

NOTES

Reactivity Ratios of *N*-dodecylacrylamide in Copolymerization with Methyl Methacrylate and Langmuir–Blodgett Multilayer Formation of the Copolymers

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Langmuir–Blodgett (LB) films have received much attention from the viewpoint of functional ultrathin films.¹ The LB method is one of the best way to prepare thin films with controlled thickness at a molecular size and well-defined molecular orientation.² Many kinds of amphiphilic compounds such as long-chain fatty acids have been investigated and the application to various functional devices has been expected.^{1–3} These LB films, however, have poor mechanical and thermal stabilities, or poor resistance to dissolution by organic solvents.

In order to improve these weakness, many efforts to prepare polymer LB films have been carried out.^{4–11} Generally, it is difficult to prepare polymer LB films, although condensed polymer monolayers are formed on a water surface. Recently, we have succeeded in the preparation of fairly uniform polymer LB films using *N*-alkylacrylamides. First, it was found that *N*-octadecylacrylamide (ODA) forms a stable condensed monolayer, which can be deposited onto solid supports with a transfer ratio of unity. The monomer LB multilayers are polymerized completely by UV irradiation¹² and the possibility of application to a new type of high resolution resist (a deep UV- and EB-sensitive negative resist) has been also indicated.¹³

Secondly, preformed poly(*N*-dodecylacrylamide) (PDDA) also forms a stable condensed polymer monolayer.¹⁴ The PDDA LB film has been used as a permselective membrane for oxygen.¹⁵ Based on this excellent ability of preformed PDDA in polymer LB film formation, we have proposed the method to incorporate various functional groups into polymer LB films in the form of the copolymers of DDA. The copolymers of DDA with *N*-vinylcarbazole¹⁶ and with Ru(bpy)₂(vbpy) (bpy, 2,2'-bipyridine; vbpy, 4-vinyl-4'-methyl-2,2'-bipyridine)¹⁷ formed stable condensed monolayers, yielding the functional polymer LB films.

It is important to know the copolymerization parameters (*Q* and *e*) of DDA monomer to prepare the copolymers with various monomers and to control the monomer sequences or hydrophobic–hydrophilic balance of the copolymers. Some values of *Q*-*e* for *N*-alkylacrylamides have been reported. For example,

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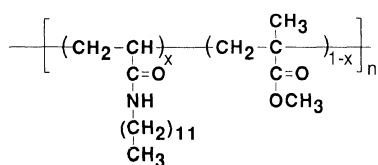


Chart 1.

the values for *N*-octadecylacrylamide (ODA) are reported to be ($Q=0.66$; $e=1.13$),¹⁸ ($Q=0.66$; $e=1.64$),¹⁹ and ($Q=0.28$; $e=0.42$),²⁰ and those for *N*-octylacrylamide (OA) are ($Q=0.18$; $e=-0.10$)¹⁸ and ($Q=0.19$; $e=-0.02$).²¹ The values of $Q-e$ for *N*-alkylacrylamides show a tendency to vary with alkyl chain lengths.²⁰

In this work, the copolymerization parameters of DDA which is of great importance in the series of our works¹²⁻¹⁷ are determined by copolymerization of DDA with methyl methacrylate (MMA). The spreading behavior of the copolymers (Chart 1) on a water surface and the formation of the polymer LB films are also investigated.

EXPERIMENTAL

N-dodecylacrylamide was synthesized by the reaction of acryloyl chloride and dodecylamine in the presence of triethylamine in 1,2-dichloroethane. The product was purified by column chromatography and by recrystallization from *n*-hexane. Radical copolymerization was carried out in benzene at 60°C with 2,2'-azobisisobutyronitrile as a thermal initiator. The copolymers were purified by precipitation from filtered chloroform solution into acetonitrile or methanol and dried under vacuum at room temperature. Molecular weights were determined by a Toyo Soda gel-permeation chromatography (GPC) using a polystyrene standard. The mole fraction of DDA was determined by ¹H NMR and elemental analysis.

