Macromolecules **2000,** *33,* 221−224

A Mesomorphic Blend Based on the Solid-State Complexes of Polymers with Surfactants

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Received July 9, 1999

Introduction

Solid-state complexes of flexible polymers with amphiphilic surfactants (surf) form a novel class of materials that exhibit interesting combinations of phase structure and properties (e.g., refs 1−10). In the bulk, polymer(surf) complexes self-organize into structural patterns of various length scales through the delicate balance of attractive and repulsive interactions. The important characteristics of the complexes include the following: (1) Comblike molecular configuration, where surf molecules are strongly associated with the polymer backbone giving rise to a comblike polymer via noncovalent interactions.[1] (2) Microphase-separated nanostructure, where the complexes may self-organize to form a nonpolar surf phase and a polar polymer phase. Lamellar morphology consisting of alternating polar and nonpolar layers was predominantly observed.[7] (3) Mesomorphic phases, where high degrees of stretching of the polymer chains and the surf alkyl tails impart liquid crystalline order to the complexes.[9,10]

Most reported studies concerning polymer(surf) complexes have dealt with the solid-state complexes of polyelectrolytes with oppositely charged surfs; in other words, complexation was achieved through electrostatic interactions. This type of ionic complexes suffers several disadvantages in its properties. For example, the glass transition temperature (T_g) of the ionic layers is normally very high, sometimes above the decomposition temperature, which could restrict the desirable melt processing.[11] Antonietti and Maskos recently reported a method for depressing the T_g of the ionic layers by incorporating the noncharged, polar units into the polymer backbone as an internal plasticizer with the alkyl chain covalently bonded to the polar unit.[11]

In an earlier study, we have shown that a highly branched poly(ethylenimine) (PEI) formed an ionic complex with dodecylbenzenesulfonic acid (DBSA), and the complex displayed mesomorphic structure as well as microphase-separated lamellar morphology.[10] The T_g of the ionic layers increased with the degree of complexation, x (x = the average number of DBSA molecules bound with a PEI unit), but the glass transition appeared to be exceedingly high for the stoichiometric complex ($x = 1$) as no T_g was observed prior to thermal decomposition. Over the whole range of degrees of complexation, the mesophase of PEI(DBSA)$_x$ complexes did not display any isotropization prior to thermal decomposition. In the present study, we report that the thermal transitions of PEI(DBSA)$_x$ complexes may be modified while still retaining the mesomorphic structure by simple blending. A PEI(DBSA)$_x$ complex with $x =$ 0.5 is blended with the polymer of its own kind, i.e., PEI. The mesomorphic structure and the thermal properties of the resultant blends will be discussed as functions of blend composition. The results presented here could offer a simple alternative for modifying the properties (while retaining the mesomorphic phase) of polymer(surf) complexes. Furthermore, it will also be demonstrated that the PEI homopolymer was incorporated into the ionic layers of PEI(DBSA)$_{0.5}$ complexes upon blending. This result could be of interest when nanoscopic dispersion of a homopolymer is desirable.

Experimental Section

Branched poly(ethylenimine) (M_w = 25 000) was acquired from Aldrich. The surfactant DBSA was obtained from Tokio Kasei, Japan. The PEI(DBSA)$_{0.5}$ complex was prepared in our previous study.[10] Blendings of PEI and PEI(DBSA)$_{0.5}$ complex were carried out by solution casting. The blending components were dissolved in xylene at room temperature, yielding a 0.5 wt % solution. The solution was subsequently poured onto a Petri dish, and the blend film was obtained after evaporating most xylene solvent on a hot plate at ca. 100 °C. The blend film was further dried in vacuo at 80 °C for 24 h.

The mesomorphic structure of PEI(DBSA)$_{0.5}$/PEI blends was observed by a Pac Hund polarized optical microscopy equipped with a Linkam HFS 91 hot stage. Small-angle X-ray scattering (SAXS) measurements were performed at room temperature (ca. 27 °C). The SAXS setup has been described in the previous study.[10] The scattering profile was output as the plot of the scattering intensity (I) vs the scattering factor, $q = 4\pi/\lambda$ sin($\theta/2$) (θ = scattering angle). Glass transitions were measured with a TA Instrument 2000 differential scanning calorimeter (DSC) equipped with the RCS cooling system. The hating scans were performed from −60 to 150 °C at the heating rate of 20 °C/min. T_g's were collected from the second heating scans.

