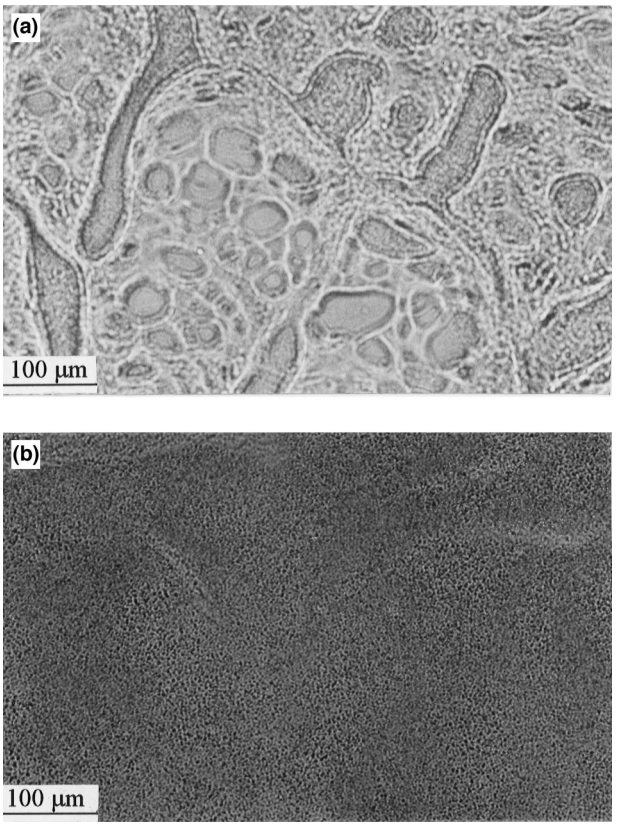

Fig. 1. Photomicrographs of (a) PDHS/PMOdS 50/50 blend and (b) PMPrS/PDHS 50/50 blend samples.

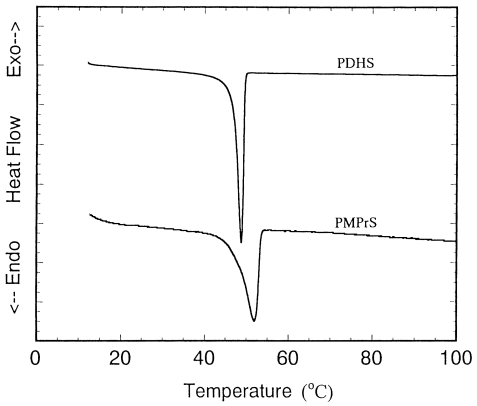

Fig. 2. D.s.c. thermograms of heating runs of PMPrS and PDHS.

a uniform dispersion, indicating some degree of compatibility. We selected PMPrS/PDHS blends for a detailed investigation by thermal and spectroscopic methods. Limited investigations were also carried out on the blends of PHDS/PMOdS for comparison purposes.

3.1. D.s.c.

D.s.c. thermograms of heating runs of PDHS and PMPrS samples are shown in Fig. 2. PMPrS shows a melting endotherm with a peak temperature of 51.85°C and PDHS shows an order–disorder transition at 48.4°C. Thermograms of heating and cooling runs of the blend of PMPrS/PDHS = 50/50 are given in Fig. 3. The thermogram of the heating run shows a single broad endotherm with a peak temperature at 45.75°C. The cooling run shows two crystallization peaks at 34.80°C and at 20.70°C. The appearance of two peaks shows that PMPrS and PDHS crystallize separately.

In polymer blends in which one of the components is crystallizable, miscibility of the system involves a decrease in the chemical potential of the blend components and this leads to a decrease in the equilibrium melting point of the crystallizable component. The melting point depression has been considered as a miscibility criterion in polymer blends.

