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Study on Ordered Structure of Poly(4-vinylphenol)-N,N-dimethyloctadecylamine Mixture in Solid State

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Phase structure of mixture of poly(4-vinylphenol) (PVPh) with N,N-dimethyl-octadecylamine (NDOA) is investigated. It is shown the PVPh-NDOA mixtures form ordered phase in solid state. The ordered structure in the mixtures is formed by 1:1 stoichiometric aggregate of NDOA and repeating unit of PVPh. Further, it is shown that short period of the structure of the mixture is almost invariant from that of NDOA crystal and long period of the structure of PVPh-NDOA aggregate is larger than that of NDOA crystal. Hence, it is predicted PVPh chain lies vertical to alkyl chain of NDOA in the ordered phase.

Keywords: Associating polymer mixture; comb-shaped polymer; poly(4-vinylphenol); N; N-dimethyloctadecylamine

INTRODUCTION

Recently, polymer-surfactant (P-S) systems have been investigated extensively [1–9]. It is predicted that P-S systems form *comb-shaped* structures due to association of hydrophilic group of S with corresponding polar group of P. Hence, it is expected that P-S systems show specific phase behavior like a *comb-shaped* polymer such as mesoscopically ordered structure [10]. Recently, the existense of the ordered phases were recognized in poly(4-vinylpyridine)-pentadecylphenol system in both solid and liquid states because hydrogen bonding of pyridine ring with hydroxy phenyl group is sperior to repulsion between alkyl group of surfactant and poly(4-vinylpyridine) [5]. Therefore, it is predicted that the mesoscopically ordered phase like a *comb-shaped* polymer appears in the P-S sys-

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tems including hydroxy phenyl group and pyridine group or tertiary amine group due to hydrogen bonding. Then, we investigate phase structure of mixture of amorphous poly(4-vinylphenol) (PVPh) and N,N-dimethyloctadecylamine (NDOA).

EXPERIMENTAL

PVPh (Maruzen Petrochemical, $\bar{M}_n = 4400$, $\bar{M}_w = 8700$) and NDOA (Tokyo Chemical Industry) were dried *in vacuo* for 12h at 80 and 40°C, respectively. NDOA was dissolved in dehydrated 2-propanol(IPA). Subsequently, PVPh was poured into NDOA solution during stirring. After the solution became clear, IPA was evaporated at room temperature. PVPh-NDOA(ϕ) mixtures were dried at 40°C for 12 h *in vacuo*. Here, ϕ represents a molar ratio of repeating unit of PVPh against NDOA. DSC measurements were performed using a Du Pont 910 DSC under N_2 flow at a heating rate of $10 deg/min$. X-ray diffraction (XRD) for PVPh-NDOA mixtures were measured at −30°C using a MAC Science MXP 3TA X-ray diffractometer. The measurements were made with a monochromatized CuKα radiation ($\lambda = 0.15405 nm$).

RESULTS AND DISCUSSION

Figures 1 and 2 show DSC thermograms for PVPh-NDOA($\phi \leq 1$) and ($\phi > 1$) mixtures, respectively. In the DSC thermograms for PVPh-NDOA($0 < \phi < 1$) mixtures, two melting peaks are recognized. One peak at around 20°C is attributed to melting peak of NDOA crystal because of the same temperature of the melting of NDOA. Another peak posing at 27°C appear characteristically in PVPh-NDOA ($\phi \leq 1.0$) mixtures. There are no transitions around 27°C in both NDOA and PVPh. The appearance of new transition suggests that new crystalline structure is formed characteristically in PVPh-NDOA mixtures. The temperature of each melting peak is invariant with composition of mixtures. Hence, crystalline structures of NDOA and PVPh-NDOA mixtures are unaltered by change in composition of mixtures at $0 < \phi \leq 1.0$. The relative magnitude of the new peak is increasing with increasing contents of PVPh and finally PVPh-NDOA(1.0) mixture shows only one peak without melting of NDOA. In addition, PVPh-NDOA(1.5) mixture shows one weak melting peak and the peak shifts to low temperature from that of PVPh-NDOA(1.0) mixture. Hence, in PVPh-NDOA($\phi > 1$) mixtures, it is suggested that the crystalline structure

