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Spreading Behaviors of Polymers Having Aromatic Chromophores in a Barium Stearate Monolayer and Preparation of the Polymer Langmuir–Blodgett Films

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ABSTRACT: The spreading behaviors of polymers with pendent aromatic chromophores, such as polystyrene (PS), poly(2-vinylnaphthalene) (PVN), and poly(9-vinylcarbazole) (PVCz), in a barium stearate monolayer were studied. The Π–*A* isotherms of the mixed monolayers were measured while varying the mixing molar ratio and the molecular weight of polymers. The isotherms indicate a relatively high miscibility of the polymers with a barium stearate monolayer, although monomolecular dispersion was not obtained. The stable mixed monolayers could be transferred onto solid supports successively by the Langmuir–Blodgett method, and the transfer ratio was equal to one in both downward and upward strokes resulting in Y-type LB films. X-ray diffraction and spectroscopic measurements were carried out with those LB films. Fluorescence measurements reveal that an energy migration occurs freely in the LB films.

Introduction

Monolayers and Langmuir–Blodgett (LB) multilayers which are prepared from amphiphilic compounds have been long studied with an interest in their interfacial properties[1–3] and as a model for physicochemical studies.[4–9] Recently the LB film has been considered as a potential candidate for application to functional devices.[10,11] The LB method has some remarkable advantages which cannot be obtained with organic compounds by other methods; the LB film provides uniform and homogeneous films with a thickness of less than 10 nm; moreover, a well-defined molecular orientation can be achieved by the LB technique. Many attempts to fabricate a highly functionalized LB film have been carried out on the basis of these advantages. For example, the uniform thin LB film is used as an insulator in MIS (metal–insulator–semiconductor) devices;[12–14] a piezoelectric device[15] is based on the molecular orientation of the LB film, and photo and electron beam resists[16–18] are based on both the advantages. However, these LB films with low molecular amphiphilic compounds have poor stability for application to practical devices. In order to improve the stability, efforts to prepare polymerized LB films have proceeded. Two main methods have been investigated; one is polymerization of LB films prepared from polymerizable amphiphilic monomers.[19–22] The other is the preparation of LB films with preformed amphiphilic polymers[23,24] or copolymers.[25,26]

In this paper, we report an attempt to incorporate well-known vinyl aromatic polymers, i.e., poly(9-vinylcarbazole), poly(2-vinylnaphthalene), and polystyrene, into an LB film in the form of a mixed monolayer with a fatty acid and discuss the dispersion of the polymers in the monolayer.

Experimental Section

Poly(9-vinylcarbazole) (PVCz), poly(2-vinylnaphthalene) (PVN), and polystyrene (PS) were prepared in benzene by free radical polymerization at 60 °C with 2,2′-azobis(isobutyronitrile) as a thermal initiator. The polymers were purified by several reprecipitations. Molecular weights of the polymers were measured on a Toyo Soda GPC. Distilled and deionized water was used. Chloroform used for spreading on the water surface was of fluorescence spectroscopy grade. Quartz slides on which the LB film was deposited were cleaned in boiling H_2SO–HNO_3 (2:1) solution and made hydrophobic with dimethyldichlorosilane. The surface pressure–area (Π–*A*) isotherms were measured with an automatic Langmuir trough (Kyowa Kaimen Kagaku HBM-AP using a Wilhelmy type film balance). Fluorescence spectra and X-ray diffraction measurements were carried out by a Shimadzu RF 503A spectrofluorophotometer and a Shimadzu VD-1 X-ray powder diffractometer, respectively.

