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Spreading Behavior of Short-Branched *N*-Alkylacrylamide Polymers and the Formation of Langmuir−Blodgett Films

Tatsuo Taniguchi, Yoshiyuki Yokoyama, and Tokuji Miyashita*

Institute for Chemical Reaction Science, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-77, Japan

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ABSTRACT: The spreading behavior of poly(*N*-alkylacrylamides) with short-branched alkyl substituents (isobutyl (p*i*BA), *tert*-butyl (p*t*BA), isopentyl (p*i*PA), *tert*-pentyl (p*t*PA), and *neo*pentyl (p*N*PA)) on the water surface was investigated by measurement of surface pressure (π)−area (A) isotherms. These isotherms showed that condensed monolayers are formed for all the short-branched alkylacrylamide polymers. Branched alkyl substituents in the alkylacrylamide polymers were found to be more suitable to formation of a stable monolayer than are straight alkyl substituents with the same chain length that had been investigated in a previous study. The condensed polymer monolayers can be transferred successively onto solid supports by both downward and upward strokes, yielding Y-type uniform polymer LB films. Film thickness was measured by X-ray diffraction measurement. The quality of the polymer LB films deposited onto glassy carbon electrodes was estimated by means of cyclic voltammetry of the redox couple of potassium ferri- and ferrocyanide in aqueous solutions.

Introduction

Langmuir−Blodgett (LB) films have recently received much attention as functional ultrathin films.[1,2] The LB technique provides uniform films with controlled thickness and well-defined molecular orientation. Thus far, LB films have been prepared with amphiphilic compounds, such as long-chain fatty acids and dyestuffs with long hydrocarbon chains. These LB films, however, have poor stability with respect to mechanical and thermal treatment or poor resistance to dissolution by organic solvents. In an effort to overcome these drawbacks, polymer LB films have been investigated extensively.[3−6]

A previous study found that *N*-dodecylacrylamide polymer (pDDA) forms a stable monolayer on the water surface and stable LB film.[7−9] Moreover, the present authors have proposed a copolymerization method to incorporate various functional groups into the polymer LB films with the help of the excellent properties of pDDA.[10−13] Electron-transfer and energy-transfer processes in a layered structure of LB films are known to depend on the distance between donor and acceptor molecules in the layer structure,[14−16] wherein long alkyl chains often constitute a disadvantage in acting as a barrier to electron transport. A layer structure with various distances, especially short distances, is required for the design of various functional molecular-organized assemblies.

In the present study, the properties of short branched *N*-alkylacrylamide polymer monolayers and the formation of the LB films were investigated. The layer structure and the quality of the polymer LB films were also investigated by XRD measurement and cyclic voltammetry, respectively.

Experimental Section

Materials. All *N*-alkylacrylamide (alkyl substituents: *tert*-butyl (*t*BA), *tert*-pentyl (*t*PA), isopropyl (PrA), isobutyl (*i*BA), isopentyl (*i*PA), neopentyl (*N*PA), and dodecyl (DDA)) monomers were synthesized in dichloromethane by the reaction of acryloyl chloride and corresponding alkylamines in the presence of triethylamine. *t*BA, *t*BA, and DDA monomers were purified by column chromatography and recrystallization. *i*BA, *i*PA, and *N*PA monomers were purified by distillation under reduced pressure.