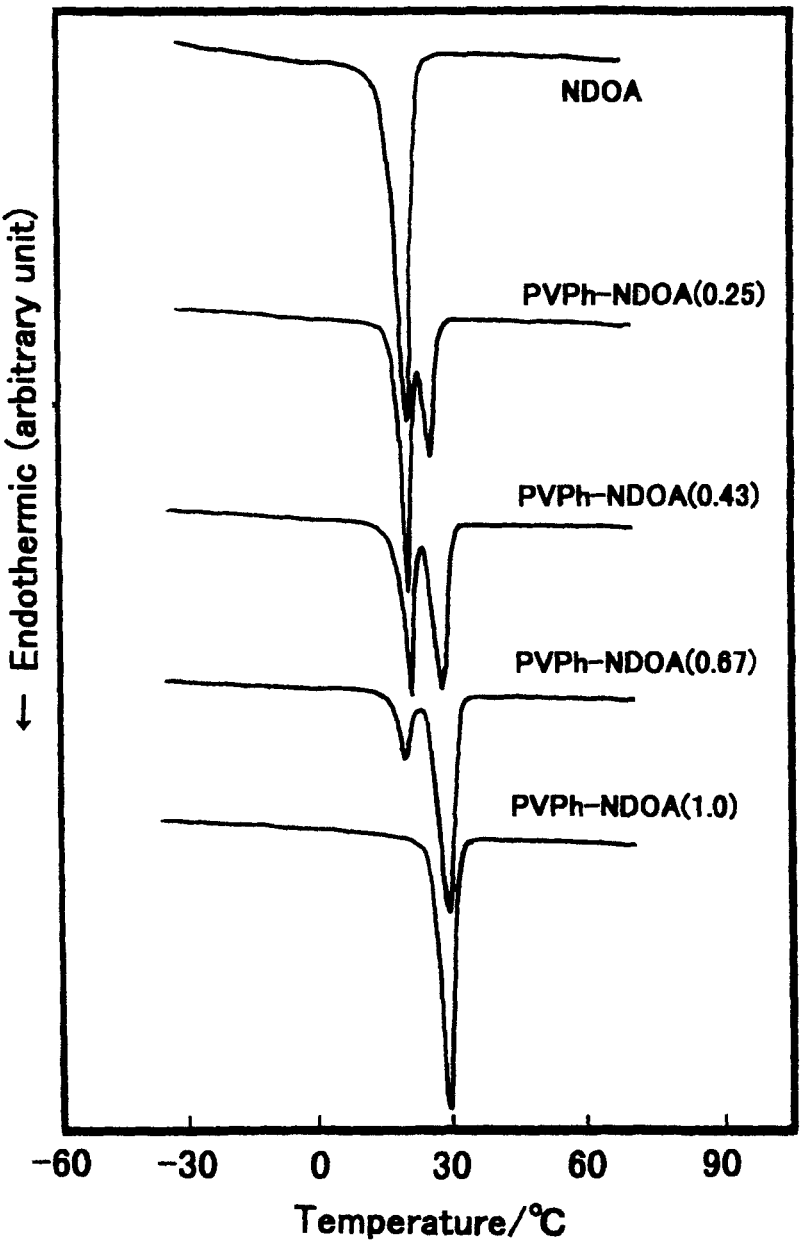

FIGURE 1 DSC thermograms of PVPh – NDOA mixtures including high amount of NDOA against repeating unit of PVPh

become irregular compared to that of PVPh-NDOA($\phi \leq 1.0$) mixtures due to lack of NDOA molecules against repeating units of PVPh. On the other hand, PVPh-NDOA($\phi > 1.5$) mixtures show only a glass transition without any melting peaks. Hence, it is considered that the new peak indicates the melting of crystal constructed by PVPh-NDOA(1.0) aggregate.

