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Improved Stability of a Polyion-Complexed Monolayer of a Maleic Acid Copolymer by Using Alkoxyethyldimethylamines as Hydrophobic Counterparts at the Air-Water Interface

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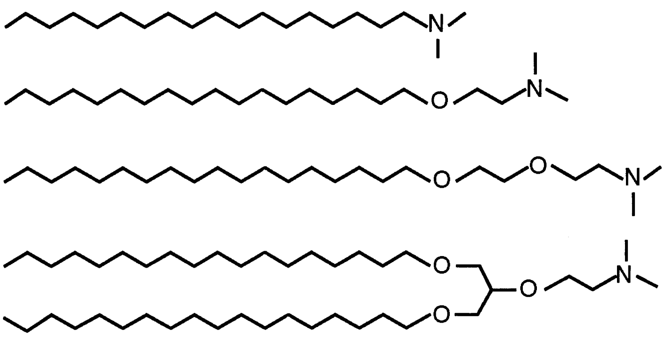
Amphiphilic tert-amines, 2-(dimethylamino)ethyl octadecyl ether(C_{18}ODA), 2-(dimethylamino)ethyl octadecyl ethylene glycol diether($C_{18}O_2$DA), and 1,3-dioctadecyl-2-(2-(N,N-dimethylamino)ethyl) glyceryl triether (2$C_{18}O_3$DA), were synthesized and employed as hydrophobic counterparts for spreading a water-soluble copoly(maleic acid-methyl vinyl ether) by polyion complexation at the air-water interface. The amines stabilized the monolayers with the order of 2$C_{18}O_3$DA > C_{18}ODA > $C_{18}O_2$DA > N,N-dimethyloctadecylamine. The stabilized monolayer could be transferred on solid substrates.

The formation of polyion complex at the air-water interface has broadened the scope of materials which can be used for monolayer formation, and it has opened the possibility to prepare LB films with various functionalities.[1)] For example, water-soluble polymers such as potassium poly(styrenesulfonate)[2)], polyamines[3)], polyammonium salts[3)], and poly(ethyleneimine)[4)] could be incorporated into LB film by attaching electrostatically with the low molecular weight hydrophobic counterparts. Thin films of poly(imide)[5)] and poly(arylenevinylene)[6)] were prepared by the LB method by fixing electrostatically hydrophobic amines to the precursor polymers which, by themselves, are incapable of monolayer formation. We have reported formations of salt bridges between a polymerized ammonium monolayer and an anionic polymer at the air-water interface[7)] and of two-dimensional polymer network of LB films of a polyamine-polycarboxylate salt.[8)]

When polyamic acids were spread with the hydrophobic amines such as N,N-dimethyloctadecylamine(C_{18}DA) and 4-(17-octadecenyl)pyridine, the monolayer with the former amine was found to transfer Z type or to start Y type and convert to Z type.[9,10)] Meanwhile, in case of the latter amine, ordinarily, Y type deposition occurs.[11)] S.Baker et al. found that two factors are important to obtain Y type LB films in case of the former



C_{18}DA

C_{18}ODA

$C_{18}O_2$DA

2$C_{18}O_3$DA

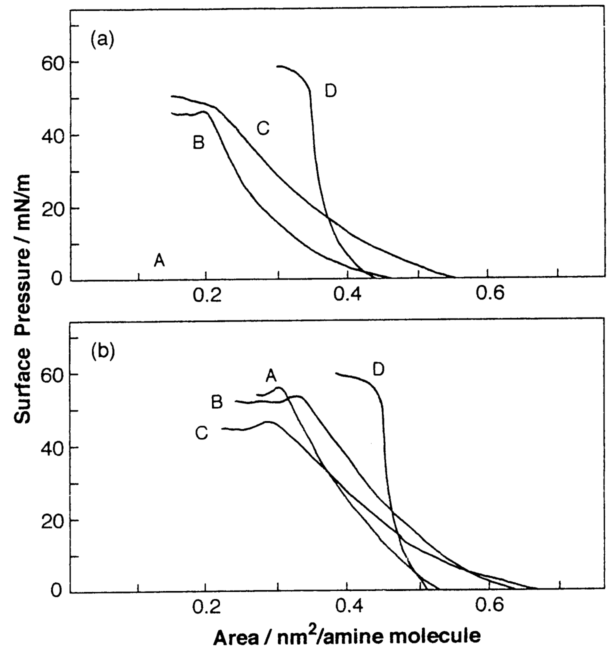


Fig.1. Surface pressure-area isotherms of (a) the amines and (b) the amine-MAMVE at 30 °C; A:$C_{18}DA$ B: $C_{18}ODA$ C:$C_{18}O_2DA$ D: $2C_{18}O_3DA$; pure water subphase; compression speed of 0.4 mm/sec; spreading solution of 1.5 x 10^{-3} M with respect to the amine.