The samples were isothermally crystallized at

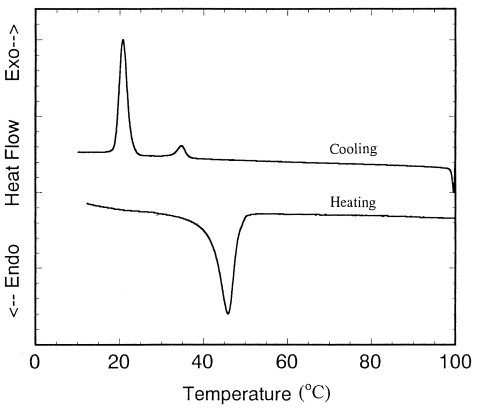

Fig. 3. D.s.c. thermograms of heating and cooling runs of the PMPrS/PDHS 50/50 blend sample.

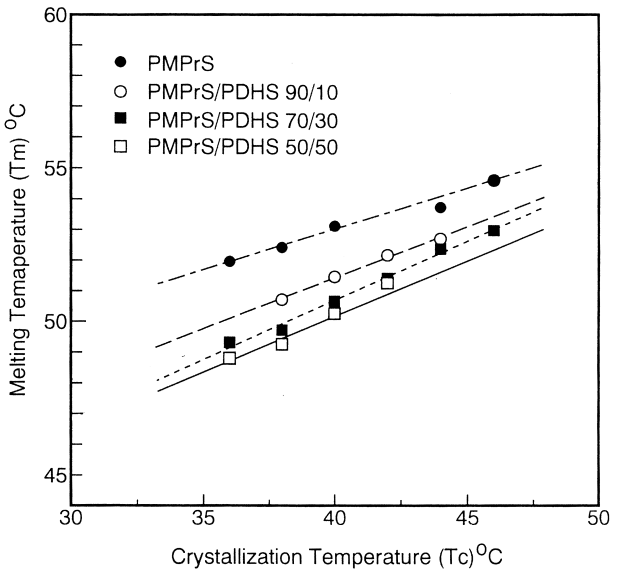

Fig. 4. Plot of melting temperature versus crystallization temperature for various blend samples.

temperatures in which only PMPrS crystallizes. The melting points are plotted against the crystallization temperatures (Fig. 4). In this case PDHS can be considered the non-crystallizable component in the blend. The melting point of PMPrS decreases with an increasing PDHS content. It has been reported that the apparent melting point depression in a blend can be due not only to thermodynamic factors, but also to kinetic factors [34]. These are related to variations in crystal morphology with blend composition. Kinetic effects can be discarded by using the equilibrium melting point, which can be estimated from the apparent melting point by the Hoffman–Weeks equation [35] as described in the literature [30]. The estimated values are plotted against the blend composition in Fig. 5. As can be seen, the melting

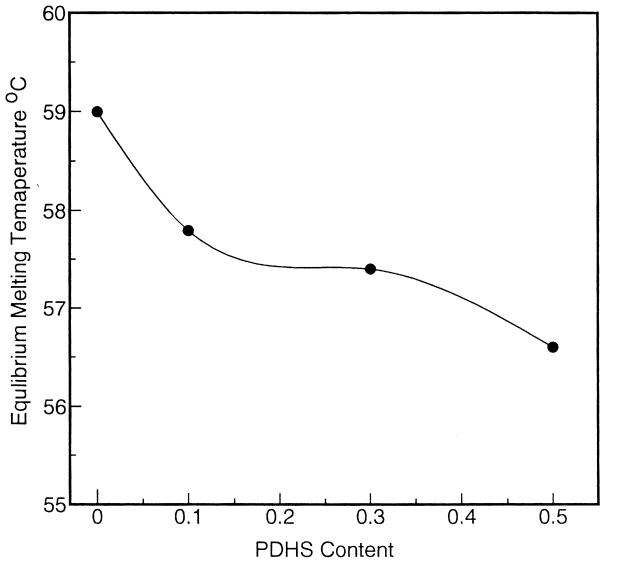

Fig. 5. Equilibrium melting temperature of PMPrS as a function of PDHS composition.

point of PMPrS decreases with an increasing PDHS content, indicating some degree of compatibility of the two components.

