Mesomorphic Interpolymer Complexes and Blends Based on Poly(4-vinylpyridine)−Dodecylbenzenesulfonic Acid Complex and Poly(acrylic acid) or Poly(*p*-vinylphenol)

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ABSTRACT: Poly(4-vinylpyridine)−dodecylbenzenesulfonic acid [P4VPy(DBSA)$_x$] complexes form interpolymer complexes with poly(acrylic acid) (PAA) in ethanol. The layer structures with nearly unchanged long periods are retained in the interpolymer complexes even when the PAA content is as high as 50 wt %. P4VPy(DBSA)$_x$ complexes form miscible blends with poly(*p*-vinylphenol) (PVPh). The miscible blends also possess well-defined layer structures. PAA and PVPh are confined and dispersed in the polar layer of the P4VPy(DBSA)$_x$ complex.

Introduction

Supramolecular polymeric materials based on polymer/low-molecular-weight compound systems have received increasing attention in recent years.[1−8] Specific interaction such as hydrogen bonding or ionic interaction between a polymer and an amphiphilic surfactant can result in a material with new properties and a phase structure not possessed by either component.[3,4,9−23] In the bulk, polymer−surfactant complexes self-organize into structural patterns through a delicate balance of attractive and repulsive interactions. Mesomorphic phases with liquid crystalline order form in some of these complexes wherein the alkyl tails of surfactants are highly stretched.[10,18] Recently, Hsiao et al.[20] reported that mesomorphic blends with ordered structures were obtained by blending poly(ethylenimine) (PEI) with poly(ethylenimine)−dodecylbenzenesulfonic acid complexes with a low degree of complexation.

Two dissimilar polymers can mix intimately to form a miscible blend if they are able to interact through favorable specific interactions. When the interpolymer interaction is strong, the mixing of two polymer solutions in a common solvent leads to the formation of precipitates which are commonly known as interpolymer complexes.[24] Poly(4-vinylpyridine) (P4VPy), a proton-accepting polymer, forms miscible blends and interpolymer complexes with a large number of proton-donating polymers including poly(acrylic acid) (PAA)[25−28] and poly(*p*-vinylphenol) (PVPh).[29−32] When P4VPy is complexed with dodecylbenzenesulfonic acid (DBSA), a mesomorphic phase with ordered structure exists both in the bulk and in xylene solution when the DBSA content is relatively high.[21] P4VPy−DBSA complexes containing free pyridine units are expected to interact with proton-donating polymers. It is of interest to investigate the effect of blending a P4VPy−DBSA complex with a proton-donating polymer such as PAA or PVPh on the ordered structure of the pristine complex. It will be shown that P4VPy−DBSA can form interpolymer complexes with PAA in ethanol and that the mesomorphic layer structures with nearly unchanged long periods are retained in the interpolymer complexes even when the PAA content is as high as 50 wt %. Miscible P4VPy−DBSA/PVPh blends are obtained when the PVPh content is relatively low (<17 wt %). The blends possess layer structures with nearly the same long period as that of the pristine complex. It is envisaged that PAA and PVPh are incorporated among the polar polymer backbones of P4VPy−DBSA complexes.

Experimental Section

Materials. P4VPy (weight-average molecular weight (M_w) = 60 000), PAA (M_w = 450 000) and PVPh (M_w = 20 000) were all supplied by Aldrich. DBSA (98%, soft type) was obtained from Tokyo Kasei, Tokyo.

Preparation of P4VPy(DBSA)$_x$ Complexes. Appropriate amounts of P4VPy and DBSA were separately dissolved in absolute ethanol (2% w/v). The DBSA solution was then added dropwise to the P4VPy solution. The mixture was stirred continuously at room temperature for 2 days before evaporating off the solvent. The complex was further dried at 60 °C in vacuo for 2 days and then stored in a desiccator. The complexes are denoted as P4VPy(DBSA)$_x$, where x denotes the number of DBSA molecules per repeating unit of 4-vinylpyridine. P4VPy(DBSA)$_{0.75}$ and P4VPy(DBSA)$_{0.50}$ were then used for blending studies.

Preparation of Blends and Interpolymer Complexes of P4VPy(DBSA)$_x$. Appropriate amounts of P4VPy(DBSA)$_x$ complex and proton-donating polymer were separately dissolved in absolute ethanol (1% w/v). Mixtures were prepared by dropping the proton-donating polymer solution into the P4VPy(DBSA)$_x$ solution. They were then stirred at room temperature for 2 days. In the case where precipitation occurred, the interpolymer complex in the form of precipitates was isolated by centrifugation, washed with ethanol, and then dried in vacuo at 60 °C for 2 days. The ratio of the amount of dried complex to the total weight of the polymer and the P4VPy(DBSA)$_x$ complex in the initial solutions gives the yield of the complex. When the mixing of two solutions did not lead to precipitation, the solution was evaporated to dryness. The resulting blend was also dried in vacuo at 60 °C for 2 days.

