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Phase Diagram of Poly(4-vinylphenol)−*N*,*N*-Dimethyloctadecylamine Mixture

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ABSTRACT: The phase diagram of poly(4-vinylphenol)−*N*,*N*-dimethyloctadecylamine (PVPh−NDOA) mixture is investigated by X-ray diffraction measurements and optical microscopy. In the low-temperature region PVPh−NDOA mixtures take the mesoscopically ordered phase like a comb-shaped polymer above the melting temperature of the crystal of PVPh−NDOA aggregates. With elevating temperature PVPh−NDOA mixtures undergo an order−disorder phase transition that is a characteristic phase transition in block- or comb-shaped polymers and take homogeneous single phase. Furthermore, at higher temperatures PVPh−NDOA mixtures show the LCST-type phase transition and macroscopically separate into two homogeneous phases. These complex phase behavior in the PVPh−NDOA mixture is explained in relation to the balances of association between the hydroxyphenyl group of PVPh and the dimethylamino group of NDOA, repulsion between PVPh and the octadecyl group of NDOA, and the variation of the entropy contribution with varying temperature.

Introduction

In recent years associating polymers have been investigated extensively due to various mesoscopic phase behavior such as thermoreversible gels.[1−4] Among them, polymer−surfactant systems and in particular polyelectrolyte−surfactant systems have been focused extensively on both theoretical and experimental aspects.[5−14] Associating polymer−surfactant systems can take a comblike structure due to the association between the hydrophilic headgroup of surfactant and the corresponding polar group of polymer and repulsion between the polymer and the hydrophobic group of surfactants. Therefore it is expected that the associating polymer−surfactant systems will show the same phase behavior as comb-shaped polymers.

Recently Ruokolainen et al. found an ordered mesomorphic structure in the hydrogen-bonding poly(4-vinylpyridine)−pentadecylphenol (P4VP−PDP) system that resembled a comb-shaped polymer in both solid and liquid states.[7,10,14] According to their results, in associating polymer−surfactant systems, a specific ordered structure is formed in the solid state and a mesoscopically ordered structure reflecting the ordered structure in the solid state appears in the liquid state.[7,10] Furthermore for the P4VP−PDP system they also found an order−disorder transition phase behavior, which is a characteristic phase behavior in block or graft copolymers.[14] These results are of great value because of the evidence that the associating polymer−surfactant systems show the same phase behavior as a comb-shaped polymer. However in associating polymer−surfactant systems, a polymer as a main chain and surfactants as side chains are bonded noncovalently each other by physical bonds, for example a hydrogen bond, whereas side chains are covalently bonded with the main chain in comb-shaped polymers. Therefore, it is predicted that the phase diagram of an associating polymer−surfactant system is more complicated compared with that of covalently bonding block or graft copolymer due to the thermoreversible nature of the noncovalent bond between the main and side chains.[15]

Tanaka et al. and Dormidontova et al. predicted theoretically the phase diagram of associating polymer−surfactant systems.[6,13] The shapes of the resulting phase diagrams in their theories seem to differ from each other. However, in their phase diagrams, there are some common aspects. Both theories predict a lower critical solution temperature (LCST) that is a characteristic feature in polymer solution or blends in the high-temperature region and an order−disorder transition (ODT) that is a characteristic aspect in comb-shaped polymers in the low-temperature region. Therefore, it is expected that the LCST and ODT coexist in actual phase diagrams of associating polymer−surfactant systems. The actual phase diagrams have been found by Ruokolainen et al. on the P4VP−PDP(methane sulfonic acid) system which show both microphase separation and macrophase separation.[16] Hence, it is expected that a similar phase diagram, including various phase transitions, can be found in another associating polymer−surfactant system.

In our previous study, we reported on crystalline structure in an associating poly(4-vinylphenol)−*N*,*N*-dimethyloctadecylamine (PVPh−NDOA) mixture.[17] In the PVPh−NDOA mixture, PVPh and NDOA form specific crystalline structure cooperatively due to the stoichiometric association between the hydroxyphenyl group of PVPh and the dimethylamino group of NDOA and repulsion between PVPh and the octadecyl group of NDOA.[17] Since the PVPh−NDOA mixture is regarded as an associating polymer−surfactant system, it is expected that it shows various phase behaviors in both macro- and mesoscopic regions. Then we investigated the phase diagram of PVPh−NDOA mixtures using cloud point measurements and small-angle X-ray diffraction.

