Melting Behavior of Associating Mixtures of Poly(4-vinylphenol) and *N,N*-Dimethyloctadecylamine with Selective Solvent

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ABSTRACT: In this study, melting behavior in comb-shaped aggregates of poly(4-vinylpheol) (PVPh) and *N,N*-dimethyloctadecylamine (NDOA) with xylene which is a good solvent only for NDOA is investigated. For comb-shaped PVPh−NDOA aggregates with sufficient side chains, the melting temperature is simply depressed by addition of a small amount of xylene. Hence, xylene acts as only diluents for side chain crystals for PVPh−NDOA aggregates with sufficient side chains. On the other hand, it is found that for PVPh−NDOA aggregates with small portions of side chains the presence of a small amount of xylene caused elevation of melting temperature. Therefore, it is suggested that the presence of a small amount of good solvent for only side chains promotes assembly and rearrangement of alkyl chains of NDOA in the comb-shaped aggregates with small portions of side chains.

Introduction

Recently, phase behavior in associating polymer−amphiphile mixtures has been studied extensively because the mixtures form various mesomorphic phases, such as microphase separation, gelation, and liquid crystallization with variation of balances of associative and repulsive interactions.[1−17] Especially, lyotropic behavior in concentrated solutions of comb-shaped aggregates of a flexible polymer and a surfactant is of great interest. Fredrickson indicates theoretically that nematic order is formed in the flexible polymer−surfactant mixtures in solution due to stiffening of the flexible polymer chains.[3] In addition, Ikkala et al. found poly(vinylpyridine)−dodecylbenzensulfonic acid complexes in xylene form mesomorphic ordered structures and optical anisotropy suggesting formation of nematic order.[8] Thus, it is expected that the existence of solvent causes characteristic phase formation of the comb-shaped aggregates.

In our previous studies,[9,10,18,19] mesomorphic, crystalline structures and melting behavior in associating poly(4-vinylphenol)−*N,N*-dimethyloctadecylamine (PVPh−NDOA) mixtures which form comb-shapes aggregates have been investigated. Among them, it has been found by X-ray diffraction that octadecyl chains in a 1:1 stoichiometric mixture between repeating units of PVPh and NDOA are closely packed in comparison with pure NDOA, and the aggregate forms the ordered structure as schematically represented in Figure 1.[10] However, when the molar ratio of the repeating unit of PVPh against NDOA is larger than 1, the regularity of the crystal of the comb-shaped aggregates is spoiled due to the lack along the PVPh chains. For these systems, it is interesting to investigate effects of solvent on assembly of the components. Especially, if the good solvent only for side alkyl chains enhances assembly of alkyl chains, crystallization might be induced in the PVPh−NDOA aggregates. Then, in this study, we focus on the melting behavior in PVPh−NDOA mixtures in which the repeating unit of PVPh/NDOA ≥ 1.0 (mol/mol) with xylene which is a good solvent only for alkyl chains.

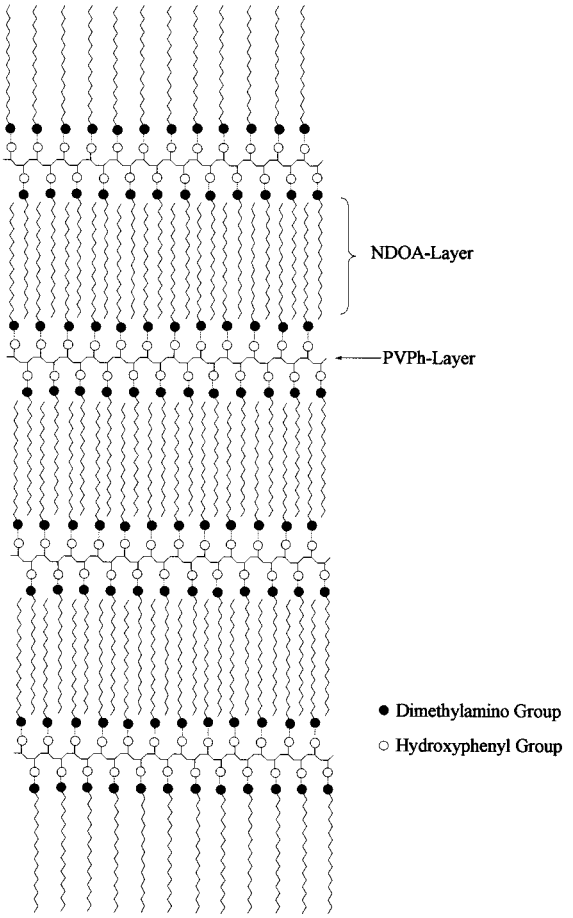

Figure 1. Schematic representations of ordered structures of comb-shaped PVPh−NDOA aggregates.