Figures 3 and 4 show XRD profiles measured at −30°C for the mixtures. Diffract peaks are detected at around $2\theta = 22°$ for NDOA and a diffuse halo is recognized at around $2\theta = 20°$ for PVPh. On the other hand, diffract peak is detected at around $2\theta = 23°$ for PVPh-NDOA(1.0) mixture. In addition, diffract peaks arisen from NDOA crystal disappear in PVPh-NDOA(1.0) mixture. This result indicates that the ordered structure distinguished from crystalline structure of NDOA is formed in PVPh-NDOA(1.0) mixture. Further, overlapping profile of XRD patterns for NDOA and PVPh-NDOA(1.0) is obtaied in PVPh-NDOA(0.43) mixture. Hence, in PVPh-NDOA($\phi < 1$) mixtures, there are two types of crystals, one is NDOA crystal and another is crystal constructed by PVPh-NDOA(1.0) aggregate. Short period of the ordered structure in PVPh-NDOA(1.0) mixture (0.41*nm*) is slightly diminished from that of NDOA crystal (0.42*nm*). These values correspond to period of helix formed by 2 repeating units of PVPh per a cycle. On the contrary, the long period of PVPh-NDOA(1.0) mixture (4.26*nm*) is longer than that of NDOA (3.11*nm*) which is slightly larger than the length of fiber axis of octadecyl chain with a planer zigzag conformation. These results are similar to the results for atactic poly(octadecylethylene) as a *comb-shaped* polymer [11]. According to the literatures[10, 11], the presence of short period about 0.4nm is attributed to hexagonal packing of the alkyl side chain. Therefore, in PVPh-NDOA(1.0) mixture, it is predicted that hexagonal packing of the NDOA chains with planer zigzag conformation and fiber axis of PVPh chains with helical conformation lie perpendicular to that of NDOA chains between NDOA layers. However, the crystalline structure of PVPh-NDOA(1.0) mixture evidently include a lot of imperfections because of broaden diffract peak of XRD reflecting an imperfaction of packing of alkyl chains. The imperfection arises from stereo irregular structure of PVPh.

CONCLUDING REMARKS

In DSC measurements, new transition was found in PVPh-NDOA mixture. The new transiton is attributed to the melting of PVPh-NDOA(1.0) aggregate. From XRD, we concluded PVPh-NDOA(1.0) in solid state takes the ordered structure in which alkyl side chains are packing with planer zigzag conformation and fiber axis of PVPh chains lie perpendicular to that of NDOA chains between NDOA layers.