The thermodynamic aspect of the melting point depression was studied by estimating the polymer–polymer interaction parameter χ by using the equation of Nishi and Wang [36]:

$$\frac{1}{T_m} - \frac{1}{T_{mo}} + \frac{RV_2}{\Delta H_f V_1}\left[\frac{\ln \phi_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1}\right)\phi_1\right] = -\frac{RV_2}{\Delta H_f V_1}\chi_{12}\phi_1^2 \quad (1)$$

Here subscripts 1 and 2 refers to PDHS and PMPrS respectively, T_m is the equilibrium melting point of PMPrS in the blend, T_{mo} is the equilibrium melting point of the pure PMPrS. V is the molar volume of the polymer repeat unit (estimated from the unit cell dimensions obtained by X-ray diffraction studies); ϕ is the volume fraction of the component in the blend; m is the degree of polymerization; ΔH_f is the heat of fusion of the perfect crystal of PMPrS. ΔH_f of PMPrS was estimated as follows: the fraction of crystalline and amorphous (disordered) phases in the maximum crystallized PMPrS sample was estimated by resolving the corresponding band of the u.v. spectrum by assuming that the 330 nm band originates from the all-trans conformation in the crystal phase and the 300 nm band from the disordered phase. ΔH_f of the crystalline phase was then estimated from the measured value of heat of fusion of maximum crystallized PMPrS sample obtained using d.s.c. The heat of fusion of the crystalline fraction estimated using these values is 18 J g^{-1}. R in Eq. (1) is the gas constant and χ_{12} is the polymer–polymer interaction parameter which was estimated as being -0.044 and -0.02559 for the present blends of PMPrS/PDHS = 70/30 and 50/50 respectively. The negative value of interaction parameter indicates that the present blends are thermodynamically compatible in the composition range studied.

3.2. Liquid crystalline nature of the blends

It has been reported that PDHS [37] exists in a liquid crystalline mesophase above a temperature of 42°C and shows a hexagonal columnar symmetry, with columns formed of single polymer chains. It has also been reported that far from being all-trans, as in the low-temperature crystal, the backbone conformation in the high-temperature mesophase is presumably close to an all-gauche helical conformation [37].

Fig. 6a shows the photomicrograph of PDHS film taken under crossed polarizers at 55°C. The persistent birefringence of the PDHS film above its disorder temperature is clearly visible. This was reported [37] to be an indication of the existence of a liquid crystalline mesophase. The persistence of birefringence was observed up to a very high temperature of 200°C. In the case of PMPrS, the sample appeared birefringent at room temperature, indicating the