Experiments

PVPh ($\bar{M}_n = 4.4 \times 10^3$, $\bar{M}_w = 8.7 \times 10^3$) was supplied from Maruzen Petrochemical Co., Ltd. NDOA was purchased from Tokyo Chemical Industry Co., Ltd.

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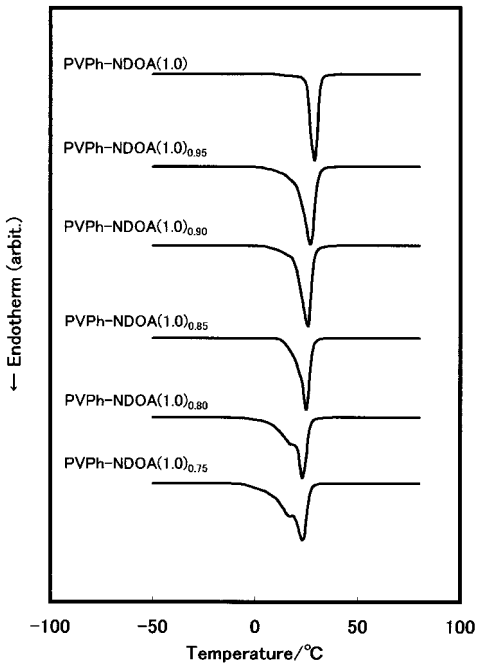

Figure 2. DSC thermograms of PVPh−NDOA(1.0)$_y$ mixtures crystallized in a cooling process at a cooling rate of 1 deg min^{-1}.

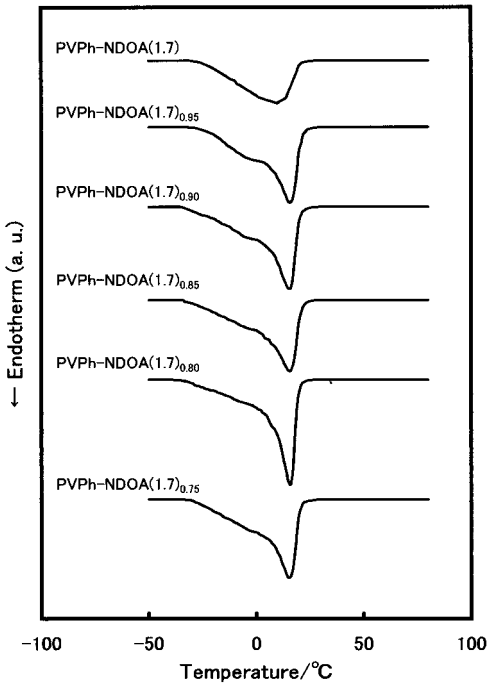

Figure 3. DSC thermograms of PVPh−NDOA(1.7)$_y$ mixtures crystallized in a cooling process at a cooling rate of 1 deg min^{-1}.

PVPh and NDOA at desired compositions were dissolved in 2-propanol (IPA). The solution was stirred until it become clear. Then, IPA was evaporated on a glass plate at 80 °C. The resulting samples were further dried at 40 °C for 12 h in a vacuum. The resulting samples were described as PVPh−NDOA(x), where x denoted the molar ratio of the repeating unit of PVPh against NDOA.

Xylene (Xy) was selected as a good solvent only for the alkyl chain of NDOA. Xy was poured into PVPh−NDOA(x) to be the desired concentration. Then, the solution was homogenized and seasoned at 40 °C for 12 h. All the resulting PVPh−NDOA(x)/Xy mixtures were optically transparent at 40 °C. They were described as PVPh−NDOA(x)$_y$. Here, y represents the weight fraction of PVPh−NDOA(x) in mixtures of PVPh−NDOA(x) and xylene.

Crystallizations of PVPh−NDOA(x)$_y$ systems were performed by two methods. One was crystallization in the cooling process at a cooling rate of ca. 1 K min^{-1}. The other was isothermal crystallization at 3 °C for 3 h.

The melting behavior of PVPh−NDOA(x)$_y$ was investigated by differential scanning calorimetry (DSC). DSC measurements were performed using a Du Pont 910 DSC equipped with 990 thermal analyzer at a heating rate of 10 K min^{-1} under a dry N_2 atmosphere.