Results and Discussion

Complexation between PEI and DBSA occurs via proton transfer from DBSA to the amine groups in PEI, giving rise to the complexes with electrostatic interaction.[10] The mesomorphic phases of PEI(DBSA)$_x$ complexes had been identified from the birefringent pattern under polarized optical microscopy (POM).[10] Figure 1 shows the POM micrographs of PEI(DBSA)$_{0.5}$/PEI blends observed at 30 °C. Uniform mesomorphic phases are observed up to 27 wt % PEI, indicating that the mesomorphic structure initially displayed by the complexes retains with slight dilution of PEI. No mesophase is identified for PEI composition above 27 wt %, where the blend only exhibits a disordered melt with no sign of macrophase separation. It is noted that when PEI was blended with the complex with high degree of complexation (e.g., the stoichiometric complex with $x =$ 1), the blend showed macrophase separation with one phase containing predominantly the mesomorphic complex and the other consisting of the isotropic PEI-rich phase.

The mesomorphic phases in polymer(surf) complexes are associated with the lamellar structure wherein the polymer backbone and the alkyl tails of surf are highly

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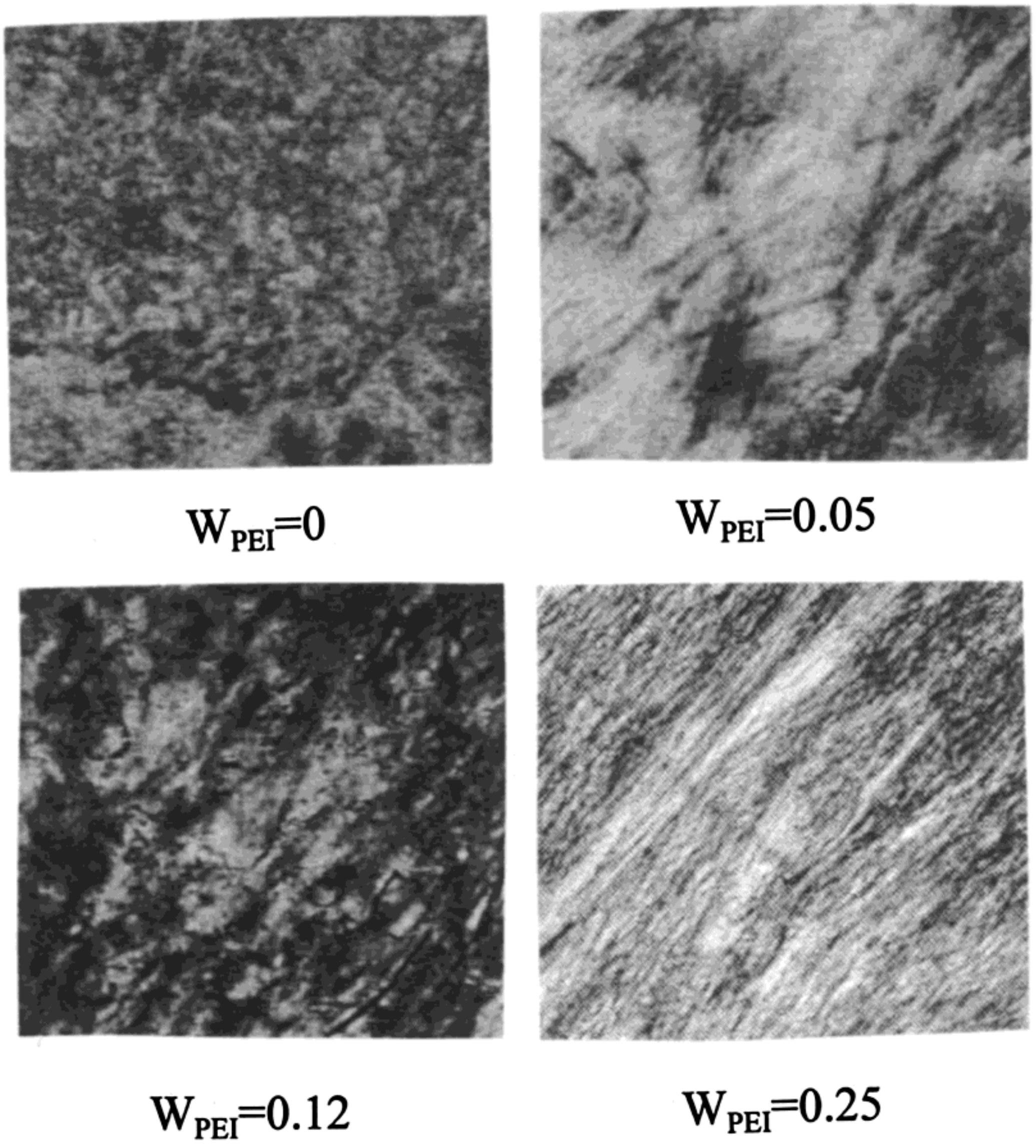
W_{PEI}=0 W_{PEI}=0.05