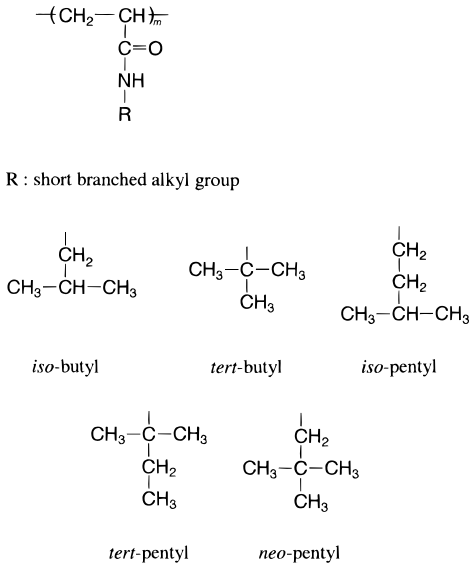

Chart 1. Chemical Structures of Short-Branched Alkylacrylamide Polymers

Poly(*N*-alkylacrylamides) with various alkyl substituents (Chart 1) were prepared in benzene at 60 °C by free-radical polymerization of *N*-alkylacrylamide monomers with AIBN as a thermal initiator. The polymers were purified by dissolution in chloroform, filtering, and precipitation into a large excess of *n*-hexane or acetonitrile and were subsequently dried under vacuum at room temperature. The molecular weights and polydispersities for P*t*BA, P*t*PA, P*i*BA, P*i*PA, and P*N*PA are 8.3×10^4 ($M_w/M_n = 1.53$), 9.9×10^4 (1.6), 12.3×10^4 (2.2), 12.9×10^4 (1.61), and 9.4×10^4 (1.73), respectively.

Monolayer and Multilayer Formation. Measurement of the surface pressure (π)−area (A) isotherms and deposition of the monolayers was carried out with an automatic Langmuir trough (Kyowa Kaimen Kagaku HBM-AP using a Wilhelmy-type film balance) at a compression rate of 14 cm^2/min. Distilled, deionized water was used for the subphase of the polymer monolayers. On the deposition of barium stearate monolayer, the subphase contains $BaCl_2$ (3.0×10^{-4} M) and $KHCO_3$ (3.0×10^{-4} M). Chloroform used for spreading the monolayer on the water surface was of spectroscopic grade. Quartz slides for the deposition of the monolayers were

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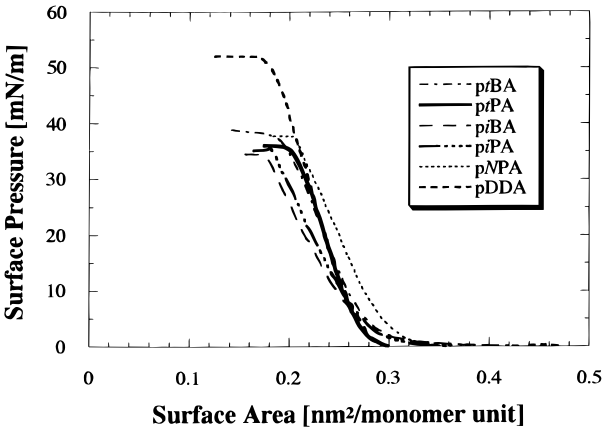
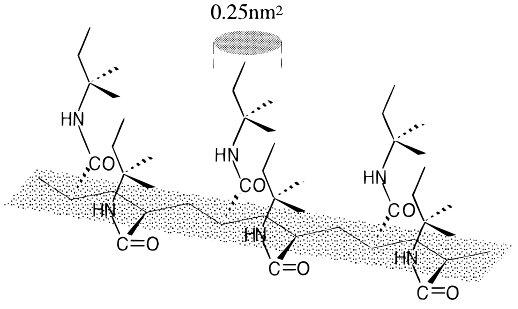


Figure 1. Surface pressure (π)−area (A) isotherms of poly(*N*-alkylacrylamide) on the air−water interface at 20 °C.

Chart 2. Molecular Conformation of p*t*PA Monolayer on the Water Surface



previously cleaned in a boiling HNO$_3$ solution and were made hydrophobic by treatment with trimethylchlorosilane.

Measurement. X-ray diffraction spectra were obtained on a Rigaku X-ray diffractometer RU-200 equipped with a copper anode operating at 40 kV and 30 mA as the X-ray source (wavelength λ = 1.542 Å). A counter monochromator of graphite was used to reduce the peak noise in XRD measurement. Potentiostatic control of the electrodes was maintained using Hokuto Model HA-501 potentiostat and a Model HB-104 function generator. A conventional Pyrex glass electrochemical cell (50 mL capacity) was used for electrochemical measurement. The counter and reference electrodes were Pt wire and saturated calomel electrode (SCE), respectively. An aqueous solution of 0.1 M Na$_2$SO$_4$ was used as the supporting electrolyte. Oxygen was removed from the solution by the bubbling of N$_2$ gas for 1 h.