Experimental Section

Materials. Poly(4-vinylphenol) (PVPh) was kindly supplied from Maruzen Petrochemical Co., Ltd. Number and weight

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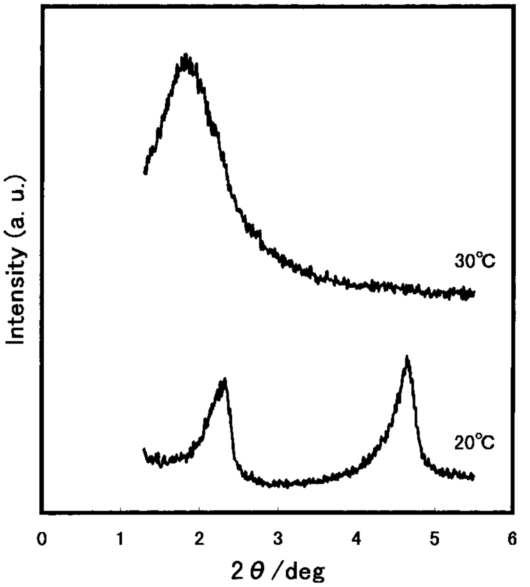

Figure 1. X-ray diffraction profiles for the PVPh−NDOA(1.0) mixture at 20 and 30 °C.

average molecular weights (M_n, M_w) of PVPh were 4400 and 8700 gmol^{-1}, respectively. *N*,*N*-Dimethyloctadecylamine (NDOA) was purchased from Tokyo Chemical Industry Co., Ltd. 2-Propanol (IPA) as a solvent was purchased from Wako Pure Chemicals Co., Ltd. PVPh and NDOA were dried at 40 °C for 12 h in reduced pressure before using. IPA was dehydrated by 3A molecular sieves.

Sample Preparation. PVPh−NDOA(*x*) mixtures were prepared by solution mixing. Here *x* in parentheses denotes the molar ratio of the repeating unit of PVPh vs NDOA. First NDOA was dissolved in IPA. Then, PVPh weigh to the desired composition was poured into the solution under mechanical stirring. The solution was stirred until it became clear. After the solution became clear, IPA was evaporated at 30 °C. The resulting PVPh−NDOA(*x*) mixtures were dried at 40 °C for 12 h under reduced pressure.

X-ray Diffraction. X-ray diffraction measurements were performed using an MXP3TA X-ray diffractometer of MAC Science Co., Ltd. The measurements were made with an X-ray beam (Cu Kα radiation, $\lambda = 0.15405$ nm) monochromatized with a diffracted beam monochromator. The measurements were performed between 20 and 100 °C.

Optical Microscopy. For PVPh−NDOA(*x*) mixtures, optical microscopy studies were carried to detect cloud points. All the experiments were performed between 100 and 150 °C by using a Nikon S−Ke optical microscope equipped with a heating stage.

Results and Discussion

Figure 1 shows X-ray diffraction patterns for the PVPh−NDOA(1.0) mixture at 20 and 30 °C. In our previous study we reported that melting points (T_m) of the PVPh−NDOA(1.0) aggregate is about 25 °C.[17] Hence the results shown in Figure 1 are obtained below and above T_m of the PVPh−NDOA(1.0) mixture. In the diffraction pattern for PVPh−NDOA(1.0) mixture at 20 °C, first and second-order diffraction peaks appear at 3.2 and 6.4°, respectively. This result corresponds to our previous study.[17] Therefore the first-order diffraction peak is attributed to the long period of crystalline structure formed by stoichiometric aggregates of PVPh−NDOA(1.0). On the other hand, in the diffraction pattern at 30 °C, second-order diffraction disappears and first-order diffraction is broaden and shifted to a lower angle. Hence the crystalline ordered structure of the PVPh−NDOA(1.0) mixture is distorted by melting of the crystal of the PVPh−NDOA(1.0) aggregate. However since first-order diffraction remained even above the melting temperature, the mesoscopically ordered structure of the PVPh−NDOA(1.0) mixture is still maintained in the liquid state. Therefore it is expected that association between the hydroxyphenyl group of PVPh and the dimethylamino group of NDOA and repulsion between PVPh and the octadecyl group of NDOA still remain at above T_m and repulsive and associative forces are balanced. Therefore it is predicted that the features of the mesoscopically ordered structure of the PVPh−NDOA(1.0) mixture are similar to those of a comb-shaped polymer and the as same as those of the crystalline structure of the PVPh−NDOA(1.0) mixture.