Results and Discussion

Spreading Behaviors of Aromatic Polymers in a Barium Stearate Monolayer. A chloroform solution of a polymer and stearic acid mixture was spread onto the surface of water which contains 3×10^{-5} M $BaCl_2$ and 5×10^{-4} M $KHCO_3$. Figure 1 shows Π–*A* isotherms at 17 °C for the mixture of PVCz ($M_n = 3000$) and stearic acid in various molar ratios of the monomer unit and the acid. All the isotherms showed a monotonous increase of surface pressure up to a collapse pressure with compression, except for a slight bending around 10 mN/m. The collapse pressure varied systematically with the molar ratio, which suggests a relatively good miscibility of both components (PVCz and stearic acid). When phase separation into a polymer phase and a barium stearate phase is occurring, the isotherms should have two collapse states, being due to the collapse pressure of each phase. The average limiting surface area was estimated from the isotherms by extrapolating the steep rising of surface pressure (20–40 mN/m) to zero surface pressure. The average limiting areas obtained were all below 0.2 nm^2/molecule which is the limiting area of stearic acid, and the change in area with mixing molar ratio is shown in Figure 2. The plots deviated positively from the additivity line. In general, a negative deviation from additivity is seen in good miscible systems due to intermolecular interactions, and an additivity rule is held in the case of either an ideal mixing system or a perfect immiscible system.[27] Positive deviation is thought to occur in thermodynamically unstable systems. However, the example of such a case is not common in literatures and sufficient discussions for it have not been made.[28,29] The positive deviation in the present case is not attributed to the phase separation into a large polymer domain and a barium stearate phase, because the collapse pressure of the mixed monolayer changes with the mixing molar ratio, not having two collapse states. The positive deviation from additivity seems to be due to a change of the spreading form of the polymer chain. The surface area per PVCz monomer is calculated at various mixing ratios by assuming the area of stearic acid to be constant at 0.2 nm^2/molecule. The areas obtained were several times smaller than the value derived from CPK molecule models

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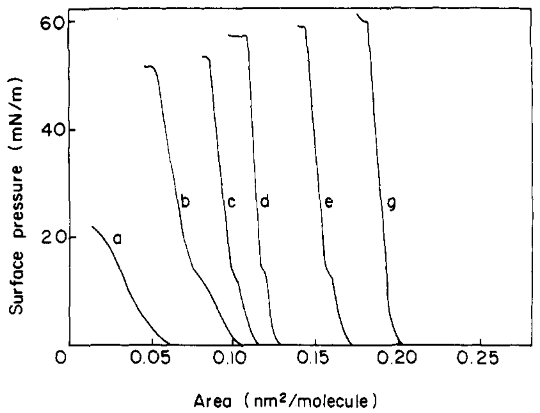

Figure 1. Surface pressure-area isotherms of PVCz (M_n = 3000)-barium stearate mixed monolayers. Subphase 3×10^{-5} M $BaCl_2$, 5×10^{-4} M $KHCO_3$. PVCz monomer unit:stearic acid = (a) 1:0; (b) 4:1; (c) 2:1; (d) 1:1; (e) 1:2; (g) 1:10.

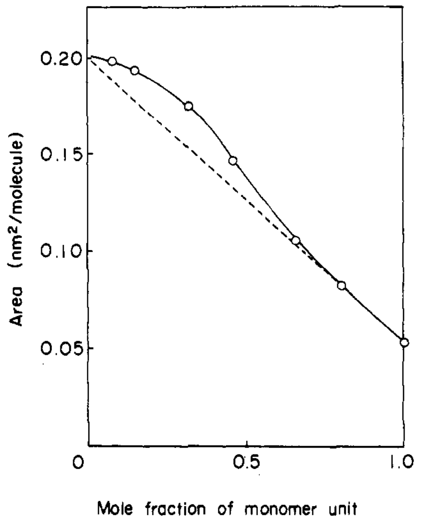

Figure 2. Plots of the average limiting surface area versus mole fraction of PVCz monomer unit for PVCz-barium stearate mixed monolayers.

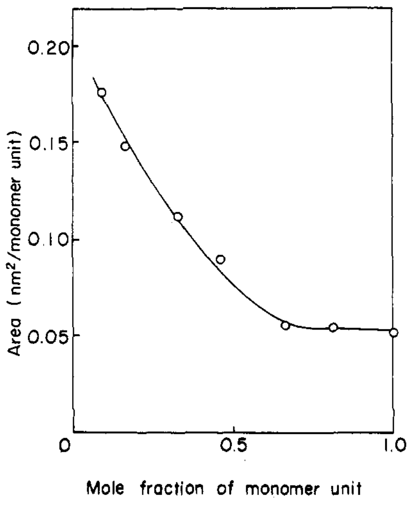

Figure 3. Plots of the surface area of PVCz (M_n = 3000) monomer unit versus the mole fraction of PVCz monomer unit for PVCz-barium stearate mixed monolayers.