Results and Discussion

Monolayer Behavior. Poly(*N*-alkylacrylamides) with various alkyl substituents were spread from a chloroform solution onto pure water. The π−A isotherms at 20 °C for p*t*BA, p*t*PA, p*t*BA, p*i*PA, and p*N*PA are shown in Figure 1, together with that of pDDA. All of the π−A isotherms for the branched polymers show a steep rise in surface pressure, similarly to that of pDDA, whereas the collapse pressure is relatively lower than that of pDDA. Clearly, the short-branched alkylacrylamide polymers form stable and condensed monolayers on the water surface in the same manner as does pDDA. The limiting surface area per monomer unit of the polymers is determined by extrapolating the linear portion of the steep rise in the π−A isotherms to zero surface pressure. For the short-branched *N*-alkylacrylamide polymers, the surface area per monomer unit is approximately 0.28 nm^2. A series of previous studies by the present authors investigated the spreading behavior of poly(*N*-alkylacrylamide) with various straight alkyl chains, from hexyl to octadecyl, on the water surface. Alkylacrylamide polymers having alkyl chains longer than octyl were found to form a stable monolayer, and pDDA was found to form the most stable condensed monolayer. Interestingly, the branched alkyl chain was found to be more suitable for monolayer formation than are straight alkyl substituents that have the same chain length. The surface area for *N*-alkylacrylamide polymer as calculated from the CPK model, wherein the polymer main chain is laid on the water surface horizontally and the alkyl substituent is oriented perpendicular to the chain, is estimated to be in the range of 0.24−0.32 nm^2/monomer unit. Chart 2 shows the possible molecular conformation for the monolayer of p*t*PA polymer on the water surface.

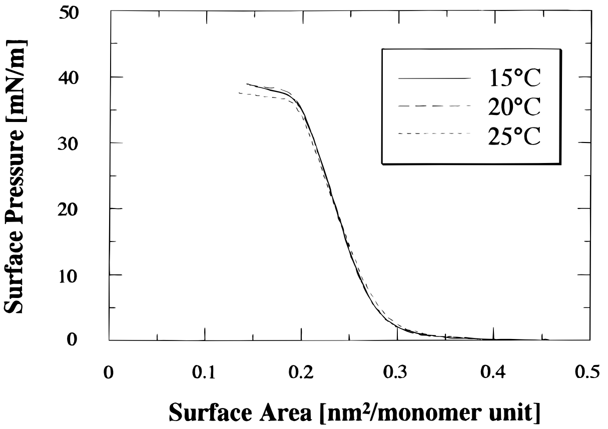


Figure 2. Surface pressure (π)−area (A) isotherms of poly(*N*-alkylacrylamide) at various subphase temperatures.

The effect of subphase temperature on monolayer behavior was also investigated based on the π−A isotherms. Figure 2 shows as a typical example the π−A isotherms of the p*t*PA monolayer at various subphase temperatures. No significant dependence of the π−A isotherms on temperature was observed in the present short-branched *N*-alkylacrylamide polymers. In the monolayers of long straight alkylacrylamide polymers, π−A isotherms were observed to change with temperature, in a manner similar to the change of the isotherm with alkyl chain length. In the spreading behavior of fatty acid monolayers, the isotherm changes with temperature are generally known to be very similar to the changes with chain length, and the π−A isotherm change with the addition of one carbon atom to the chain is considered to correspond to the change with an 8−10 °C decrease in temperature of the subphase. These behaviors are attributed to the interaction between hydrocarbon chains, that is, the molecular packing of hydrocarbon chains constitutes a dominant factor for stable monolayer formation. The stability of poly(alkylacrylamide) monomers with straight alkyl chains is governed by the packing of the side alkyl chains. Closer packing of alkyl substituents in the polymer forms more stable condensed monolayers, just like in the case of fatty acid monolayers. In the present polymer monolayers, the short-branched alkyl substituent forms a stable monolayer, and no temperature effect is observed. This indicates that the packing of the side alkyl chains is not such an important factor. The interaction (packing) of polymer main chains, which is regulated by the short-branched alkyl chains, may be a dominant factor for stable monolayer formation. Similar results have been found with respect to the stability of the monolayer of polyglutamate, so-called "hairy-rod" polymers.[17]