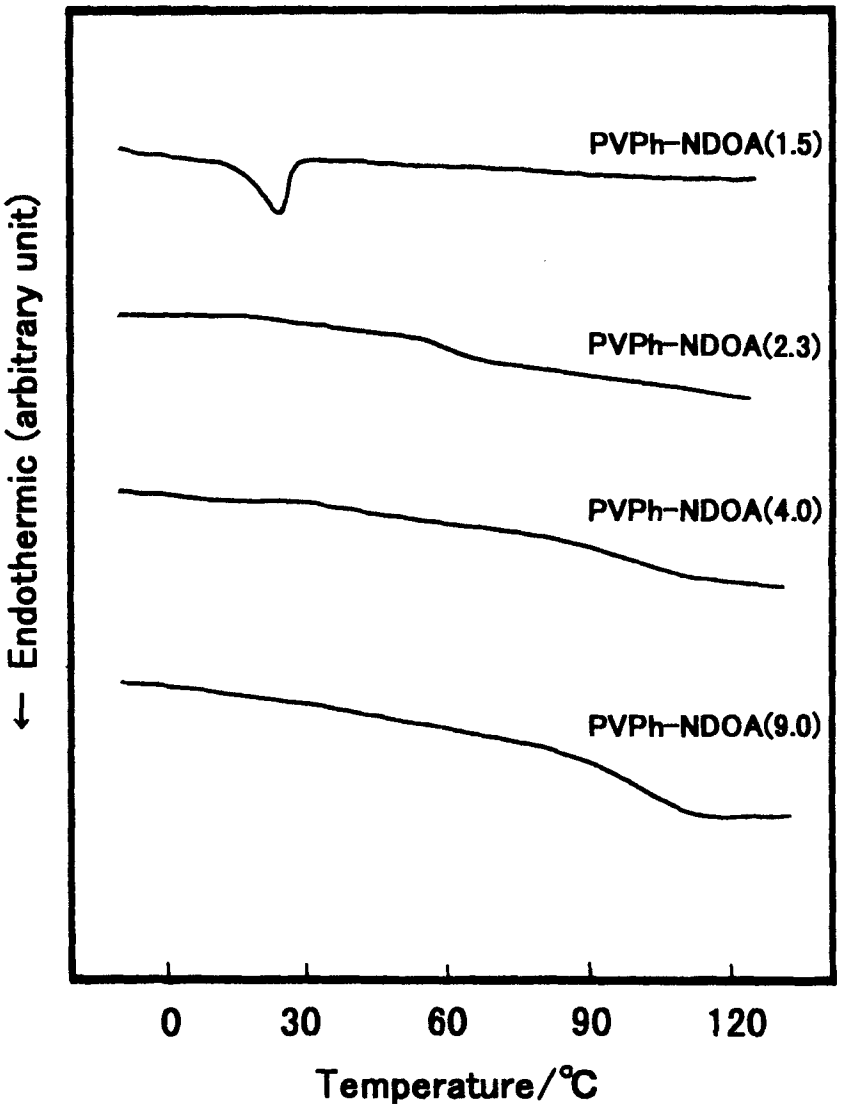

FIGURE 2 DSC thermograms of PVPh – NDOA mixtures including high amount of repeating unit of PVPh against NDOA