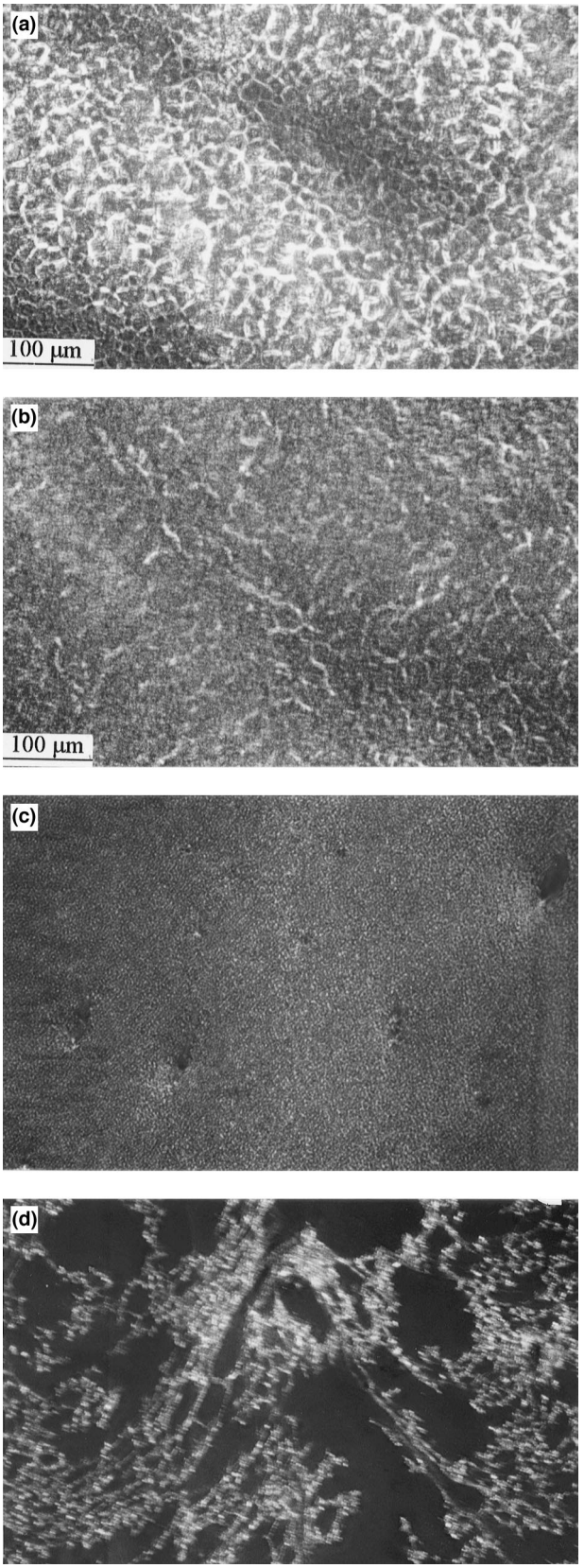

Fig. 6. Photomicrographs of blends films of (a) PDHS (b) PMPrS/PDHS 30/70 (c) PMPrS/PDHS 70/30 (d) PMPrS/PDHS 90/10 under crossed polarizers at 55°C.

presence of crystals which disappear when heated above 40°C without entering into a liquid crystalline mesophase. Since one of the components in the blend is PDHS, we have examined the liquid crystalline nature of the blend. Fig. 6b–d shows photomicrographs of some of the blend samples. The sample with PMPrS/PDHS = 30/70 (Fig. 6b) is also birefringent, although PMPrS becomes completely isotropic above 50°C. A noteworthy observation is that the PDHS component is uniformly distributed. Also, the PMPrS-rich phase is not completely isotropic, indicating the existence of thoroughly mixed PDHS in PMPrS. The blend with more than 50% of PMPrS also shows very fine birefringent particles uniformly distributed in the PMPrS-rich phase (Fig. 6c). Here also the PMPrS-rich phase seems to be liquid crystalline. This observation clearly indicates that PMPrS and PDHS are compatible in these compositions. On the other hand, the 90/10 blend (Fig. 6d) shows a phase separation into a birefringent PDHS-rich phase and the isotropic PMPrS phase.

3.3. Spectroscopic studies on crystallized blend samples

Fig. 7. shows the u.v. absorption spectra for various blends crystallized by cooling at 8°C. As seen from Fig. 7, PMPrS and PDHS show their characteristic crystalline peaks at 328 nm and at 370 nm respectively. The disordered phase of PDHS appeared as a low intensity peak at 315 nm. The 328 nm band shows a marked shift towards the shorter wavelength side in the blend with PMPrS/PDHS = 90/10, indicating that the crystallinity of PMPrS is lowered by blending PDHS in PMPrS/PDHS = 90/10 blend. In the longer wavelength range, the 378 nm band of PDHS shifts towards the longer wavelength side with increasing PMPrS content, indicating the increase in the segment length of PDHS with an all-trans conformation.

It has been shown that the energy transfer occurs in PDHS from the disordered to the crystalline phase [16,24]. Klingensmith et al. [24] suggested that the polysilane chain is effectively separated into series of chromophores communicating by rapid energy transfer. Calculations suggested that these chromophores are all-trans segments separated by gauche links within which extensive σ-delocalization occurs [24]. The shortest trans segments are believed to be essentially non-fluorescent [38]. Solution experiments and calculations suggest that emission from longer all-trans segments results in a shift of the emission peak position to lower energy [39]. Despotopoulou et al. [16] showed that similar energy transfer phenomena also occur in the solid state. Fluorescence spectroscopic studies on PDHS thin and thick films showed that, in the case of thicker films, where crystalline and disordered phases coexist, most of the emission comes from the low energy chromophores in the crystalline phase even when the crystallinity is low [16]. This is an indication that the energy transfer occurs from the disordered to the crystalline phase. They have also observed a shift in the emission from the crystalline phase as the thickness of the film increased, presumably due to the presence of a large number of longer all-trans segments in the crystalline phase. In the present case we have examined the fluorescence spectra of various PMPrS/PDHS blends in order to check any energy transfer between the components.