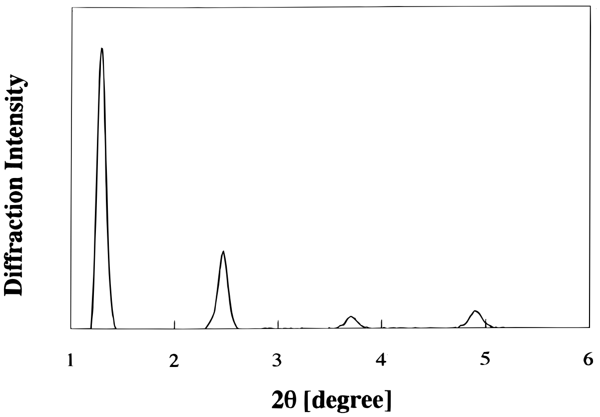


Figure 3. X-ray diffraction patterns of a p*t*PA/BaSt mutual deposition LB film.

The monolayer of the short-branched alkylacrylamide polymers on the water surface can be transferred onto hydrophobic quartz plates by a vertical dipping method. In upward stroke the transfer ratio is almost unity. On the other hand, in downward (deposition on a hydrophobic surface) the transfer ratio is almost unity. Since a cooperative hydrophobic interaction between short-branched alkyl substituents in the polymer side chain is weak relative to that in pDDA, the deposition of the polymer monolayers on a hydrophobic surface would be expected to become less efficient. In the case of the monolayer of p*t*PA, which forms the most stable monolayer, the transfer ratio was measured at various surface pressures. The ratio for p*t*PA monolayer at 15, 20, 25, and 30 mN/m was found to be 0.75, 0.80, 0.85, and 0.87, respectively. Monolayer deposition at higher surface pressure improves the transfer ratio.

X-ray Diffraction Measurements. The layer structure and the film thickness of the branched alkylacrylamide polymer LB film was investigated by X-ray diffraction measurement (XRD). As a typical example, the X-ray diffraction patterns for the p*t*PA LB multilayers are shown in Figure 3. As p*t*PA contains no heavy atoms that could account for the diffraction, the two layers of p*t*PA (Y-type) were sandwiched between two layers of barium stearate (BaSt) by the alternating deposition of two Y-type layers (two strokes of down and up) of BaSt and p*t*PA, respectively. The regular peaks arising from the 1st to 4th diffraction patterns were observed in the region $2\theta = 1-6°$. A diffraction pattern characterized by layer spacing at 68.5 Å was obtained. Considering the BaSt monolayer thickness (24 Å),[18,19] the p*t*PA monolayer thickness is calculated to be approximately 10 Å, which closely agrees with the film thickness estimated from the CPK model, where the alkyl substituent is oriented perpendicular to the water surface.

Electrochemical Measurements for Evaluation of Quality in Polymer LB Film. Apparently, an ultrathin polymer LB film with a thickness 8 Å thinner than that of the pDDA monolayer (18 Å) can be formed on solid supports. The quality of the polymer LB films was investigated by electrochemical measurement. An electrochemical redox reaction, which is readily monitored by cyclic voltammetry, was employed for evaluation of quality. The number of defects in the LB films that cover the electrode surface should be readily evaluated based on the amount of redox peak current, because the redox reaction proceeds only when the electrolyte ion comes in contact with the electrode surface through the defects.[20] The redox reaction between potassium ferr-$[Fe^{II}(CN)_6]^{4-}$ and ferrocyanide $[Fe^{III}(CN)_6]^{3-}$ was employed for the present work.