Results and Discussion

Figure 2 shows DSC thermograms for PVPh−NDOA(1.0)$_y$ crystallized in cooling process at a cooling rate of ca. 1 K min^{-1}. When $1.0 \geq y \geq 0.85$, a sharp and single melting peak is detected in each thermogram. However, when $y < 0.85$, the premelting peak appears. Hence, crystals of alkyl chains in the PVPh−NDOA(1.0) mixture become unstable with increasing Xy. Similar results are obtained for PVPh−NDOA($1.5 \geq x \geq 1.0$) mixtures. On the other hand, in xylene solution of PVPh−NDOA($x > 1.5$), the melting behavior is much different from that of PVPh−NDOA($1.5 \geq x \geq 1.0$). Figure 3 shows DSC thermograms for PVPh−NDOA(1.7)$_y$ crystallized in a cooling process at a cooling rate of ca. 1 K min^{-1}. The thermogram of the PVPh−NDOA(1.7) mixture shows a broad and weak peak of melting. On the contrary, when a small amount of Xy is added to PVPh−NDOA(1.7) mixtures, a sharp and strong signal of melting is observed at a higher temperature than the melting region of PVPh−NDOA(1.7) mixtures. Especially, in the PVPh−NDOA(1.7)$_{0.80}$ mixture, the signal peak of melting is no longer detectable. This phenomenon is a common feature for PVPh−NDOA($x \geq 1.7$)$_y$ systems.

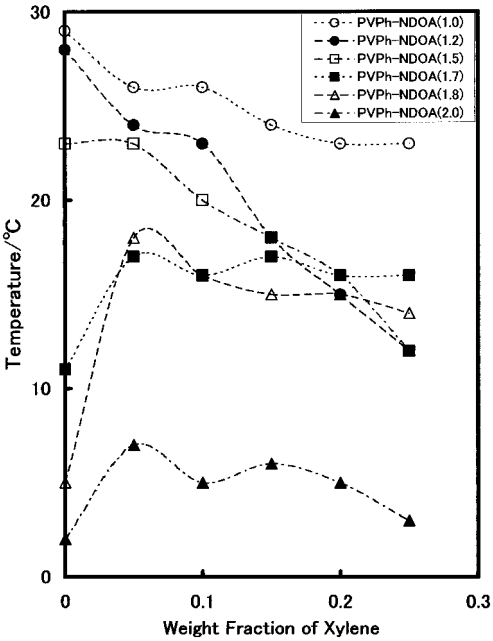

Figure 4. Plots of T_m of PVPh−NDOA(x)$_y$ mixtures crystallized in a cooling process at a cooling rate of 1 deg min^{-1} against weight fraction of xylene.

Figures 4 and 5 show plots of melting temperature (T_m) and heat of fusion per mole of NDOA (ΔH_u) of PVPh−NDOA(1.7)$_y$ systems crystallized in a cooling process against weight fraction of Xy, respectively. Since both T_m and ΔH_u tend to decrease with increasing PVPh contents in PVPh−NDOA mixtures, packing of side chain in PVPh−NDOA aggregates crystallized in a

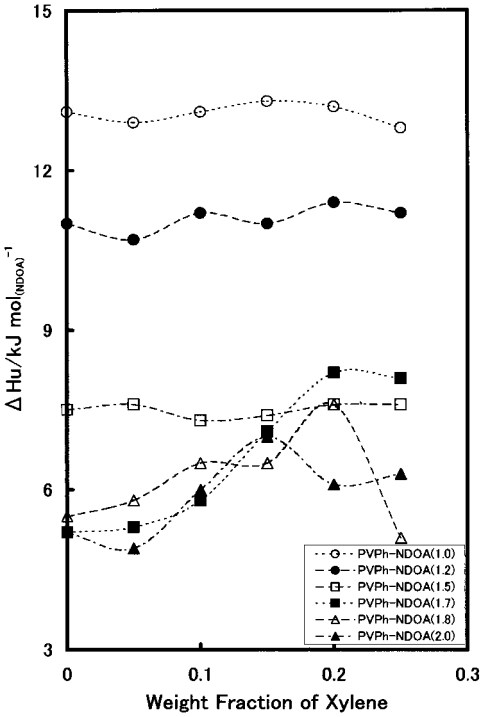

Figure 5. Plots of ΔH_u's per mole NDOA of PVPh−NDOA(x)$_y$ mixtures crystallized in a cooling process at a cooling rate of 1 deg min^{-1} against weight fraction of xylene.