Fig. 8 shows the emission spectra of various samples crystallized at 8°C when excited at 300 nm. The fluorescence intensity was normalized to 200 nm sample thickness. As seen from the figure, the PMPrS sample shows emission with a peak at around 352 nm, whereas the PDHS sample shows a peak at around 378 nm, and these are seen in the blends. Except for the PMPrS/PDHS = 90/10 sample, all samples show relatively stronger emission at 378 nm. This was observed even in the samples in which the composition of PMPrS is higher than the PDHS.

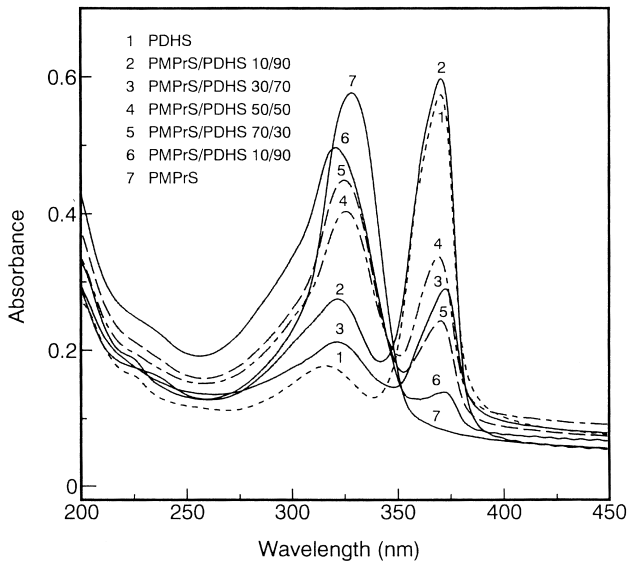

Fig. 7. U.v. spectra of various samples crystallized at 80°C.

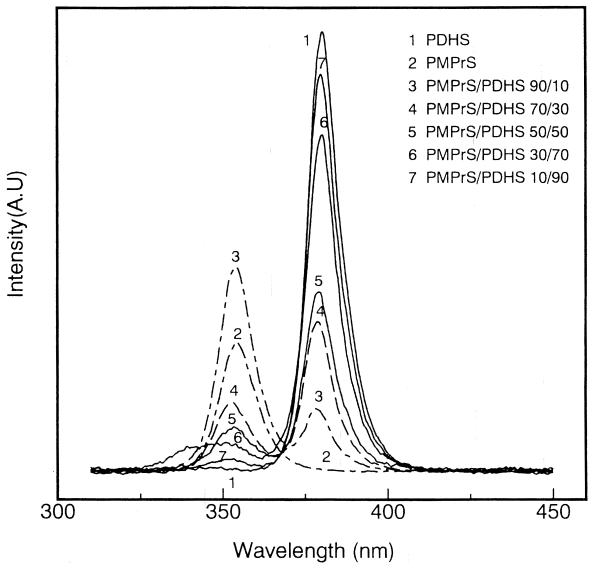

Fig. 8. Fluorescence emission spectra of various crystallized samples when excited at 300 nm (normalized to 200 nm sample thickness).