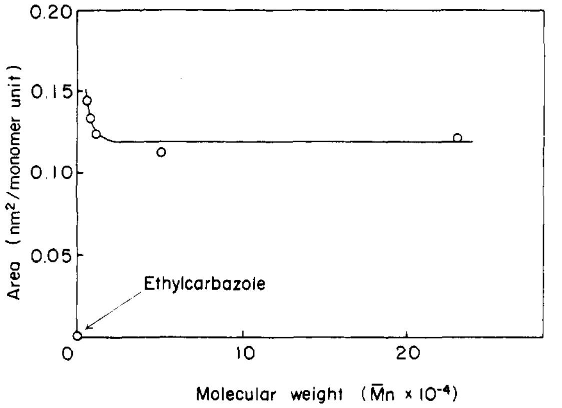

Figure 4. Dependence of the surface area of the PVCz monomer unit on molecular weight.

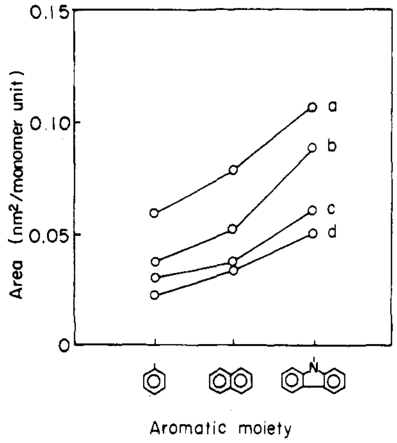

Figure 5. Change of surface area of monomer unit by pendent aromatic chromophore at various mixing ratios. Monomer unit:stearic acid = (a) 1:5; (b) 1:2; (c) 1:1; (d) 1:0.

(0.8–0.3 nm²/molecule), indicating a folded form of polymer chains as the spreading form. On the other hand, ethylcarbazole which is the model compound of PVCz has no surface area on the water surface (Figure 4). The polymer structure assists the spreading of the polymer on the water surface. As can be seen from Figure 3, the surface area of the polymer increases with decreasing concentration of the polymer in the mixture, that is, the polymer chain becomes an expanded form by dilution with stearic acid.

The influence of the molecular weight of the polymer on the surface area was investigated. The surface area per PVCz monomer unit with various molecular weights was measured at a fixed mixing molar ratio (PVCz monomer unit:stearic acid = 1:5) (Figure 4). It is noteworthy that the limiting surface areas per monomer unit were nearly constant for the polymers with molecular weight larger than 10^4. This means that the polymers have a similar spreading form in barium stearate monolayer at a fixed concentration of monomer unit irrespective of the molecular weight.

The spreading behaviors of polystyrene and poly(2-vinylnaphthalene) in a barium stearate monolayer were also examined. The Π–A isotherms for the mixed monolayers of the polymers and barium stearate were similar to those for PVCz. Figure 5 shows the change of the surface area by the pendent aromatic moieties at several mixing molar ratios. The areas increased in the order PS < PVN < PVCz at a fixed molar ratio, which agrees with the order of the size of the aromatic moieties, i.e., phenyl < naphthyl < carbazolyl, indicating that the spreading behavior is determined by the monomer structure and the mixing molar ratio. Conclusively, these polymers have a relatively high miscibility with barium stearate monolayer on the water surface.

Formation of Multilayers. The stable polymer mixed monolayers were transferred successively onto solid supports in both downward and upward strokes (Y-type de-

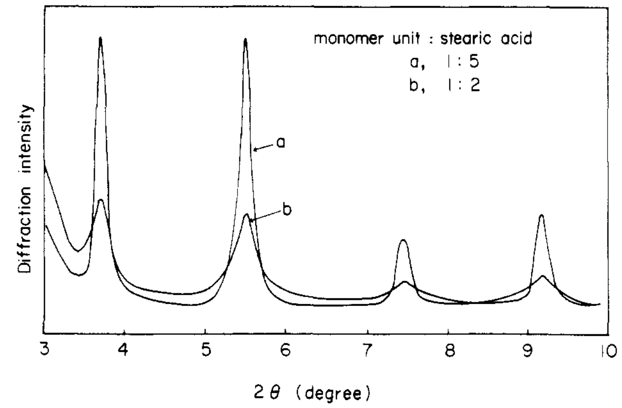

Figure 6. X-ray diffraction patterns for barium stearate mixed monolayer with PVN. Monomer unit:stearic acid = (a) 1:5; (b) 1:2.