The copolymer compositions (Table I) were calculated from the relative intensity ratios

Table I. Copolymerization conditions and molecular weight of polymers^a

No.	Feed	Convsn.	Copolymerization composition	M_n
	DDA mol%	%	DDA mol%	
1	100	10	100	3700
2	80	6.5	60	70000
3	60	5.4	38	80000
4	50	3.8	28	69000
5	40	2.0	20	70000
6	20	3.1	8	68000
7	0	10	0	24000

^a $[\text{AIBN}] = [\text{monomer}]_T \times 10^{-2} \text{ mol l}^{-1}$

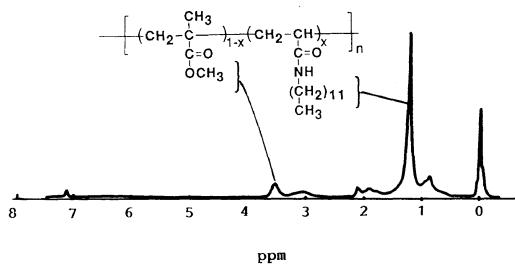


Figure 1. ¹H NMR spectrum of copolymer of DDA ($M_2 = 59 \text{ mol}\%$) and MMA ($M_1 = 41 \text{ mol}\%$).

of the NMR signal due to the methylene (1.2 ppm) of dodecyl substituent to that due to the methyl (3.6 ppm) of ester group (Figure 1). The compositions were also calculated from elemental analysis of the copolymers. Both results were consistent with each other.

The measurement of surface pressure-area isotherms and the deposition of the monolayers were carried out with an automatically working Langmuir-trough (Kyowa Kaimen Kagaku HBM-AP using a Wilhelmy type film balance). Distilled, deionized water was used for the subphase. Chloroform used for spreading monolayer on a water surface was of spectroscopy grade. Glass slides on which LB multilayer was deposited were cleaned in a boiling $\text{H}_2\text{SO}_4\text{--HNO}_3$ (2:1) solution and made hydrophobic with dichlorodimethylsilane.

RESULTS AND DISCUSSION

Copolymerization of DDA with MMA for Q - e Value Determination

DDA monomer (M_2) was copolymerized with MMA (M_1) at various monomer feeds shown in Table I. The relationship between the copolymer composition and the monomer feed is plotted in Figure 2, showing an upward curvature. From the plots by Fineman–Ross method²² (Figure 3), the monomer reactivity ratios were determined to be $r_1 = 1.73$ and $r_2 = 0.52$. Thus, by considering the reported Q - e value for MMA ($Q = 0.78$; $e = 0.40$),²² the Q and e values for DDA can be calculated to be 0.51 and 0.73, respectively. The values are placed between ODA ($Q = 0.66$; $e = 1.13$ ¹⁸ or $Q = 0.66$; $e = 1.64$ ¹⁹) and OA ($Q = 0.18$; $e = -0.10$ ¹⁸ or $Q = 0.19$; $e = -0.02$ ²¹). The calculation by Keler–Tüdös method,²³ which is one of improved method of Fineman–Ross method, gave also a similar result ($r_1 = 1.67$; $r_2 = 0.58$).

In general, homologous series of vinyl monomers with linear side alkyl chain shows similar reactivity in copolymerization. Reactivity ratios for octadecyl acrylate and shorter alkyl acrylates with methyl methacrylate were reported to be similar. In *N*-alkylacrylamide series, the values of Q and e increased with alkyl chain length, that is, the acrylamides with longer alkyl substituents showed more electron withdrawing properties and the derived radicals are more stable. It is not clear at the present work why the effect of alkyl chain length on the reactivity ratio appears in the *N*-alkylacrylamide series, whereas the effect is lacked in alkyl acrylate series. The Q (0.51) and e (0.73) values show that DDA is a conjugated monomer and will undergo easily radical copolymerization with electron-donating and conjugative comonomers. From the value of $r_1 \cdot r_2 = 0.9$, the DDA copolymers with MMA show a poor tendency for alternating copolymerization. In the following section, the monolayer properties of the copolymers are

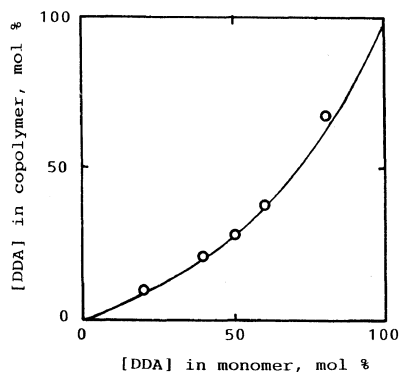


Figure 2. Relationship between monomer feed and copolymer composition.