W_{PEI}=0.12 W_{PEI}=0.25

Figure 1. Mesomorphic phases of PEI/PEI(DBSA)$_{0.5}$ blends observed by polarized optical microscopy. The blend compositions expressed by the weight fraction of PEI (w_{PEI}) are indicated in the figure.

stretched.[1,3] The microphase-separated lamellar structure in neat PEI(DBSA)$_x$ complexes had been established by SAXS in our prior study.[10] Figure 2 displays the SAXS profiles of PEI(DBSA)$_{0.5}$/PEI blends. The SAXS peak shifts toward lower angle with increasing PEI composition, meaning that the long period associated with the lamellar structure increases. The swelling of long period is attributed to the incorporation of PEI into the lamellar structure, where PEI is enclosed in the polar and/or nonpolar layers. To examine whether PEI may be included into the nonpolar layers, the solubility of PEI with dodecylbenzene (which corresponds to the nonpolar alkyl tails in DBSA) was tested. PEI was found to be insoluble in this nonpolar compound; therefore, PEI molecules were enclosed in the polar layers formed predominantly by the protonated PEI chains. Figure 3 plots the long period calculated from the Bragg's law against the weight fraction of PEI (w_{PEI}). The long period rises monotonically with PEI composition, and the swelling at $w_{PEI} = 0.27$ is ca. 7 Å. This slight swelling indicates that the PEI chains in the polar layers are highly stretched. It is noted that although no mesophase is observed, the SAXS profile for $w_{PEI} = 0.5$ still shows a very broad peak. This broad

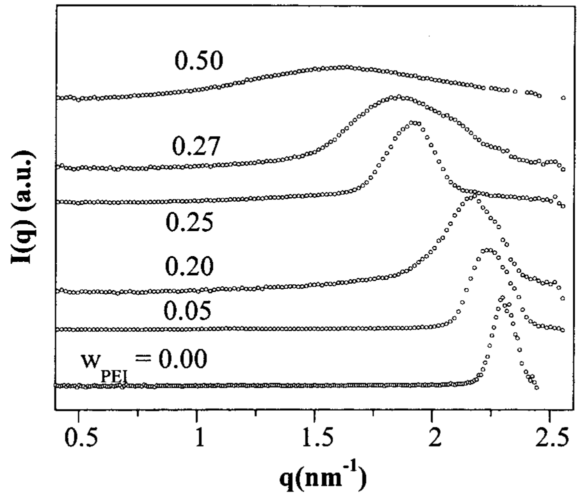

Figure 2. SAXS profiles of PEI/PEI(DBSA)$_{0.5}$ blends. The scattering peak shifts toward lower angle and broadens with increasing PEI composition. An extremely broad peak associated with correlation hole is observed for the composition of $w_{PEI} = 0.5$.