cooling process becomes imperfect with decreasing NDOA, side chain, content. For PVPh−NDOA($1.5 \geq x \geq 1.0$), the apparent T_m is decreasing systematically with increasing Xy contents. On the other hand, ΔH_u's are almost constant against Xy contents. Hence, a small amount of Xy acts as diluents for side-chain crystals of comb-shaped PVPh−NDOA aggregates because alkyl chains are closely packed in a confined area in bulk. On the other hand, the addition of a small amount of Xy to PVPh−NDOA($x \geq 1.7$) mixtures causes a drastic rise of apparent T_m. In addition, ΔH_u's of PVPh−NDOA($x \geq 1.7$) systems tend to increase with increasing Xy contents compared with that of PVPh−NDOA($x \leq 1.5$) systems. This means that the existence of a small amount of good solvent only for side chain induces or promotes packing of side chain in comb-shaped PVPh−NDOA aggregates of $x \geq 1.7$. In our previous studies,[9,10] we showed that T_m's of PVPh−NDOA($x > 1.0$), especially PVPh−NDOA($x > 1.5$) mixtures, are lower than that of the PVPh−NDOA(1.0) mixture because alkyl chains in PVPh−NDOA($x > 1.0$) are packed imperfectly due to weak segregation of microphase-separated PVPh-rich and NDOA-rich phases. Then, it is expected that the good solvent only for side chains causes strong segregation of alkyl chains in the confined NDOA−Xy-rich phase. Since the octadecyl chains are assembled in a confined area due to this reason, it is considered that the side chains of PVPh−NDOA−Xy mixtures are packed more closely than the bulk PVPh−NDOA($x > 1.5$) mixtures. However, these results are obtained for the Xy solution of a PVPh−NDOA mixture crystallized in the cooling process. Therefore, the melting behavior in Xy solution of PVPh−NDOA mixture as shown above might include kinetic effects of crystallization of octadecyl chains. Then, melting behavior in the Xy solution of PVPh−NDOA mixtures crystallized in isothermal condition is investigated below.

Figures 6 and 7 show DSC thermograms for PVPh−

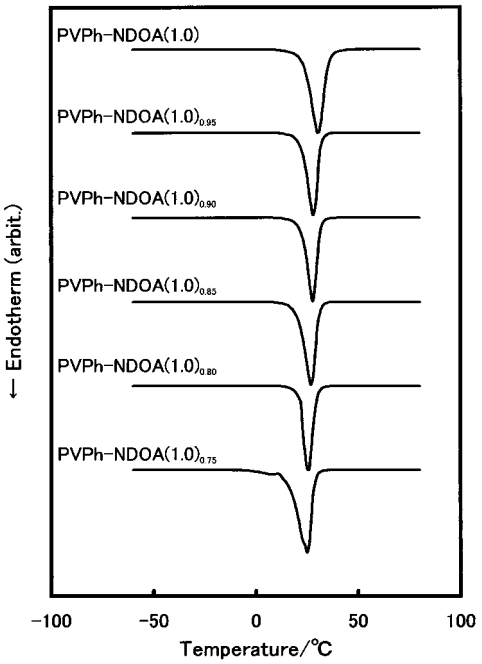

Figure 6. DSC thermograms of PVPh−NDOA(1.0)$_y$ mixtures crystallized by isothermal crystallization at 3 °C for 3 h.

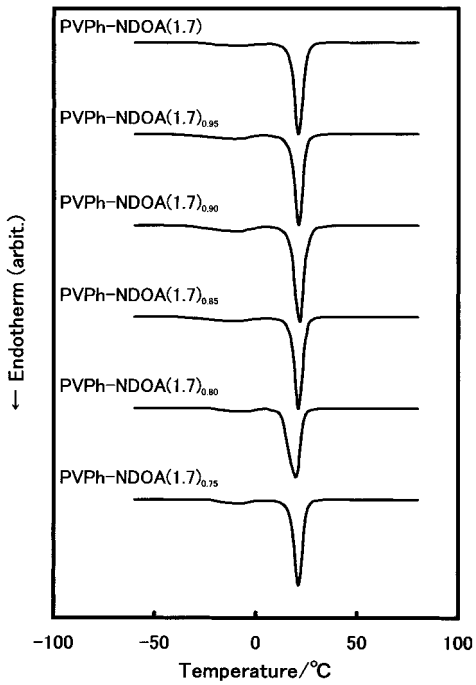

Figure 7. DSC thermograms of PVPh−NDOA(1.7)$_y$ mixtures crystallized by isothermal crystallization at 3 °C for 3 h.