Characterization. Glass transition temperature (T_g) measurements were made on a TA Instruments 2920 differential scanning calorimeter (DSC). Measurements were conducted under a nitrogen atmosphere using a heating rate of 20 °C/min.

The mesomorphic structures of various samples were observed with an Olympus BH2-UMA polarizing optical microscope. XRD patterns of the samples were recorded on a

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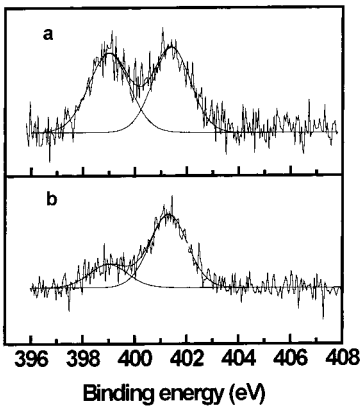


Figure 1. N 1s spectra of (a) P4VPy(DBSA)$_{0.50}$ and (b) P4VPy(DBSA)$_{0.75}$.

Siemens D5005 X-ray powder diffractometer with Cu Kα (1.540 51 Å) radiation (40 kV, 40 mA). Samples were mounted on a sample holder with Stick & Fix (Bostik) and scanned with a step size of $2\theta = 0.01°$ between $2\theta = 1.5$ and 35°. For both POM and XRD measurements, samples were made by smearing 2−3 drops of ethanol to a thin layer of dried powder sample on a cover glass, followed by drying at atmosphere pressure and then in vacuo at room temperature.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG Scientific ESCALAB MKII spectrometer equipped with a Mg Kα X-ray source (1235.6 eV photons) and a hemispherical energy analyzer. Detailed information about measurements and data processing has been reported elsewhere.[28,32,33]

Results and Discussion

Figure 1 shows the N 1s spectra of P4VPy(DBSA)$_{0.50}$ and P4VPy(DBSA)$_{0.75}$ complexes. Each N 1s peak can be deconvoluted into two component peaks. The peak at 399.0 eV is due to neutral pyridine nitrogens while that at 401.3 eV is due to positively charged pyridinium ions.[33] The extent of protonation of pyridine units in the complexes can be calculated from the areas of the deconvoluted N 1s peaks. The N^+/N ratios are 1 and 3 for P4VPy(DBSA)$_{0.50}$ and P4VPy(DBSA)$_{0.75}$, respectively, in agreement with the stoichiometry of the complex. Polarized optical microscopy shows that complexes with high DBSA contents ($x > 0.25$) are birefringent, indicating liquid crystalline order. The long periods of the ordered layer structure in various P4VPy(DBSA)$_x$ complexes as determined by XRD measurements are around 30 Å, comparable to the results reported by Ikkala et al.[21]

We have previously reported that P4VPy forms interpolymer complexes with PAA.[28] Similarly, both P4VPy(DBSA)$_{0.75}$ and P4VPy(DBSA)$_{0.50}$ form interpolymer complexes with PAA over a wide composition range in ethanol solutions. The yield of complex increases with increasing PAA content in the feed. As compared to the P4VPy/PAA interpolymer complexes,[28] the P4VPy(DBSA)$_{0.75}$/PAA and P4VPy(DBSA)$_{0.50}$/PAA interpolymer complexes possess lower T_gs (about 163−168 °C). It has been well established that microphase-separated ordered structures exist in polymer−surfactant complexes wherein the polar phase consists of polymer chains and surfactant heads and the nonpolar phase consists of alkyl chains of the surfactants.[10,18] The ordered layer structures in the P4VPy(DBSA)$_x$ complexes have been established.[21] Figure 2 shows the POM micrographs of some P4VPy(DBSA)$_x$/PAA interpolymer complexes observed at room temperature. They are all birefringent. XRD studies indicate that the mesomorphic structure initially displayed by the P4VPy(DBSA)$_x$ complex is retained in all interpolymer complexes. Broadening and reduced intensity of the diffraction peaks suggest that disturbance is exerted on the layer structure of the pristine complex during interpolymer complex formation. Figure 3 shows the expanded XRD patterns of the P4VPy(DBSA)$_{0.75}$ complex and two P4VPy(DBSA)$_{0.75}$/PAA interpolymer complexes to give a clear view of the peak position. The pristine P4VPy(DBSA)$_{0.75}$ complex shows three peaks with positions following a ratio of 1:2:3 (the two higher-order peaks are weak but can be clearly detected in a plot of log(intensity) vs 2θ), indicating a well-defined lamellar