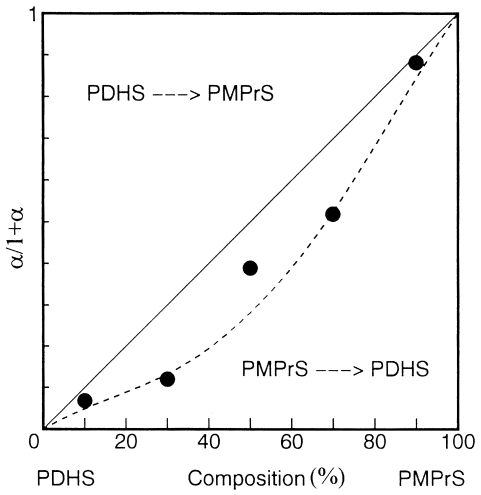

Fig. 9. Plot of $\alpha/1 + \alpha$ versus blend composition.

On the other hand, the fluorescence intensity at 352 nm decreased significantly in the blend samples with respect to the emission intensity of pure PMPrS, except for the PMPrS/PDHS = 90/10 blend. This indicates the energy transfer from PMPrS to PDHS.

In polysilanes the alkyl side chains influence strongly the backbone conformation. In the PMPrS synthesized by the Wurtz condensation reaction, the configuration of molecular chains is expected to be atactic. The irregularity of the configuration limits the stability and the length of the all-trans segments, whereas the long all-trans segments are stable in PDHS. Most of the excited energy is transferred from the shorter and/or twisted trans segments of PMPrS to the longer all-trans segments having a lower electronic energy level. In order to clarify the condition for energy transfer, we have plotted the quantity $\alpha/1 + \alpha$ against the blend composition, where α is the ratio of the intensity I of emission in the higher energy level (associated with PMPrS) to the intensity of emission in the low energy level (associated with PDHS) normalized with the intensity of pure PMPrS and PDHS with same thickness, using the expression

$$\alpha = \frac{I_{\mathrm{PMPrS(blend)}} \times I_{\mathrm{PDHS(pure)}}}{I_{\mathrm{PMPrS(pure)}} \times I_{\mathrm{PDHS(blend)}}}$$

The plot of $\alpha/1 + \alpha$ *versus* blend composition is shown in Fig. 9. The straight line corresponds to the fluorescence intensity of blends which is averaged by weighing the fraction of each component. If the quantity $\alpha/1 + \alpha$ for the blend samples falls below the straight line, the fluorescence intensity of PDHS, relative to the intensity of PMPrS, is higher than the value expected from the content of PDHS in the blend. This occurs as a result of energy transfer. As seen from the figure, in the present case, energy transfer occurs from PMPrS to PDHS for all the blend compositions studied.

Fig. 10 shows the excitation spectra of various crystallized samples recorded at an emission wavelength of 382 nm, at which only the emission of PDHS is expected.

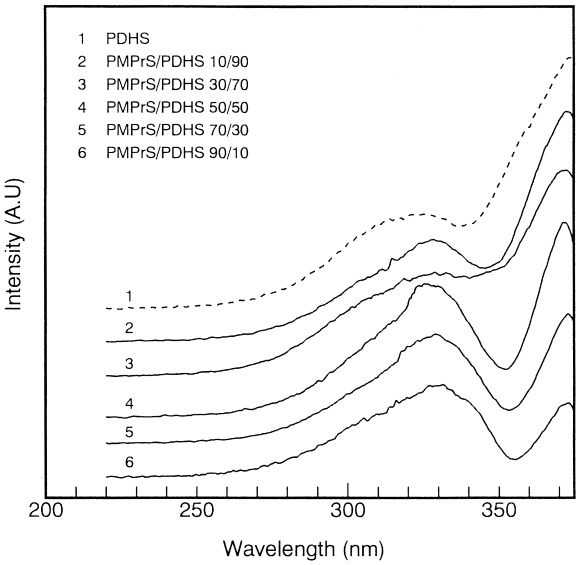

Fig. 10. Fluorescence excitation spectra of various crystallized samples (emission at 382 nm).

The excitation spectra are recorded from 220 nm to 375 nm. In the case of PDHS, two peaks observed at 370 nm and 320 nm corresponded to the excitation of all-trans segments and the disordered phase respectively. The excitation peak at 320 nm indicates energy transfer from the disordered phase to all-trans segments. In the case of blends, a new peak was observed at around 329 nm, and the peak was attributed to excitation of the trans segments of PMPrS. The intensity of the 329 nm peak increased with increasing PMPrS content. The excitation peak at 329 nm indicated energy transfer from PMPrS to PDHS.