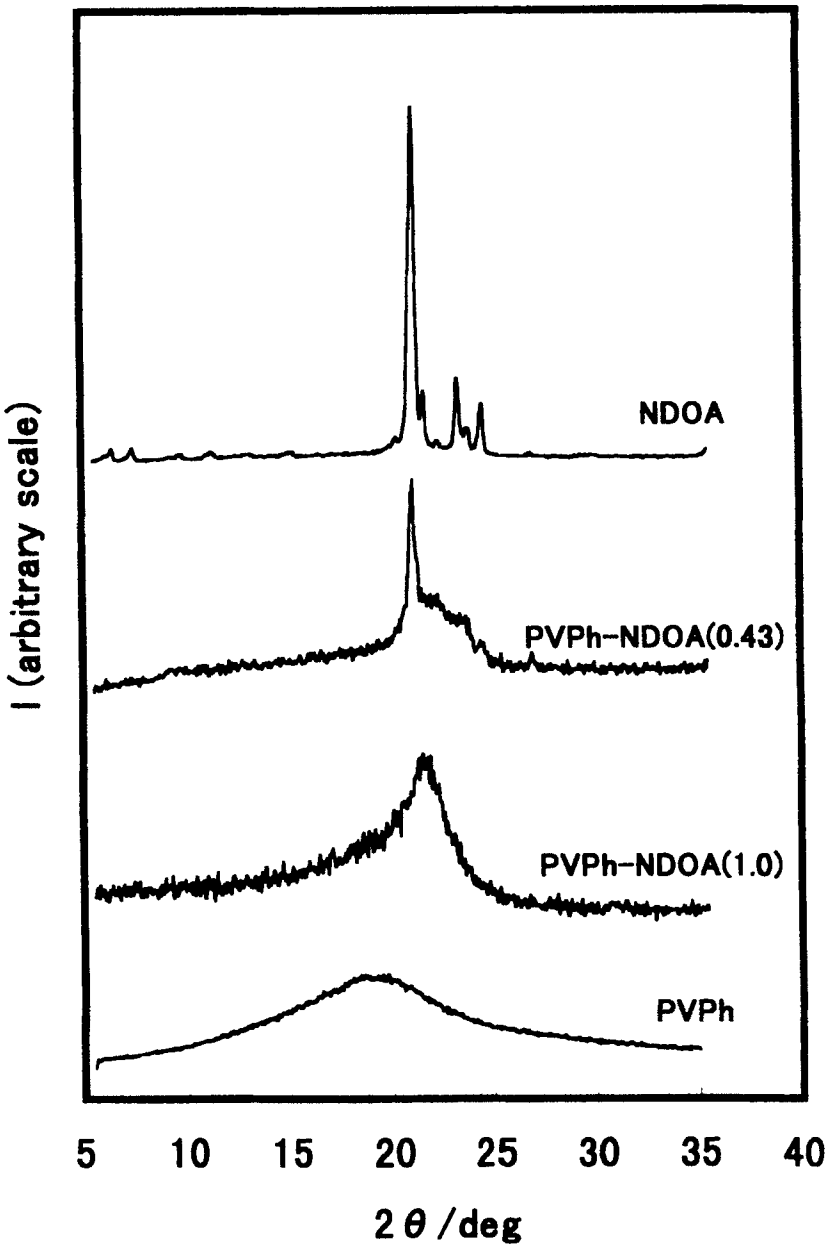

FIGURE 3 X-ray diffraction profiles in wide angle region for PVPh – NDOA mixtures measured at −30°C

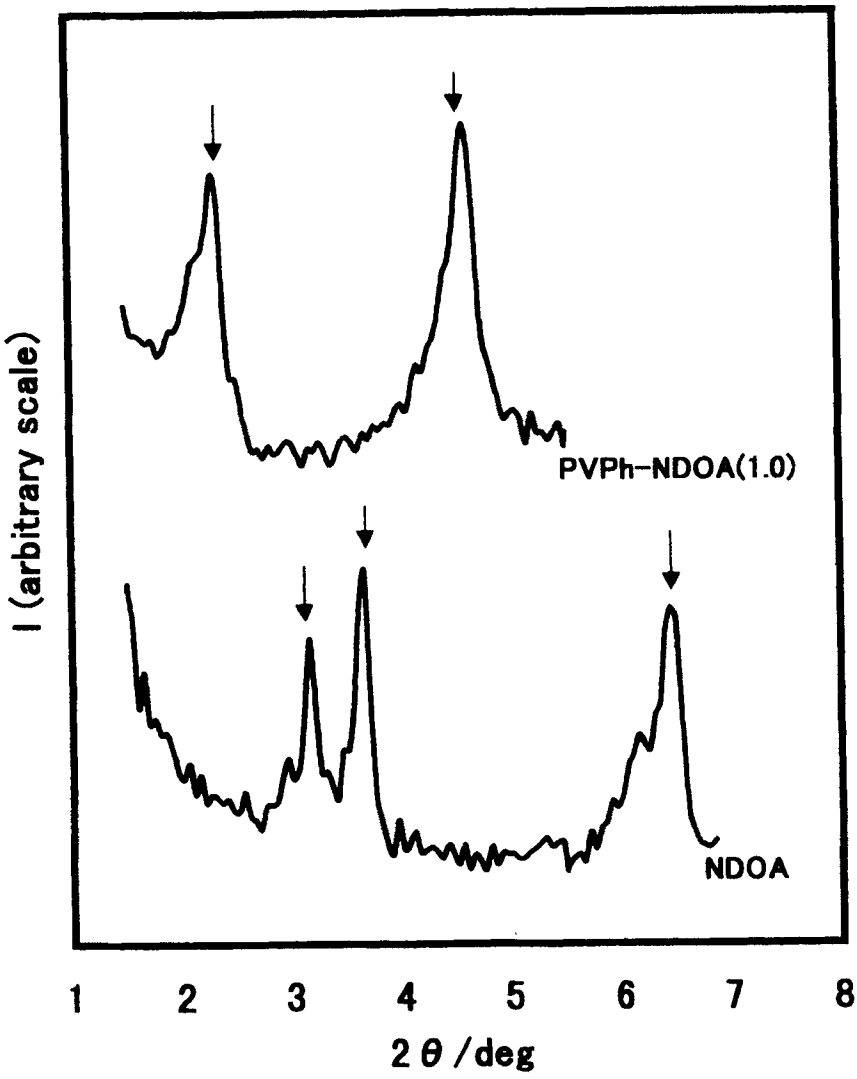

FIGURE 4 X-ray diffraction profiles in small angle region for PVPh – NDOA mixtures measured at −30°C

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