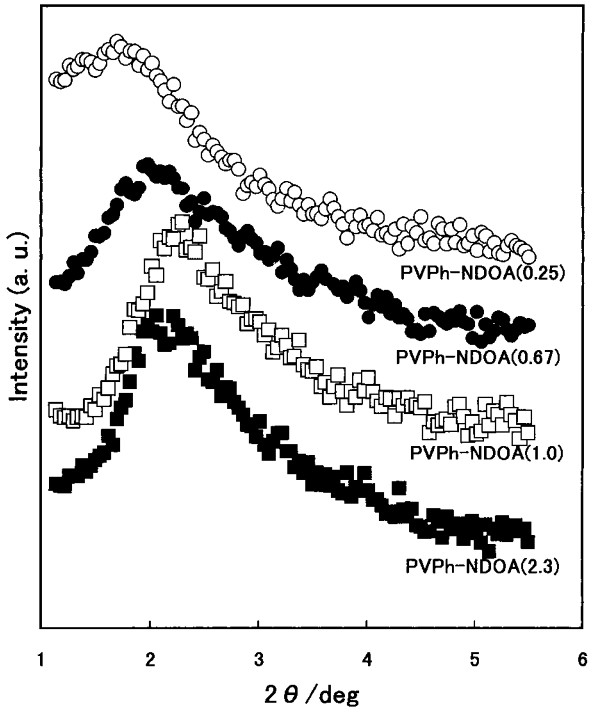

Figure 2. Compositional change in X-ray diffraction patterns for PVPh−NDOA(*x*) mixtures at 40 °C: (○) $x = 0.25$; (●) $x = 0.67$; (□) $x = 1.0$, (■) $x = 2.3$.

Since the PVPh−NDOA(1.0) mixture takes the mesoscopically ordered structure in liquid state due to the association and repulsion between PVPh and NDOA, it is considered that the mesoscopically ordered structure can be varied with varying composition of the PVPh−NDOA(*x*) mixture. Figure 2 indicates compositional change in X-ray diffraction patterns of PVPh−NDOA(*x*) mixtures at 40 °C. In PVPh−NDOA($x > 1.0$) mixtures, X-ray diffraction peaks are shifted to lower angle with increasing mole fraction of PVPh. On the contrary, in PVPh−NDOA($x < 1.0$) mixtures X-ray diffraction peaks are shifted to lower angle with decreasing *x*. This result indicates that compositional dependence of the long period of the mesoscopically ordered structure in PVPh−NDOA(*x*) mixtures show a minimum at a stoichiometric composition of the mixture. Then Bragg spacings (*d* spacings) of PVPh−NDOA(*x*) mixtures are calculated by Bragg's equation.

The compositional change in *d* spacings of PVPh−NDOA(*x*) mixture at 40 °C is shown in Figure 3. The *d* spacings show a minimum around $\phi = 0.5$, i.e., $x = 1.0$, where ϕ represents the mole fraction of NDOA in PVPh−NDOA(*x*) mixture. It is considered that the

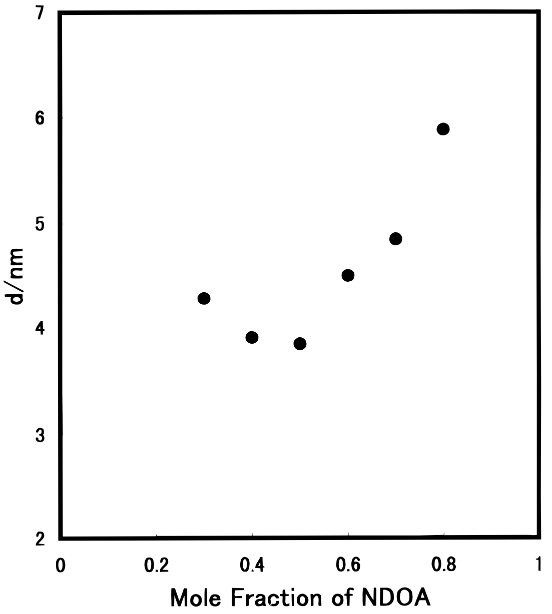

Figure 3. Compositional dependence of *d* spacing for PVPh−NDOA(*x*) mixtures at 40 °C.