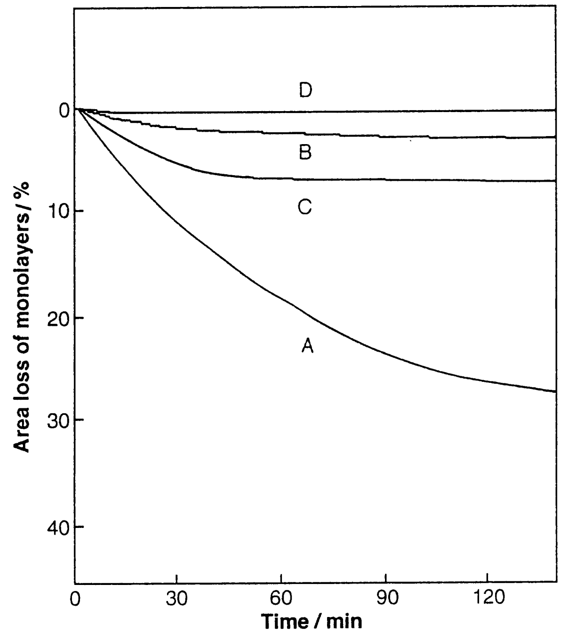


Fig.2. Area loss of monolayers of the amine-MAMVE during incubation at 20 mN/m and at 30 °C; A: $C_{18}DA$ B: $C_{18}ODA$ C: $C_{18}O_2DA$ D: $2C_{18}O_3DA$; pure water subphase; spreading solution of 1.5 x 10^{-3} M with respect to the amine.

amine, i.e., the time between preparation of the spreading solution and its use, and the pressure-annealing time of the Langmuir film.[12] We have also found the change of deposition type, poor transfer ratio, and spontaneous area loss at definite surface pressure in cases of maleic acid copolymers spread with $C_{18}DA$. In this paper, we describe the synthesis of new amphiphilic tert-amines and their uses as supporting monolayers for a water-soluble polymer at the air-water interface. The enhancement of monolayer stability by using the new amines and possible transfer as the complexed state on solid substrates are discussed.

The amphiphilic amines, 2-(dimethylamino)ethyl octadecyl ether($C_{18}ODA$), 2-(dimethylamino)ethyl octadecyl ethylene glycol diether($C_{18}O_2DA$), and 1,3-dioctadecyl-2-(2-(N,N-dimethylamino)ethyl)glyceryl triether ($2C_{18}O_3DA$), were prepared by reactions of the corresponding tosylates with 2-dimethylaminoethanol or 2-(2-dimethylaminoethyl)ethanol.[13]

Figure 1a shows that the amphiphilic amines of $C_{18}ODA$, $C_{18}O_2DA$, and $2C_{18}O_3DA$ form monolayers by themselves (FSD 50, San-esu Keisoku). Meanwhile, in case of $C_{18}DA$, any development of surface pressure by area compression was not observed. Contrary to the double-chained $2C_{18}O_3DA$, the single-chained amines reveal expanded phases. The tetrahydrofuran/dimethyl sulfoxide(6/4, by volume) solutions of equimolar amounts of the amine and copoly(maleic acid-methyl vinyl ether)(MAMVE; with respect to repeat units, Scientific Polymers Products, Inc.) were spread on pure water. Figure 1b shows the surface pressure-area(π-A) isotherms of the two-component monolayers. All the monolayers of $C_{18}DA$-MAMVE, $C_{18}ODA$-MAMVE, $C_{18}O_2DA$-MAMVE, and $2C_{18}O_3DA$-MAMVE give more expanded phases than those of the amines themselves. This change between the two isotherms is attributed to the formation of a polyion complex at the interface and the consequent change of the monolayer organization, as already described for other systems.[8,14)]

The monolayer stability against surface pressure was investigated at 20 mN/m of surface pressure and at 30 °C. The Fig. 2 shows the trend of spontaneous area loss in the two-component monolayers. The most stable monolayer was obtained in $2C_{18}O_3$DA-MAMVE system. And the monolayer sability with the amines is the order of $2C_{18}$ODA > C_{18}ODA > $C_{18}O_2$DA > C_{18}DA.

In case of $2C_{18}O_3$DA-MAMVE system, monolayer transfer(FSD-51, San-esu Keisoku) was possible onto various substrates such as a fluorocarbon membrane filter(FP-010), a CaF_2 plate, and a Si wafer. Y type deposition was found at a surface pressure of 30 mN/m and a transfer rate of 4 mm/min, although the deposition started from upward stroke in cases of CaF_2 plate and Si wafer. The transfer ratio was close to unity(1.0 to 1.1) on all the substrates. But, in cases of C_{18}ODA-MAMVE and $C_{18}O_2$DA-MAMVE systems, multilayer LB films could not be obtained, because the transferred monolayer was lost during upward(FP-010) and downward(CaF_2 plate) modes. When MAMVE was changed to other maleic acid copolymers such as copoly(maleic acid-ethylene) (MAE) and copoly(maleic acid-styrene) (MAS), the monolayer transfer occurred as X type(MAE system) or Y type which is gradually changed to Z type(MAS system).