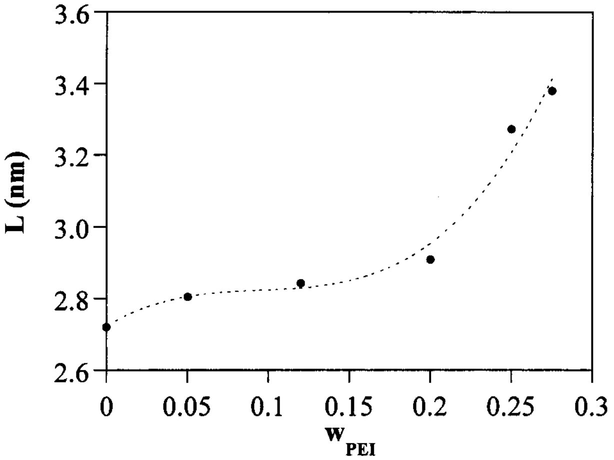

Figure 3. Composition variation of long period of PEI/PEI-$(DBSA)_{0.5}$ blends.

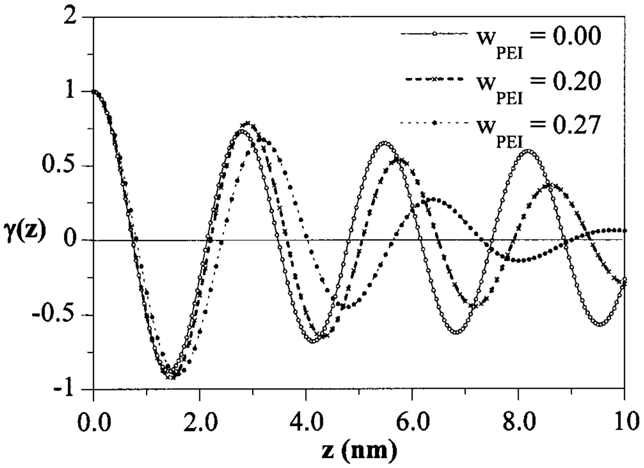

Figure 4. One-dimensional correlation functions calculated from the SAXS profiles of PEI/PEI$(DBSA)_{0.5}$ blends. The correlation functions of the blends display more rapid damp than that of the neat complex, showing the disturbance of long-range correlation in the lamellar structure.

peak is attributed to the presence of block copolymer like concentration fluctuation (correlation hole) in the disordered melt.[7,12]

The SAXS peaks for the blends exhibiting mesophase broaden with increasing PEI composition, showing the disturbance of long-range correlation in the lamellar structure. This may be more clearly manifested from the one-dimensional correlation function shown in Figure 4. The correlation functions of the blends apparently exhibit more rapid damp than that of the neat complex.

The present SAXS results have demonstrated the incorporation of PEI into the lamellar structure of the complex. Such a "nanoscopic dispersion" is somewhat similar to the intercalation of polymer chains in polymer/layered silicate nanocomposites.[13] Incorporation of PEI chains into a nanoscopic layer is entropically unfavorable because the chain loses a significant amount of conformational entropy when highly stretched. However, inclusion of PEI into the ionic polar layers may help screen the repulsive interaction among the ions of the same charge. The loss of conformational entropy may be compensated by such an energetically favorable effect and also the entropic gain from disturbing the ordered stacking of lamellae.