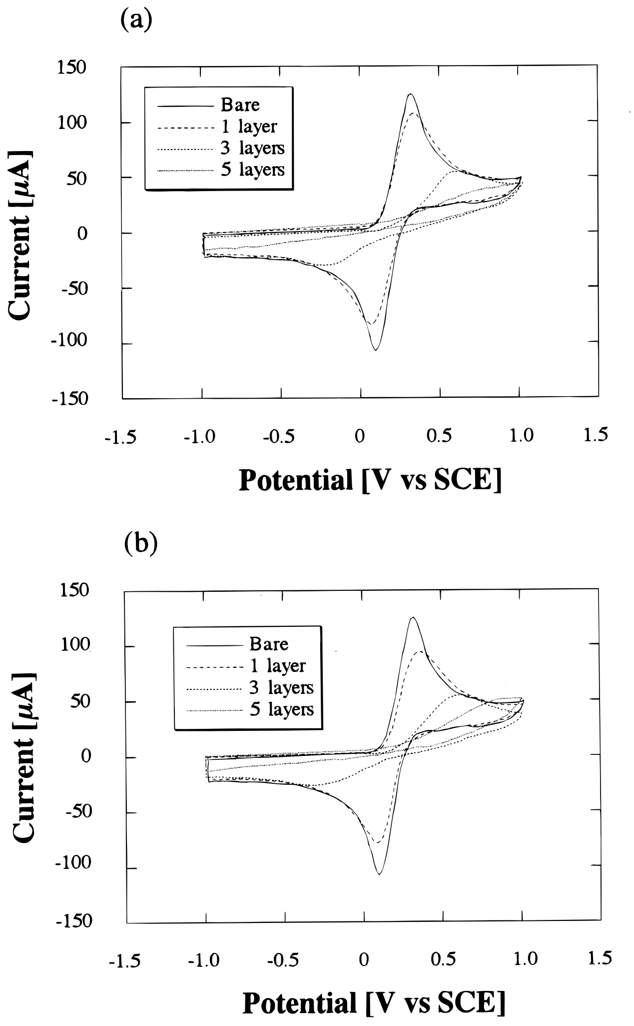


Figure 4. Cyclic voltammogram of a $K_4[Fe(CN)_6]$ aqueous solution: (a) glassy carbon electrode coated with pDDA 0−5 layers; (b) glassy carbon electrode coated with p*t*PA 0−5 layers. $K_4[Fe(CN)_6]$ (1 mM)−KCl (100 mM) aqueous solutions were used as electrolyte. The scan rate was 100 mV/s.

The monolayer of pDDA of p*t*PA was transferred onto a glassy carbon disk electrode, and the current induced by the $[Fe^{II}(CN)_6]^{4-}/[Fe^{III}(CN)_6]^{3-}$ redox couple on the electrode was measured under a nitrogen atmosphere at room temperature as a function of the number of deposited layers (Figure 4). The redox peak current apparently decreases with increasing number of layers, indicating that the redox reaction on the electrode is suppressed by deposition of the LB films. Both pDDA and p*t*PA LB films are of relatively high quality, with a small amount of defects. With over five layers, both polymer LB films can completely restrict the contact of the ferrocyanide ion with the surface of the electrode. Consequently, the branched alkylacrylamide polymer LB films can suppress ion penetration of the redox species at considerably thinner film thickness (total thickness, 50 Å) than can pDDA films (total thickness, 90 Å).

In conclusion, poly(*N*-alkylacrylamides) with short-branched alkyl groups as *N*-substituents, such as isobutyl (*i*BA), isopentyl (*i*PA), *tert*-pentyl (*t*PA), and neopentyl (*N*PA), form condensed monolayers in a manner similar to that of alkylacrylamide polymers with long alkyl chains such as poly(dodecylacrylamide). The monolayers can be transferred onto solid supports in both downward and upward strokes, yielding Y-type polymer LB films. The monolayer thickness of a p*t*PA LB film (1 nm), determined by the X-ray diffraction measurement, suggests that the branched pentyl substituent is oriented nearly perpendicular to the LB surface. The p*t*PA LB films is of high quality, with a small number of defects, and the electrode coated by a p*t*PA LB film with a thickness of 5 nm (five layers) showed no contact with the ferrocyanide redox ion in an aqueous solution.

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