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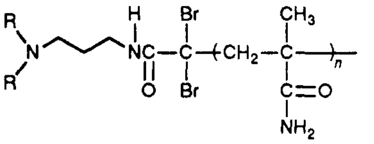
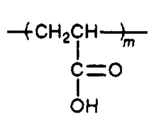
Chain-Length Recognition of Poly(acrylic acids) by a Surface Monolayer of Poly(methacrylamide)-Based Amphiphile

The interaction between two different macromolecules plays an important role in living systems because biological phenomena such as enzymatic processes and molecular recognition on the biomembrane surfaces are indebted mainly to specific intermolecular interactions. Organized monolayers and bilayers provide peculiar environments for molecular interactions and consequently for molecular recognition.[1] Novel molecular interaction systems can be developed by using monolayer assemblies, which may possess characteristics different from those in bulk phases. Few investigations have been reported, however, concerning polymer–polymer interaction by well-defined monolayer systems, probably due to the difficulty of preparing monolayer formers carrying a well-characterized polymer segment. We have established that the catalytic system of halo-terminated polymer and manganese carbonyl ($Mn_2(CO)_{10}$) is useful in designing and preparing an amphiphile diblock polymer with a well-defined structure.[2] By using this catalytic system, double-chain amphiphiles containing a poly(methacrylic acid) or poly(acrylic acid) segment have been prepared. The monolayers of them recognize the chain length of poly(ethylene glycol) as an additive in the subphase based on a specific interpolymer interaction at the air–water interface.[3]

Interpolymer complexation from poly(acrylamide) and poly(methacrylic acid) has been well-known to occur in aqueous media primarily through hydrogen bonding between $CONH_2$ and COOH.[4,5] In the present study, we prepared monolayers from new amphiphiles, $2C_{18}$-PMAm(n), and studied binding of poly(acrylic acids) (PAA(m)) with different chain lengths (m = 14–114) from the water subphase.



$2C_{18}$-PMAm(n), n = 28, 52, R = $C_{18}H_{37}$

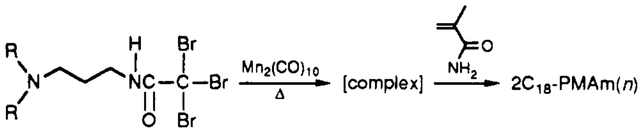


PAA, m = 14–114

Amphiphiles ($2C_{18}$-PMAm(n)) were prepared according to Scheme I. Polymerizations of methacrylamide with a tribromomethane derivative (DODTB, *N*-[3-(*N'*,*N'*-dioctadecylamino)propyl]tribromoacetamide)[6] were carried out in the presence of $Mn_2(CO)_{10}$ in THF in a manner similar to that described in the previous reports.[2,3] The resulting amphiphiles were confirmed to consist of two long alkyl chains ($C_{18}H_{37}$) as the hydrophobic part and a poly(methacrylamide) (PMAm) segment as the hydrophilic part whose chain length was controlled by polymerization conditions to be n = 28 and 52, on the basis of structural analyses.[7] PAAs as the subphase additives were prepared by photopolymerization of acrylic acid initiated with bis(isopropylxanthogen) disulfide (BX) in ethanol.[8] The chain length (m) of PAA could be controlled in the wide range (m = 14–114) by changing feed ratios ([acrylic acid]:[BX]) and conversions of the monomer. The chain lengths were estimated from the number-average molecular weights of the polymers, which were measured by vapor-pressure osmometry.

The monolayers were obtained by spreading of benzene–acetic acid (8:2 in volume) solutions of $2C_{18}$-PMAm(n) on purified water (Milli-Q system, Millipore Ltd.) or aqueous PAA (1.4×10^{-4} unit·mol/L). The concentration of the spreading solution was about 1.0 mg/mL. The measurements of surface pressure (π)–area (A) curves were performed as described elsewhere.[3]

Scheme I



DODTB, R = $C_{18}H_{37}$

Figure 1 shows the surface pressure (π)–area (A) isotherms for $2C_{18}$-PMAm(28) and $2C_{18}$-PMAm(52) on pure water at 20 °C. They form stable monolayers. The molecular area of $2C_{18}$-PMAm(52) is larger than that of $2C_{18}$-PMAm(28), probably due to the difference in steric bulkiness of the PMAm chain between them, as has also been observed for the monolayers of amphiphilic, diblock polymers with different segment lengths.[9] pH dependences of $2C_{18}$-PMAm(n) monolayers were examined with and without PAA in the subphase. The pH was adjusted with either NaOH or HCl as required. Figure 2 gives plots of the molecular area at a constant pressure of 25 mN/m (A_{25}) on the basis of π–A curves of $2C_{18}$-PMAm(28), a typical monolayer, against pH in the subphase. The A_{25} value on pure water was not affected at all by varying pH in the range from 4 to 12, as expected, whereas at extremely low pH (pH <3) the monolayer slightly expanded relative to that in the higher pH region. It has been reported that exposing a poly(acrylamide) to an aqueous solution of pH 2 causes partial ionization of the nitrogen atom of amide groups pendent along the polymer chain.[5] Thus, the observed pH dependence of the monolayer may be ascribable to ionization of amide groups of the PMAm chain, which brought about an inter- and/or intramolecular electrostatic repulsion. Consequently, the slight increase in the A_{25} value appeared especially at pH <3.