The formation of a polyion complex in the resulting LB films (Scheme 1) could be confirmed by means of FT-IR(Nicolet 710). Figure 3a and 3c show the IR spectra of MAMVE and the LB film of $2C_{18}O_3$DA-MAMVE. The spectra show that the peak(1721 cm^{-1}) from carboxylic acid group of MAMVE is remarkably reduced in the LB film of $2C_{18}O_3$DA-MAMVE, while the peak(1565 cm^{-1}) from carboxylate salt is increased. This change shows that the polymer MAMVE forms salts with the amine $2C_{18}O_3$DA.

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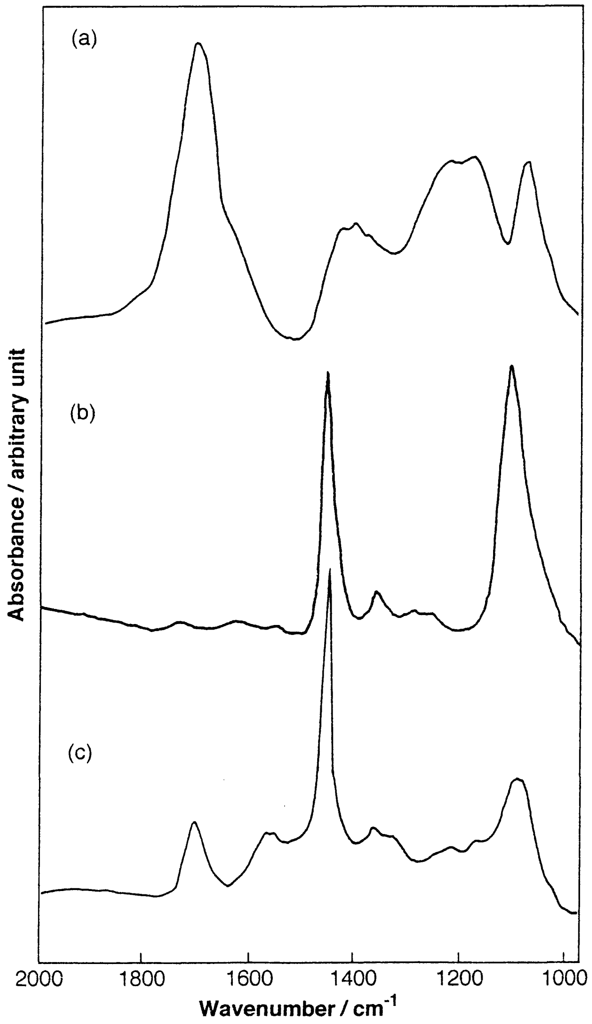
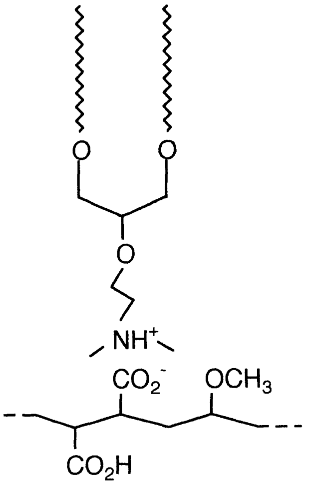


Fig. 3. IR spectra of (a) MAMVE, (b) $2C_{18}O_3$DA, and (c) LB film of $2C_{18}O_3$DA-MAMVE (13 x 2 layers) on a CaF_2 plate.



Scheme 1. Schematic representation of a polyion complexation of $2C_{18}O_3$DA-MAMVE.

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13) Synthetic procedure of $2C_{18}O_3DA$ is described in *Langmuir*, **10**, 557 (1994). $C_{18}ODA$ and $C_{18}O_2DA$ were prepared as the same procedure of $2C_{18}O_3DA$. But, instead of filtration of the precipitated amine in ice-cooled water, the extraction by chloroform was carried out. $C_{18}DA$ is commercially available. $C_{18}ODA$: viscous liquid; ^{1}H NMR ($CDCl_3$, ppm) 0.8-1.1 (t, 3H), 1.2-1.5 (m, 32H), 2.2 (s, 6H), 2.5 (t, 2H), 3.2-3.7 (m, 4H); IR (NaCl plate) 2920, 2850, 1463, 1117, 718 cm^{-1}. Anal. Found: C,77.36; H, 13.68; N, 3.97%. Calcd for $C_{22}H_{47}NO$: C, 77.35; H, 13.87; N, 4.10%. $C_{18}O_2DA$: viscous liquid; ^{1}H NMR ($CDCl_3$, ppm) 0.8-1.0 (t, 3H), 1.2-1.6 (m, 32H), 2.2 (s, 6H), 2.5 (t, 2H), 3.3-3.8 (m, 8H); IR (NaCl plate) 2918, 2848, 1464, 1121, 718 cm^{-1}. Anal. Found: C,74.77; H, 13.26; N, 3.58%. Calcd for $C_{24}H_{51}NO_2$: C, 74.74; H, 13.33; N, 3.63%.
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