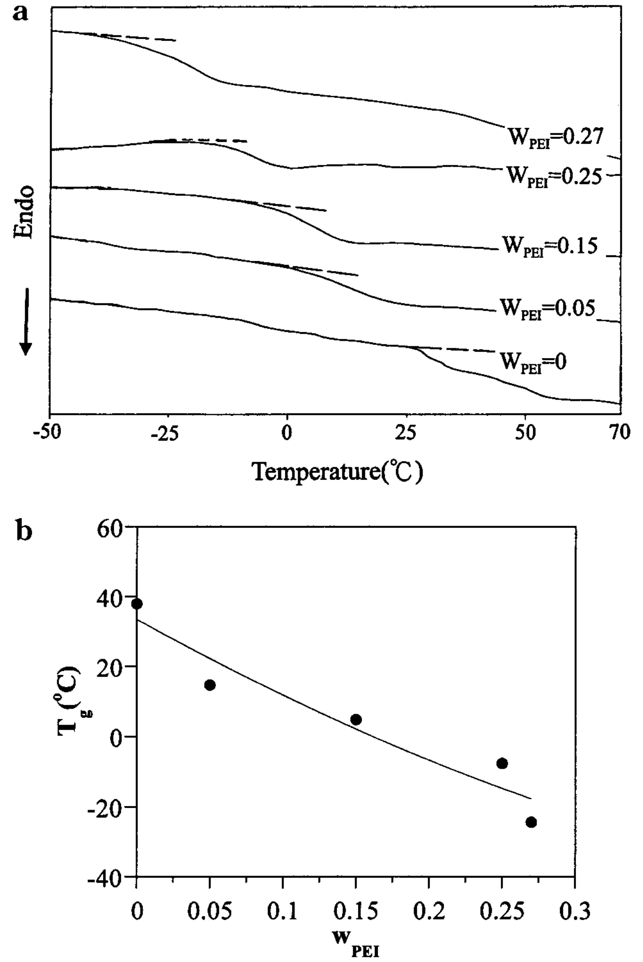

Figure 5. (a) DSC thermograms of the glass transition regions and (b) composition variation of T_g of PEI/PEI$(DBSA)_{0.5}$ blends.

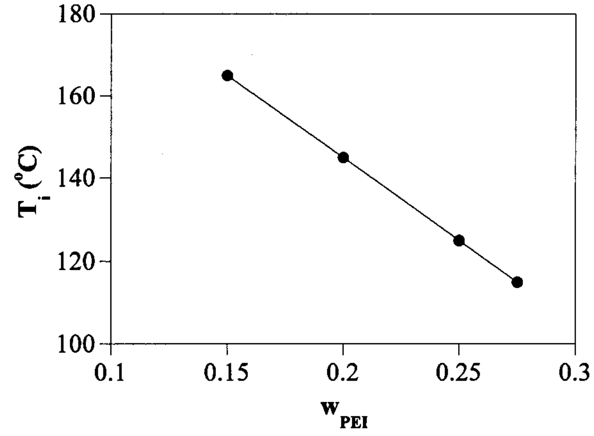

Figure 6. Composition variation of the isotropization temperature (T_i) of PEI/PEI$(DBSA)_{0.5}$ blends.

Neat PEI$(DBSA)_{0.5}$ complex shows a T_g at 38 °C associated with the polar layers. The T_g may be altered when PEI is incorporated into the polar layers. Figure 5a shows the DSC thermograms for the glass transition regions of PEI$(DBSA)_x$/PEI blends, and Figure 5b plots the observed T_g against blend composition. T_g drops monotonically with the increase of PEI composition. The presence of PEI thus exerts the "nanoscopic dilution" effect to depress the T_g of the polar layers.

The mesophase in neat PEI$(DBSA)_{0.5}$ complex does not exhibit any isotropization prior to thermal decomposition, presumably because of the extremely strong polar−nonpolar repulsion between the polymer backbone and the alkyl tails.[10] Isotropization of mesophase occurs at elevated temperature when the complex is blended with 15 wt % or more PEI. Figure 6 plots the isotropization temperature (T_i) as a function of PEI composition. T_i decreases with the increase of PEI composition. Depression of T_i has also been found in the poly(vinylpyridine)(DBSA)$_x$ complex mixed with xylene.[3] In the disordered state, the presence of PEI reduces the polar−nonpolar repulsion and consequently renders the isotropization temperature prior to thermal decomposition. The present study has demonstrated that the thermal properties of polymer(surf) complexes can be modified while retaining the mesomorphic phases via simple blending. Furthermore, a polymer may be dispersed nanoscopically into the lamellar structure of polymer(surf) complexes. The use of polymer(surf) complexes could thus be considered as an alternative for the nanoscopic dispersion of polymers.

Acknowledgment. This work is supported by the National Science Council, R. O. C., under Grant NSC 88-2216-E-007-012.

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