position) by the Langmuir–Blodgett method. The transfer ratio was almost equal to 1.0 at a dipping velocity of 5 mm/min, even at high polymer concentration (monomer unit:stearic acid = 1:1). Moreover, the mixed monolayer with a greater polymer content (monomer unit:stearic acid = 4:1) could be deposited; however, the LB film became turbid with several tens of layers. Small-angle X-ray diffraction measurements were carried out with the LB films deposited on quartz slide at about 40 layers, varying the mixing molar ratios. The diffraction pattern for the LB film with a lower polymer content (monomer unit: stearic acid = 1:5) is the same as that of a pure barium stearate LB film (Figure 6). By increasing the polymer content up to a mixing ratio monomer unit:stearic acid = 1:2, the diffraction intensity decreased; however, the diffraction angles were not changed, keeping one spacing which corresponds to twice the monolayer thickness (Figure 6).

Photochemical Measurement. In order to examine a dispersion of the polymers in an LB film, photochemical measurements of the polymer LB films were carried out in the case of PVCz. The absorption spectra of PVCz in the LB film agreed with that in a solution. On the other hand, no absorption spectrum was obtained in an LB film deposited from the mixed monolayer of ethylcarbazole, which is a monomer model of PVCz. This is consistent with the results of spreading behaviors described in the preceding section. The fluorescence spectrum of PVCz in an LB film was compared with that in a polystyrene matrix and in a solution. As a probe polymer, PVCz with a molecular weight of 3000 was used. The fluorescence spectra of the PVCz in a solution (2×10^{-4} M in chloroform) shows a maximum peak at around 370 nm corresponding to the monomer band and a shoulder above 400 nm corresponding to the excimer band[30,31] (Figure 7). In the polystyrene matrix, the emission intensity ratio of the excimer to the monomer emission varied with the mixing ratio (Figure 7). In the LB film, however, the ratio was almost unchanged with mixing ratio (Figure 8). The spectrum consists of predominantly excimer emission even in more diluted condition with a mixing ratio of monomer unit:stearic acid = 1:25. In general, the excimer formation of a polymer in a solid state is thought to occur mainly by an intramolecular and intermolecular energy migration, since the conformation change to produce an excimer form is restricted. The change of intensity ratio of the excimer to the monomer emission with the mixing ratio in polymer matrix can be interpreted by an intermolecular energy migration. The intense excimer emission in the LB film suggests that the energy migration occurs efficiently. The polymer has a favorable conformation to energy migration in the LB film, supporting the high miscibility of the polymers in the barium stearate monolayer.

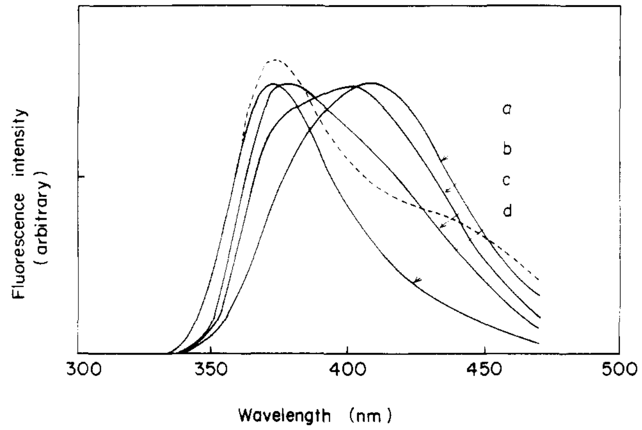

Figure 7. Change of fluorescence spectra of PVCz ($M_n = 3000$) in polystyrene matrix with mixing molar ratio. PVCz monomer unit:polystyrene monomer unit = (a) 1:0; (b) 1:1; (c) 1:5; (d) 1:20. Dotted line shows a fluorescence spectrum of PVCz in chloroform solution (2×10^{-4} M).

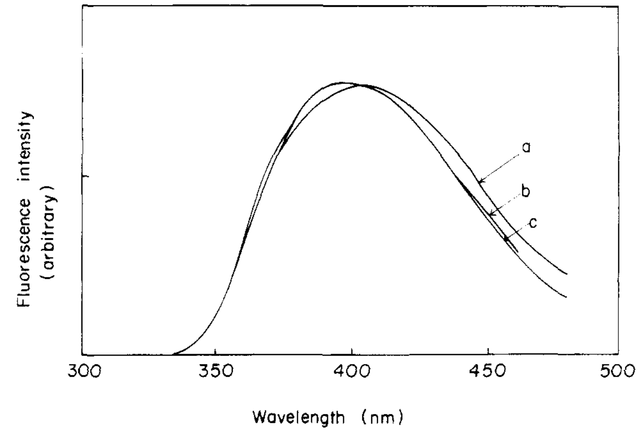

Figure 8. Change of fluorescence spectra of PVCz (M_n = 3000)–barium stearate mixed monolayer with mixing molar ratios. PVCz monomer unit:stearic acid = (a) 1:1; (b) 1:5; (c) 1:25.