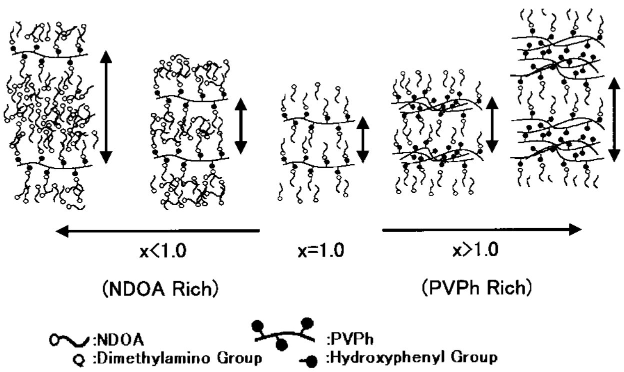

Figure 4. Schematic illustrations of compositional change in the mesoscopic ordered structure of PVPh−NDOA(*x*) mixtures.

period of the mesoscopically ordered structure in PVPh−NDOA(*x*) mixtures is dominated by deviation from $x = 1.0$. Hence compositional change in the mesoscopically ordered structures of PVPh−NDOA(*x*) mixtures in liquid state are explained as follows. Figure 4 represents schematic illustrations of compositional change in the mesoscopically ordered structure of PVPh−NDOA(*x*) mixtures. It is considered by analogy to the crystalline structure of the PVPh−NDOA(1.0) mixture reported in our previous study that the mesoscopically ordered structure of PVPh−NDOA(*x*) mixture is a layered structure of alternating PVPh and NDOA layers as shown in Figure 4. In the schematic pictures of Figure 4, only the lamellar structure is drawn. On the basis of morphological change of the block copolymer, order−order transition is predicted when $x \ll 1.0$ and $x \gg 1.0$. However, we have not detected the signals to indicate morphological transition in this system at $x \ll 1$ and $x \gg 1$ since the peak is rather weak. Moreover, Ruokolainen et al. and Antonietti et al. indicated preferences for a lamellar structure in associating polymer−surfactant complexes.[8,10,11] Hence it is considered that the lamellar structure of this system is appropriate because of its resemblance to the other polymer−surfactant systems. When $x > 1.0$, the PVPh layer becomes wider with increasing *x* due to the increment of excess repeating units of PVPh against NDOA as shown in the right-hand side pictures of Figure 4. Hence, the *d* spacing is increasing with increasing *x* in PVPh−NDOA($x > 1.0$) mixtures. On the other hand, when $x < 1.0$, *d* spacing is observed to be decreasing with decreasing *x* since the NDOA layer is thickening with decreasing *x* due to excess NDOA against repeating units of PVPh as shown in left-hand side pictures of Figure 4. Since there is no excess component against another component when $x = 1.0$, the PVPh−NDOA(1.0) mixture takes the comb-like structure as shown in the central picture of Figure 4. Therefore compositional dependence of *d* spacing of PVPh−NDOA(*x*) mixtures shows a minimum at around $\phi = 0.5$ ($x = 1.0$).

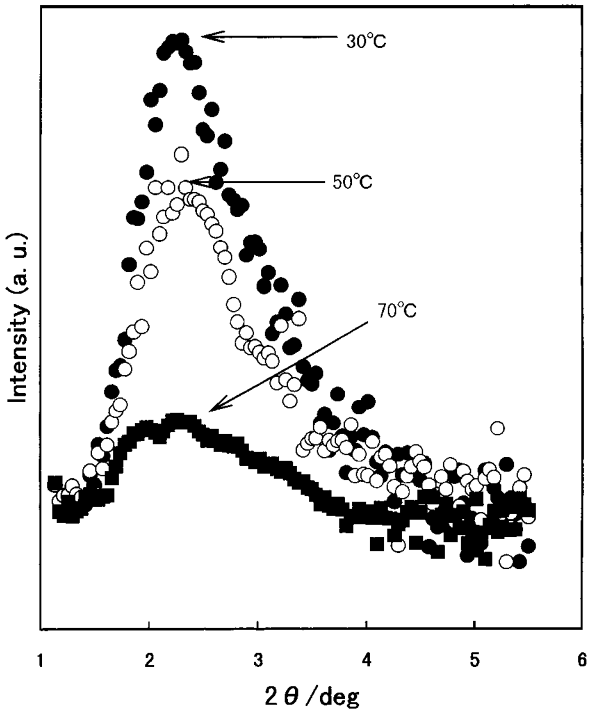

Figure 5. Temperature change in X-ray diffraction patterns for PVPh−NDOA(1.0) mixture: (●) 30 °C; (○) 50 °C; (■) 70 °C.