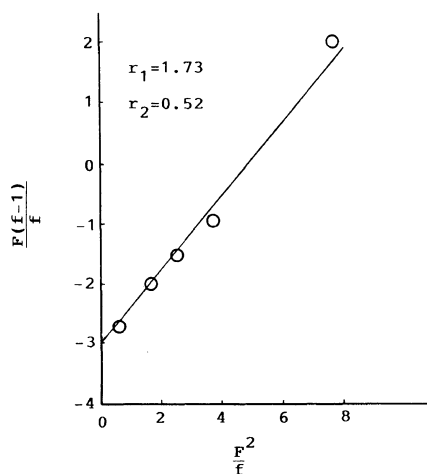


Figure 3. Determination of reactivity ratios for DDA by Fineman–Ross method [$F(f-1)/f = r_1 F^2 / \bar{f} - r_2$; F , monomer feed ratio; \bar{f} , copolymer composition ratio.]

investigated.

Monolayer Behavior of the Copolymers and LB Multilayer Formation

The surface pressure–area isotherms for the copolymers with various copolymer compositions which were spread on a water surface from chloroform solutions are shown in Figure 4. The isotherms change with MMA mole fraction: the collapse pressure decreases and the slope of the rise in surface pressure also becomes less steep with the MMA content. This indicates that the copolymer

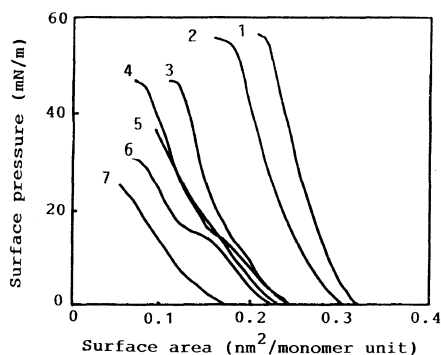


Figure 4. Surface pressure-area isotherms for poly-(DDA-co-MMA). Sample number corresponds to that in Table I.

monolayers become unstable by introduction of MMA monomer. The limiting surface areas were estimated by extrapolating the isotherms to zero surface pressure. The surface for MMA monomer unit in the copolymer monolayers was calculated to be *ca.* 0.15 nm^2 by assuming that the surface area for DDA monomer unit is 0.28 nm^2 .¹⁴ The area of about $0.15 \text{ nm}^2/\text{monomer unit}$ coincides with the isotherm of PMMA homopolymer, indicating that the copolymers of DDA with MMA have no coiled or folded form on the water surface. In general, the polymer monolayer can be divided into a condensed monolayer and an expanded monolayer class.²⁵ Both PDDA and PMMA [poly(methyl methacrylate)] monolayers are classified into the condensed monolayer from each homopolymer's isotherm. PDDA monolayer could be deposited onto solid supports with a transfer ratio of unity¹⁴ but PMMA monolayer could not be deposited onto the solid supports at all.

A recent study on the monolayer behavior of PMMA indicates that the monolayer property of PMMA is strongly dependent on the tacticity.²⁶ The isotactic PMMA monolayer could be transferred to substrates, giving a strongly oriented, highly crystalline thin film.²⁷ PMMA in this work is atactic and was not deposited. The copolymers with DDA, however, could be transferred onto a solid

support with a help of excellent property of DDA for LB film formation. The monolayers of the copolymer up to MMA mole fraction of 0.80 could be transferred onto a solid support by both down and up strokes with a transfer ratio of unity. Moreover, even the copolymer with 0.93 mol fraction could be transferred onto a solid support with both down and up strokes with a transfer ratio of *ca.* 0.6. In the previous work,²⁸ it was found that the copolymers of DDA with styrene give a stable condensed monolayer up to 0.6 mol fraction of styrene. From the reactivity ratios, the styrene copolymers ($r_1 \cdot r_2 = 0.097$) have an alternation tendency more than the MMA copolymers ($r_1 \cdot r_2 = 0.9$). The alternation nature in the styrene copolymers is favorable for stable monolayer formation, because long hydrophobic monomer sequences (styrene blocks) tend to take a coiled or folded form of the polymer chain on a water surface. Since MMA molecule has an amphiphilic nature, even the copolymers having long MMA sequences appear to form a condensed monolayer.

In conclusion, the copolymerization parameters of DDA, which has an excellent ability to prepare a stable monolayer and LB multilayer in the form of polymer, were determined in this work. The Q and e values indicate that DDA monomer tends to copolymerize with various comonomers *via* radical polymerization. It is expected that various comonomers can be incorporated into DDA polymer *via* usual radical copolymerization and the various functional polymer LB films are prepared.

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