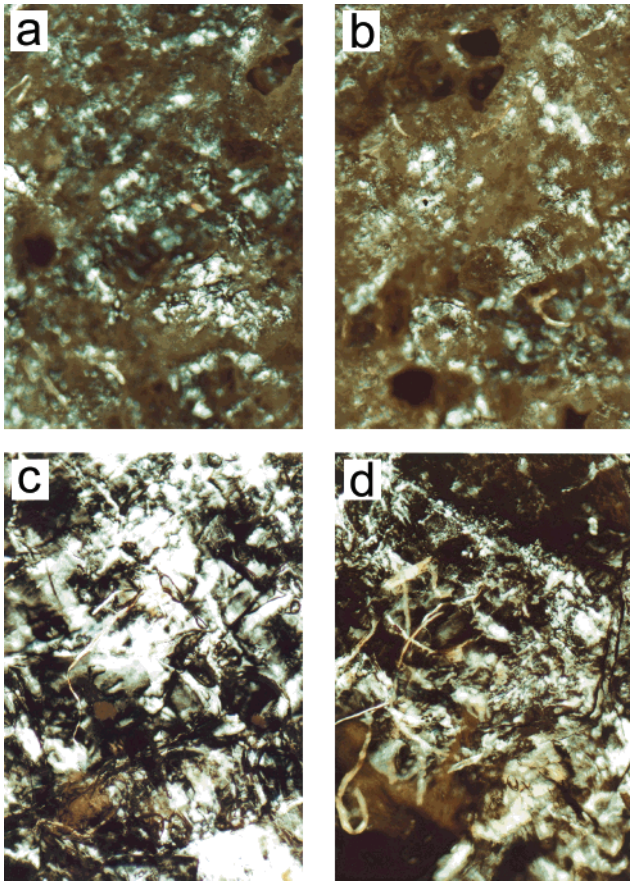


Figure 2. POM micrographs for P4VPy(DBSA)$_x$/PAA interpolymer complexes: (a) P4VPy(DBSA)$_{0.50}$/PAA (PAA feed composition 11 wt %); (b) P4VPy(DBSA)$_{0.50}$/PAA (PAA feed composition 6 wt %); (c) P4VPy(DBSA)$_{0.75}$/PAA (PAA feed composition 28 wt %); (d) P4VPy(DBSA)$_{0.75}$/PAA (PAA feed composition 13 wt %).

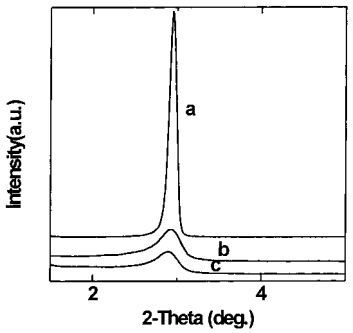


Figure 3. XRD patterns (1.5−5.0°) of the P4VPy(DBSA)$_{0.75}$ complex (a) and those of P4VPy(DBSA)$_{0.75}$/PAA interpolymer complexes obtained from various feed compositions (PAA content): (b) 18 wt %; (c) 11 wt %.

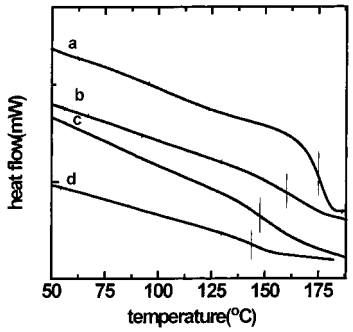


Figure 4. DSC curves. (a) PVPh and (d) P4VPy(DBSA)$_{0.75}$ complex and P4VPy(DBSA)$_{0.75}$/PVPh miscible blends: (b) PVPh 11 wt %; (c) PVPh 6 wt %.

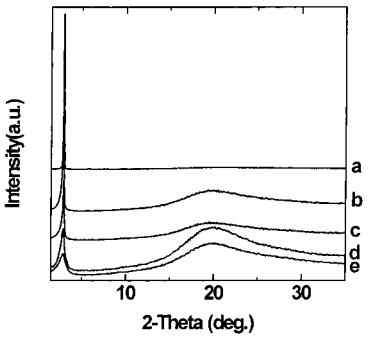
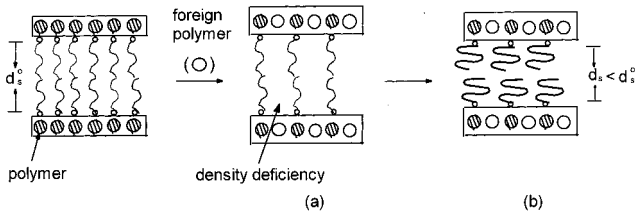


Figure 5. XRD patterns of the P4VPy(DBSA)$_{0.75}$ complex (a), P4VPy(DBSA)$_{0.75}$/PVPh miscible blends [(b) PVPh 11 wt %; (c) PVPh 6 wt %], and P4VPy(DBSA)$_{0.50}$/PVPh miscible blends [(d) PVPh 7 wt %; (e) 17 wt %].

structure. For all the interpolymer complexes, no higher order peak is detected, indicating a poorer order in the interpolymer complexes. The long periods of all the interpolymer complexes are roughly the same (30 ± 1 Å), and no systematic change in the long period as a function of PAA content is observed.