Figure 5 shows the temperature change in the X-ray diffraction pattern of the PVPh−NDOA(1.0) mixture. At low temperature, relatively sharp and strong peaks of X-ray diffraction are detected. The intensity of the diffraction peak of the mixture is observed to be decreasing with elevating temperature. This means that the regularity of the mesoscopically ordered structure of the PVPh−NDOA(1.0) mixture is disordering with elevating temperature. Therefore it is expected that there are order−disorder transition temperatures (T_{ODT}) in PVPh−NDOA(*x*) mixtures. Then the random phase approximation is applied to determination of T_{ODT}'s for PVPh−NDOA(*x*) mixtures.[18,19]

Reciprocal intensity of maximum of diffraction peaks ($I_{\max} - 1$) for the PVPh−NDOA(1.0) mixture is plotted as a function of reciprocal temperature ($1/T$) in Figure 6. $I_{\max} - 1$ is almost constant between 70 and 80 °C ($2.83 < 1000/T < 2.91$). At lower temperatures than 70 °C, $I_{\max} - 1$ decreases dramatically with increasing $1000/T$, i.e., decreasing temperature. The onset temperature of the abrupt decrement of $I_{\max} - 1$ is determined as the order−disorder transition temperature (T_{ODT}). The resulting T_{ODT} values for PVPh−NDOA(*x*) mixtures are listed in Table 1. All the T_{ODT}'s are confirmed to be

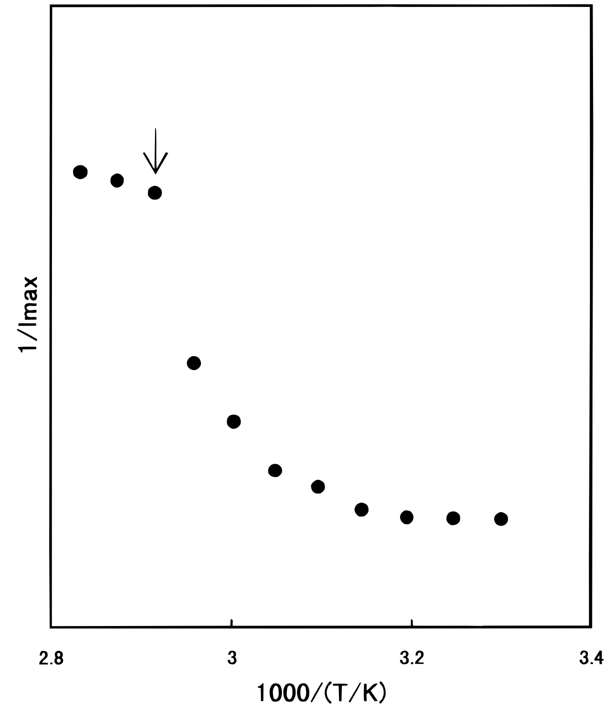

Figure 6. Plots of $I_{\max} - 1$ against reciprocal temperature.

Table 1. Order−Disorder Transition Temperature in PVPh−NDOA Mixtures

mole fract of NDOA	0.30	0.33	0.40	0.50	0.67	0.70	0.80
T_{ODT}/°C	40	55	60	70	75	70	70

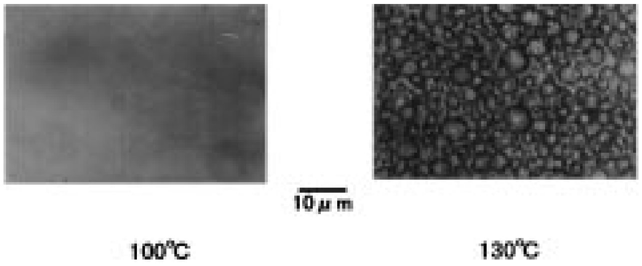

Figure 7. Optical micrographs of the PVPh−NDOA(1.0) mixture at 100 and 130 °C.

thermoreversible. It is considered that the order−disorder transitions of PVPh−NDOA(x) mixtures are caused since association between the hydroxyphenyl group of PVPh and the dimethylamino group of NDOA and the increment of the entropy contribution with elevating temperature are superior to repulsive energy between PVPh and the octadecyl group of NDOA. However since PVPh and hydrocarbon compounds are immiscible in a wide temperature and composition range,[21] it is expected that macroscopic phase separation is caused in the PVPh−NDOA mixture due to dissociation of the hydroxyphenyl group of PVPh and the dimethylamino group of NDOA at a higher temperature.[4,6]