When PAA(m=28) was added into the subphase, the pH dependence of the A_{25} value was different from that on pure water as shown in Figure 2. The A_{25} values on aqueous PAA are always larger than those on pure water over the whole pH region, suggesting formation of a surface interpolymer complex between the PMAm segment of the monolayer former and the guest PAA upon binding of PAA from the aqueous phase. It is also clear from the figure that the A_{25} values depend markedly upon pH in the subphase: with lowering pH, the A_{25} increases up to pH 3 and then decreases steeply. This result allows us to consider the existence of several interaction modes between the PMAm segment and PAA as illustrated in Figure 3. At the higher pH (>10), the PMAm–PAA interaction may be weak since carboxylic acids of PAA in the subphase are completely ionized because the subphase pH is much higher than the apparent pK_a (5.6)[10] of PAA. In fact, the A_{25} value was very close to that on pure water. Upon lowering pH, carboxyl groups of PAA are partially protonated and as a result two types of interaction (models II and III) coexist, which caused expansion of the monolayer. A maximum value in A_{25} is obviously recognized at pH 3, at which the polymer–polymer interaction might be governed predominantly by model II because of complete protonation of the PAA chain. Upon further lowering of the pH (pH 1), the A_{25} value decreases. As mentioned above, methacrylamide units of the PMAm segment are positively charged at this pH and thus a cooperative interaction of hydrogen bonding and ion–dipole interaction between methacrylamide and carboxylic acid groups (mode

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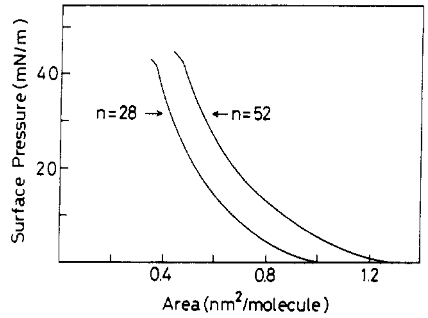

Figure 1. Surface pressure–area isotherms of $2C_{18}$-PMAm(n) on pure water at 20 °C.

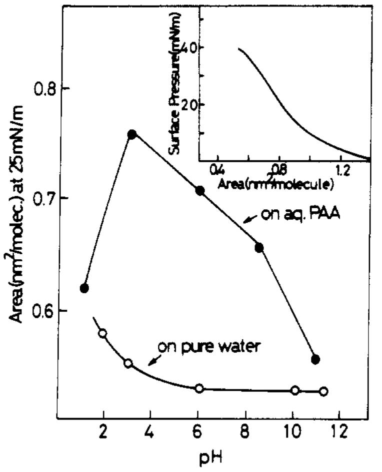

Figure 2. pH dependences of the molecular area at a constant surface pressure of 25 mN/m (A_{25}) for $2C_{18}$-PMAm(28) monolayers on pure water (○) and on aqueous PAA(m = 28, 1.4 × 10^{-4} unit·mol/L) (●) at 20 °C). Inset shows a surface pressure–area isotherm of $2C_{18}$-PMAm(28) on aqueous PAA(m=28) at pH 3, 20 °C.

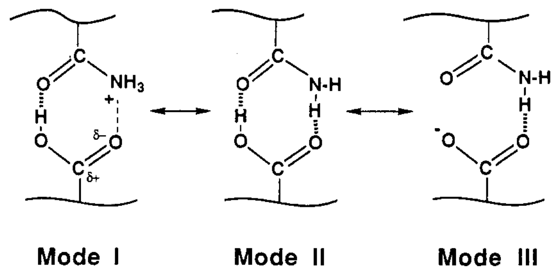

Figure 3. Schematic diagram illustrating the possible carboxylic acid–amide interaction.

I in Figure 3) seems to be dominant. However, since such an interaction may be weak, the A_{25} value on the PAA subphase likely approached that on pure water. These considerations can be rationalized only in terms of polymer–polymer interaction modes, but to obtain more detailed evidence for explaining such surface complexations, further explorations involving spectroscopic observation and the taking account of conformational properties of these polymer complexes will be required.