Fig. 11 shows excitation spectra of the crystallized blend samples of PDHS/PMOdS and PMPrS/PDHS, along with that of PDHS at an emission wavelength of 382 nm which

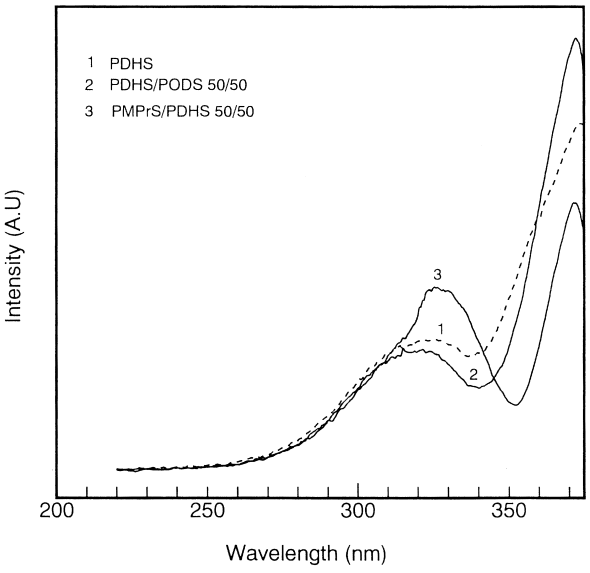

Fig. 11. Fluorescence excitation spectra of crystallized samples (emission at 382 nm).

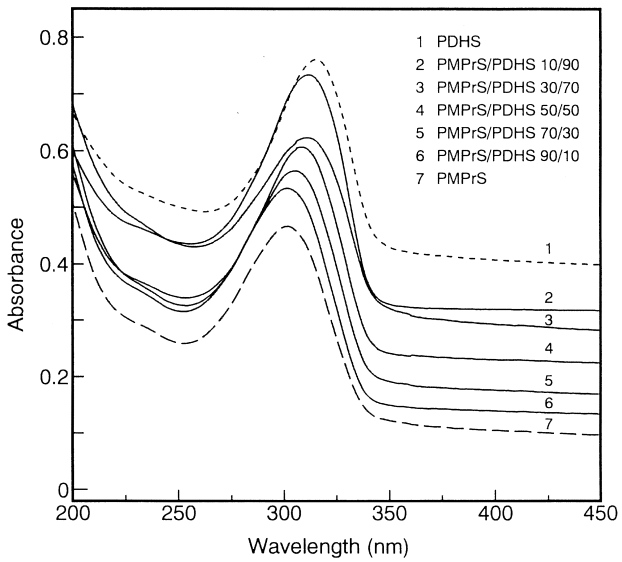

Fig. 12. U.v. spectra of various samples at 80°C.

is assigned to the emission from PDHS. The spectral shape of the PDHS/PMOdS is similar to that of PDHS, suggesting that the electronic energy comes only from PDHS in the blend. On the other hand, as mentioned earlier, the PMPrS/PDHS blend shows energy transfer from PMPrS to PDHS. This shows that some compatibility is required for the energy transfer to occur between the two blend components, as reported earlier.

3.4. Spectroscopic studies on the disordered phase

Fig. 12 shows the u.v. absorption spectra of various samples heated to 80°C. PDHS and PMPrS show peaks at 310 nm and 300 nm respectively. These absorption bands originated from the disordered conformation of the polymers, which is stable above the phase transition temperature. The u.v. absorption peak position of the blend samples moves towards shorter wavelengths with increasing PMPrS content.