Figure 7 represents optical micrographs taken for the PVPh−NDOA(1.0) mixture at 100 and 130 °C. At 100 °C the PVPh−NDOA(1.0) mixture shows homogeneous single phase. Since 100 °C is higher than T_{ODT}, the state of the PVPh−NDOA(1.0) mixture at 100 °C is homogeneous in both macro- and microscopic regions. On the other hand macroscopically heterogeneous structures appear at 130 °C in the PVPh−NDOA(1.0) mixture. Hence the PVPh−NDOA(1.0) mixture separated into two homogeneous phases with elevating temperature. This transition is thermoreversible, meaning that thermodynamic phase transition takes place. Further similar phase transitions are observed in other PVPh−NDOA(x) mixtures. It should be considered that the LCST phase behavior of PVPh−NDOA(x) mixtures appeared since repulsion between PVPh and the alkyl chain of NDOA is superior to association between the hydroxyphenyl group of PVPh and the dimethylamino group of NDOA due to the immiscible nature of PVPh and hydrocarbon compounds[20] and the thermoreversible nature of the physical bonding between the hydroxyphenyl group and the dimethylamino group. Hence the PVPh−NDOA(x) mixture shows a lower critical solution temperature (LCST) type phase transition. The temperature-sensitive heterogeneous structure is determined as the cloud point.

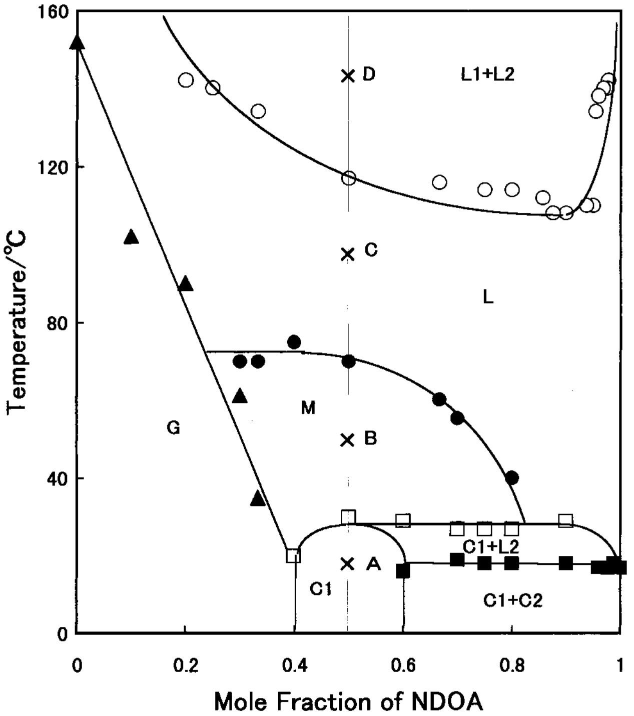

Figure 8. Phase diagram of the PVPh−NDOA mixture: (●) T_{ODT}; (○) cloud point; (■) T_m of NDOA; (□) T_m of PVPh−NDOA(1.0); (▲) glass transition temperature.

Figure 8 shows the phase diagram of a PVPh−NDOA mixture. L, M, C, and G in Figure 8 represent the homogeneous liquid phase, the mesoscopically ordered phase in the liquid state, the crystalline solid state, and the glassy solid state, respectively. The glass transition temperatures and T_m's of PVPh−NDOA mixtures used are the results of thermal analysises in our previous studies.[17,20] The relatively high T_m's represented by open squares correspond to the melting temperature of crystals of stoichiometric aggregates between PVPh and NDOA (PVPh−NDOA(1.0)) and relatively the low T_m's represented by closed squares are due to the melting of NDOA crystals. The phase diagram of the PVPh−NDOA mixture is divided into seven areas. In the PVPh-rich mixture there are simply a glassy state at low temperature and a homogeneous single phase and LCST phase separation at high temperature. On the other hand, the mixtures around $x = 1.0$ ($\phi = 0.5$) or $x < 1.0$ ($\phi > 0.5$) show complex phase behavior. In these mixtures, various phase transition temperatures appear with varying temperatures. The most characteristic feature of the