All the mixed solutions of PVPh and P4VPy(DBSA)$_{0.75}$ were clear. On the other hand, cloudy solutions were obtained when the solutions of PVPh and P4VPy(DBSA)$_{0.50}$ were mixed. Since there are more free pyridine groups in the P4VPy(DBSA)$_{0.50}$ complex, there are a large number of interaction between PVPh and P4VPy(DBSA)$_{0.50}$ complex, thus promoting interpolymer complexation. However, the particles were too fine to allow separation. Subsequently, all the P4VPy(DBSA)$_{0.75}$/PVPh and P4VPy(DBSA)$_{0.50}$/PVPh solutions were evaporated to dryness to obtain blends. Blends with PVPh content higher than 17 wt % were found to show macrophase separation. As a result, only those blends containing <17 wt % of PVPh were examined. Figure 4 shows the DSC curves of PVPh, P4VPy(DBSA)$_{0.75}$ and two P4VPy(DBSA)$_{0.75}$/PVPh blends. Each blend shows a single glass transition temperature intermediate to those of PVPh and P4VPy(DBSA)$_{0.75}$. The existence of a composition-dependent T_g is the most commonly used criterion to ascertain the miscibility of a polymer blend. Therefore, the present study shows that PVPh mixes intimately with P4VPy in the P4VPy(DBSA)$_x$ complexes. Polarized optical microscopy shows that all the miscible P4VPy(DBSA)$_x$/PVPh blends containing <17 wt % PVPh are birefringent. Figure 5 shows the XRD patterns of several miscible P4VPy(DBSA)$_x$/PVPh blends and pristine P4VPy(DBSA)$_{0.75}$ complex. Similar to the P4VPy(DBSA)$_x$/PAA interpolymer complexes, the long periods of the layer structure for all the miscible blends

Scheme 1. Simplified Illustration Depicting the Incorporation of Proton-Donating Polymer into the Polar Layer of the Pristine Complex



are roughly the same as that of the P4VPy(DBSA)$_x$ complex and no systematic change in the long period as a function of PVPh content is observed.

Hsiao et al.[20] found that the isotropization temperature is highly depressed when pure PEI is incorporated into the polar layer of PEI(DBSA)$_{0.5}$ complex. In the present study, the mesophases in the P4VPy(DBSA)$_x$ complexes, the P4VPy(DBSA)$_x$/PAA interpolymer complexes, and the P4VPy(DBSA)$_x$/PVPh blends do not show any isotropization prior to thermal decomposition. This may be due to the existence of strong interaction in all these samples.

For a layer structure in the polymer−surfactant complex, the polymer backbone is confined to a thin two-dimensional layer whereas the alkyl tails of the surfactant "anchored" on both sides of this polar layer are highly stretched.[34] When "foreign" polymer chains are incorporated into the polar layer of a polymer−surfactant complex, they are expected to be confined among the polymer backbones of the polymer−surfactant complex and cause a longitudinal expansion of the polar layer. Such an expansion will cause a density deficiency in the nonpolar layer if the alkyl tails of the surfactant retain their original conformations prior to the blending (Scheme 1a). To retain the normal density, the alkyl tails have to stretch somewhat along the direction parallel to the lamellar surface (Scheme 1b). The thickness of the nonpolar layer, in this case, will decrease. On the other hand, the polar layer thickness is expected to increase slightly through the incorporation of the "foreign" polymer. This swelling may be offset by a reduced thickness of the nonpolar layer, and this could lead to a roughly unperturbed long period upon blending (Scheme 1).[35] The confinement of a "foreign" polymer in the polar layer of a polymer−surfactant complex will cause an entropy loss of the "foreign" polymer which is compensated by both the energetically favorable interactions between the "foreign" polymer and the polymer backbone of the polymer−surfactant complex, and the entropic gain from disturbing the ordered stacking of lamellae. In view of the high PAA content in the interpolymer complexes, the ordered structure of the polymer−surfactant complex shows great tolerance to the incorporation of the "foreign" polymer.

Conclusions

P4VPy(DBSA)$_x$ (x = 0.75, 0.50) complexes form mesomorphic interpolymer complexes and miscible blends with PAA and PVPh, respectively. The layer structure with a nearly unchanged long period is retained in both miscible blends and interpolymer complexes. Proton-donating polymers are envisaged to be confined and dispersed in the polar layer of the P4VPy(DBSA)$_x$ complexes.

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References and Notes

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