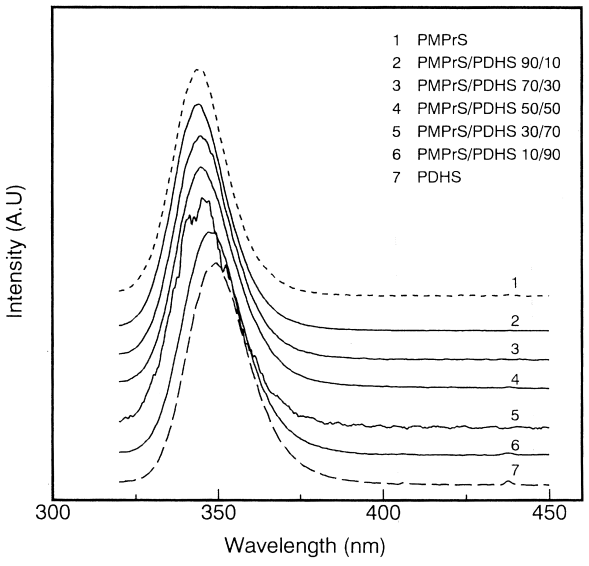

Fig. 13. Fluorescence emission spectra of various samples at 80°C when excited at 320 nm.

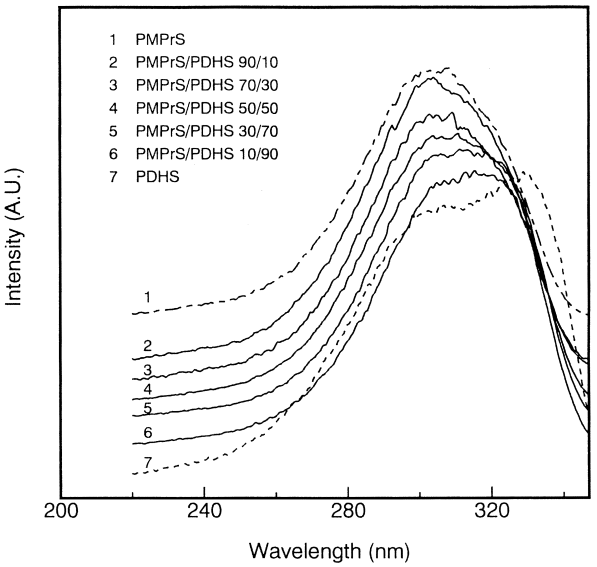

Fig. 14. Fluorescence excitation spectra of various samples at 80°C (emission at 352 nm).

Fig. 13 shows the fluorescent emission spectra of various samples at 80°C when excited at 320 nm. At 80°C both PMPrS and PDHS are known to be in a disordered (molten) state. The PMPrS and PDHS have spectra with peaks at 345 nm and 350 nm respectively. The blends have emission spectra with peaks between 345 and 350 nm. The emission peak shifts towards longer wavelengths with increasing PDHS content.

Fig. 14 shows excitation spectra of the samples at 80°C. The excitation spectra were recorded in the range 220–340 nm at an emission wavelength of 352 nm, at which both PMPrS and PDHS contribute to the fluorescence intensity, but the fluorescence is mainly emitted from the latter. Two peaks are observed in the excitation spectra of PDHS, indicating the polydispersity of the conformation of PDHS even in the disordered phase. The peak at a longer wavelength (330 nm) is markedly decreased by blending PMPrS. The spectral shape of the excitation spectra of the blends is similar to that of PMPrS in the PMPrS/PDHS = 30/70–100/0 blends. These results also show that the electronic energy was transferred from PMPrS to PDHS in the disordered phase.

4. Conclusions

Blends of PMPrS and PDHS were studied using d.s.c., optical microscopy and by u.v. and fluorescent spectroscopy. The depression of the equilibrium melting point of PMPrS with an increase in the PDHS content indicated some degree of miscibility. The polymer–polymer interaction parameter χ was found to be negative. Fluorescence spectroscopic studies showed that the energy

transfer occurs from PMPrS to PDHS. However, no energy transfer was observed for the immiscible blend of PMOdS and PDHS. This observation indicates that some degree of miscibility is required for energy transfer between components of a blend. Photomicrographs of the films of PMPrS/PDHS blend samples showed persistent birefringence at temperatures above 45°C, indicating a liquid crystalline mesophase.

Acknowledgements

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