NDOA(1.0) and PVPh−NDOA(1.7) mixtures crystallized at 3 °C for 3 h. As shown in Figure 6, for PVPh−NDOA(1.0)$_y$ systems, sharp and single melting peaks are obtained even in the mixtures with relatively high Xy contents in contrast to thermograms obtained for the mixtures crystallized in the cooling process as shown in Figure 2. In addition, for PVPh−NDOA(1.7)$_y$ systems, a sharp and single melting peak is obtained in contrast to the melting behavior in PVPh−NDOA(1.7)$_y$ systems crystallized in a cooling process as shown in Figure 3. Except for PVPh−NDOA(2.0) systems, similar thermograms are obtained for each system. Hence, assembly and arrangement of the side chain in PVPh−NDOA(x

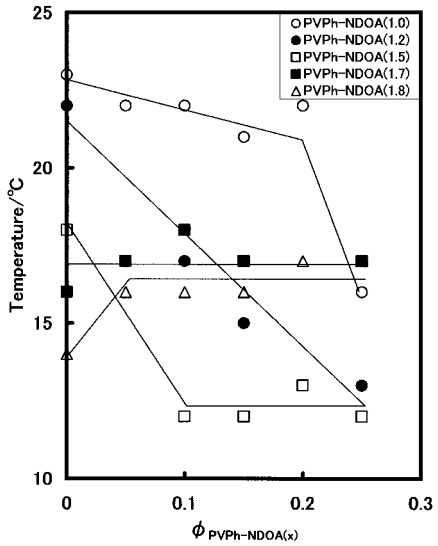

Figure 8. Plots of T_m of PVPh−NDOA(x)$_y$ mixtures crystallized by isothermal crystallization at 3 °C for 3 h.

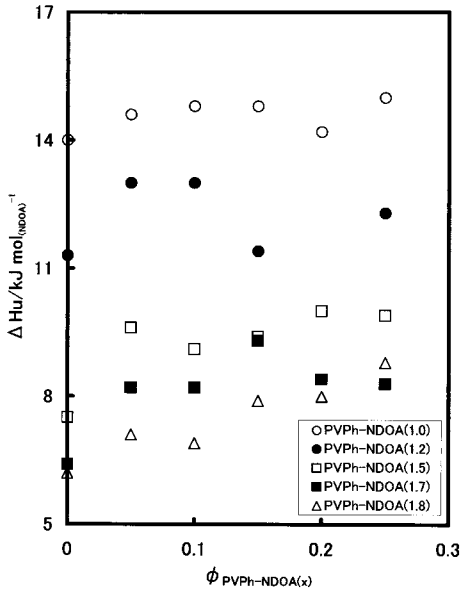

Figure 9. Plots of ΔH_u's per mole NDOA of PVPh−NDOA(x)$_y$ mixtures crystallized by isothermal crystallization at 3 °C for 3 h.

$\geq 1.0)_y$ systems are sufficiently achieved in isothermal crystallization.

Figures 8 and 9 show plots of T_m and ΔH_u's of PVPh−NDOA(x)$_y$ systems crystallized in isothermal conditions against Xy contents. For PVPh−NDOA($x \leq 1.5$) systems, the addition of a small amount of Xy causes melting temperature depression and keeps ΔH_u's almost constant. This result corresponds to the results for PVPh−NDOA($x \leq 1.5$)$_y$ crystallized in a cooling process. Therefore, it is concluded that Xy acts as only diluents for side chain crystals of comb-shaped PVPh−NDOA($x \leq 1.5$) mixtures because Xy make packing of alkyl chains looser. On the other hand, for PVPh−NDOA(1.7) and PVPh−NDOA (1.8) mixtures, T_m's are kept almost constant or tend to elevate and ΔH_u's tend to increase with adding a small amount of Xy. This means that addition of a small amount of Xy to the PVPh−NDOA($x \geq 1.7$) mixtures enhances the degree of crystallization of alkyl chains. Therefore, it is considered that for PVPh−NDOA(1.7)$_y$ and PVPh−NDOA(1.8)$_y$ systems the existence of a small amount of Xy promotes assembly of alkyl chains in confined area because Xy enhances the segregation force of microphase-separated PVPh-rich and NDOA−Xy phases.

Conclusion

For comb-shaped aggregates with sufficient side chains, the presence of a good solvent only for side chains causes melting temperature depression like the role of general diluents. On the other hand, for the comb-shaped aggregates with small portions of side chains, a small amount of good solvent only for side chains promotes assembly and arrangement of side chains since strong segregations of microphase-separated polymer-rich and hydrophobic phases are induced by adding hydrophobic solvent.

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