Figure 4 displays the chain-length effects of PAAs (m = 14–114) on the A_{25} value of $2C_{18}$-PMAm(28) and -(52) monolayers at pH 3, where the monolayer showed the largest molecular area. It is clearly seen from this figure that the A_{25} for either $2C_{18}$-PMAm(28) or -(52) monolayer gives a minimum value at certain chain lengths of PAA(m). Interestingly, the chain length of PAA at each minimum of the A_{25} is in good agreement with the chain length of the hydrophilic portion (PMAm) (n) of the monolayer formers: i.e., when n is equal to m, the monolayers are most compactly condensed. Conceivably, the complexation event occurring at the air–water interface is most efficiently transmitted to the monolayer state under the condition of n = m.

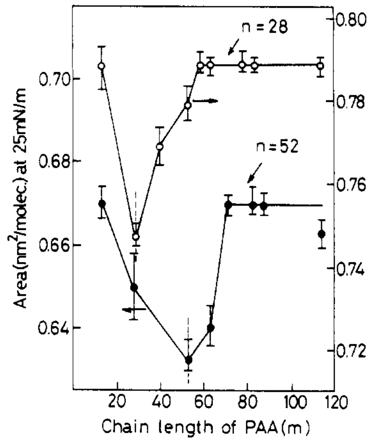

Figure 4. Chain-length (m) effect of PAA in the subphase on the molecular area (A_{25}) of $2C_{18}$-PMAm(n) monolayers. The dashed line indicates the chain length (n) of each $2C_{18}$-PMAm(n). The A_{25} values are the average of four repeated runs. The error range is shown by bars.

In conclusion, this paper demonstrated that monolayers of the amphiphilic molecules bearing a chain-length-controlled PMAm recognize the chain length of PAA in the subphase via specific polymer–polymer interactions, which can be detected by the change in the molecular area. This phenomenon was achieved owing to linked properties of the two-dimensional monolayer assembly and the structural feature of the component molecules, which possess a well-defined polymer segment having the abilities of hydrogen bonding and/or ion–dipole interaction.

References and Notes

(1) Fendler, J. H. *Membrane Mimetic Chemistry*; Wiley: New York, 1982.

(2) (a) Niwa, M.; Katsurada, N.; Matsumoto, T.; Okamoto, M. *J. Macromol. Sci. Chem.* **1988**, *A25*, 445. (b) Niwa, M.; Higashi, N.; Okamoto, M. *J. Macromol. Sci., Chem.* **1988**, *A25*, 1515.

(3) (a) Higashi, N.; Shiba, H.; Niwa, M. *Macromolecules* **1989**, *22*, 4650. (b) Higashi, N.; Shiba, H.; Niwa, M. *Macromolecules* **1990**, *23*, 5297.

(4) Nikolaev, A. F.; Shibalovich, V. G.; Perina, G. P.; Bondarenko, V. M. *Vysokomol. Soedin. Ser. B* **1976**, *18*, 222.

(5) Abe, K.; Koide, M.; Tsuchida, E. *Macromolecules* **1977**, *10*, 1259.

(6) DODTB was prepared as follows. First, 3-(N,N-dioctadecylamino)propanenitrile was synthesized by Michael addition reaction of dioctadecylamine with acrylonitrile. After reduction of 3-(N,N-dioctadecylamino)propanenitrile with $LiAlH_4$, 3-(N,N-dioctadecylamino)propylamine produced was reacted with tribromoacetyl chloride to give DODTB. The structure of the final compound was confirmed by ^1H NMR and elemental analysis.

(7) The structures of $2C_{18}$-PMAm(n) were confirmed by ^1H NMR and ^{13}C NMR spectroscopy. The molecular weight distributions (MWDs) of $2C_{18}$-PMAm(n) could not be measured because the samples were not dissolved in typical GPC solvents. In our previous reports,[2] it has been found that the vinyl polymers (poly(methyl methacrylate), polystyrene, etc.), which are prepared by polymerization of the corresponding vinyl monomers with CBr_4 or halo-terminated polymers in the presence of $Mn_2(CO)_{10}$ under the same conditions as described in this study, give considerably narrow MWDs of 1.5–2.0 on the basis of GPC analysis. Since the polymerization mechanism would not be different among these monomers and methacrylamide (this study), MWDs of $2C_{18}$-PMAm(n) are also expected to be narrow enough to discuss the effect of the chain length on the monolayer behaviors.

(8) (a) Niwa, M.; Matsumoto, T.; Izumi, H. *J. Macromol. Sci., Chem.* **1987**, *A24*, 567. (b) Niwa, M.; Sako, Y.; Shimizu, M. *J. Mac-*

romol. Sci., Chem. **1987**, *A24*, 1315. (c) Niwa, M.; Higashi, N.; Shimizu, M.; Matsumoto, T. *Makromol. Chem.* **1988**, *189*, 2187.

(9) (a) Niwa, M.; Katsurada, N.; Higashi, N. *Macromolecules* **1988**, *21*, 1878. (b) Niwa, M.; Hayashi, T.; Higashi, N. *Langmuir* **1990**, *6*, 263.

(10) Ikawa, T.; Abe, K.; Honda, K.; Tsuchida, E. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1505.

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