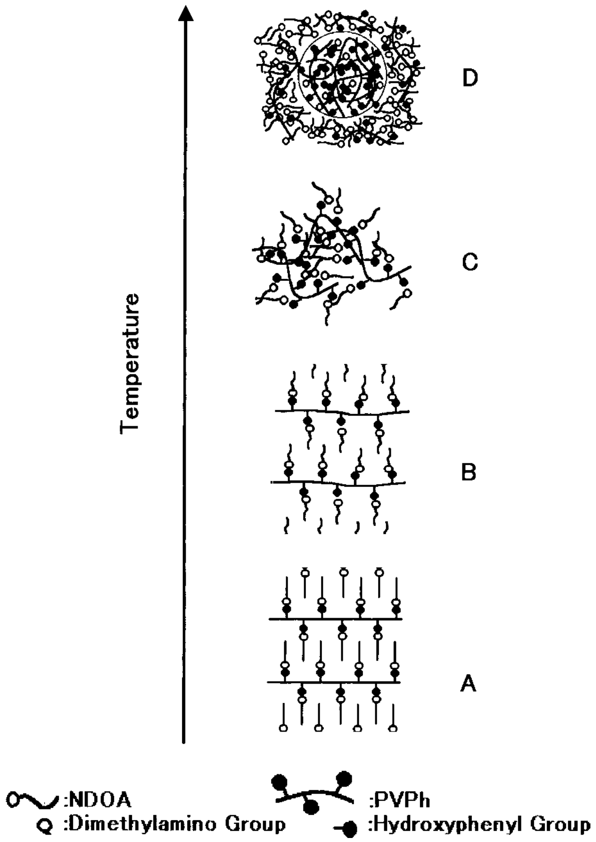

Figure 9. Schematic representations of temperature change in the phase structure of the PVPh−NDOA(1.0) mixture.

phase diagram of the PVPh−NDOA mixture appears in the variation of phase structures in the PVPh−NDOA(1.0) mixture with varying temperatures.

Figure 9 represents schematic illustrations of the change in phase structure of the PVPh−NDOA(1.0) mixture at points A, B, C, and D in Figure 8. At low temperature (A state) PVPh and NDOA form a crystalline structure cooperatively as shown in our previous study.[16] When the temperature is elevated (B state), the crystal is molten but a mesoscopically ordered structure is maintained since association between the hydroxyphenyl group of PVPh and the dimethylamino group of NDOA is superior to repulsion between PVPh and the octadecyl group of NDOA. Furthermore at the C state the PVPh−NDOA mixture takes on a homogeneous single phase. It is considered that enthalpy contribution of association between the hydroxyphenyl group of PVPh and the dimethylamino group of NDOA ($\Delta H < 0$) and entropy contribution ($T\Delta S > 0$) on free energy of mixing are superior to repulsive energy between PVPh and the octadecyl group of NDOA ($\Delta H > 0$). Finally, at high temperature (D state), the PVPh−NDOA mixture separates macroscopically into two homogeneous phases. The associating bond between the hydroxyphenyl group of PVPh and the dimethylamino group of NDOA is dissociated due to its thermoreversible nature. On the contrary, it has been found that repulsion between PVPh and the octadecyl group of NDOA is still remains in the high-temperature region because PVPh is immiscible with hydrocarbon compounds such as dodecane even at high temperature.[21] Hence, macroscopic phase separation in the PVPh−NDOA mixture is occurring due to repulsion between PVPh and the octadecyl group of NDOA and becomes predominant to association between PVPh and NDOA and the entropy contribution on free energy of mixing.

Concluding Remarks

A complex phase diagram of the poly(4-vinylphenol)−*N*,*N*-dimethyloctadecylamine (PVPh−NDOA) mixture is prepared by X-ray diffraction measurements and optical microscopy. In the phase diagram of the PVPh−NDOA mixture, the order−disorder phase transition (mesoscopic phase transition) and the LCST phase transition (macroscopic liquid−liquid-phase transition) coexist. The order−disorder phase transition in the mixture with elevating temperature arises since the enthalpy contribution of association between the hydroxyphenyl group of PVPh and the dimethylamino group of NDOA and the increment of entropy contribution with elevating temperature are superior to the repulsive energy between PVPh and the octadecyl group of NDOA. The LCST phase separation in the mixture is caused due to the dissociation of the associating bond between PVPh and NDOA and the consequent predominant repulsion between PVPh and the octadecyl group.

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