In conclusion, a conventional aromatic vinyl polymer could be dispersed in a barium stearate monolayer. The mixed monolayers are stable even if the polymer concentration is considerably high and could be transferred onto solid supports successively. Fluorescence study suggests that the energy migration along aromatic moieties occurs freely in the LB film. A functional thin film using various functional polymers would be obtained easily by the method described here.

Registry No. PS, 9003-53-6; PVN, 28406-56-6; PVCz, 25067-59-8; barium stearate, 6865-35-6.

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Macromolecules **1989**, *22*, 2709-2720 **2709**

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Entanglement Scaling in Polymer Melts and Solutions

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ABSTRACT: In this paper, we develop several universal scaling laws for molecular entanglements in polymer melts and solutions and compare our predictions against experimental data. The model used here is a generalization of our previous work where entanglements were described by a universal topological parameter, $\tilde{N}$. Predictions for the mean entanglement spacing as a function of the polymer chemical and structural properties were found to be in good agreement with experimental data. The model also predicts a transition from entangled chains to unentangled chains at a degree of polymerization, N_c, that correlates well with values determined from steady-state compliance measurements. The model transition is shown to be analogous to the liquid–gas critical point predicted by the van der Waals equation of state and leads directly to departures from the reptation theory scaling laws for shear viscosity without invoking new mechanisms. Scaling laws are developed for entanglements in solution and are in good agreement with experimental data. Predictions made for the onset of entanglement effects in solution closely parallel earlier work on chain overlap by de Gennes. A relationship between the overlap threshold density and entanglement threshold density is predicted in terms of the parameter $\tilde{N}$.

1. Introduction

The reptation or tube model of de Gennes[1] and Doi and Edwards[2] has provided the framework for understanding many of the transport and mechanical properties of entangled polymers both in the melt and in solution. The model, which builds on earlier work on rubber elasticity,[3] assumes the presence of a certain average number of entanglements per polymer chain. Using the noncrossability of chains, a kinetic equation was developed to describe the evolution of the polymer conformation. This equation described the polymer as evolving in a tube formed by the surrounding chains. The degree of entanglement amongst chains was described by a phenomenological parameter, N_e, which represents the mean number of polymer skeletal bonds between entanglements. A relationship between N_e and the polymer properties was not given.

A quantitative description of molecular entanglements and their interactions is still one of the more challenging problems in polymer physics. The difficulty of topological classification of entanglements is compounded by the mathematical difficulty of describing the entanglement interaction. A "first-principles" derivation of the reptation theory perhaps hinges on developments along these lines. Such a theory would merge continuously with the Rouse theory for short chains and also describe the transition from the highly entangled state to the unentangled state. A missing element thus far has been a mathematical criterion for describing entanglements.

Despite the absence of a unifying theory, significant progress has been made toward understanding the shortcomings of the reptation theory in the transition region. For example, Graessley[4] has shown that the tube renewal process can effectively compete with reptation for finite length chains. Improved agreement between experiment and theory was observed when a tube renewal effect was considered. The original tube renewal model, however, lacks self-consistency. For example, the nonreptative corrections applied to the test chain are derived assuming bare reptation dynamics for the surrounding chains. This feature makes the model unsuitable for describing the dynamics near the transition. Perhaps an iterative procedure would improve the model in this regime.

Doi[5] recognized that tube length fluctuations can be important for finite length chains and proposed a model for incorporating this effect in the reptation theory. Doi's solution of the length fluctuation model included a variational parameter that could quantitatively account for departures from the $\eta_0 \sim M^3$ power law. Des Cloizeaux's[6] in-depth analysis of a similar model concluded that the effect of length fluctuations is not as large as Doi had predicted.

Recently, Hess[7] has taken a more fundamental approach. Starting with a Fokker–Planck equation, for the phase space distribution function for all polymer segments,

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