Chain-length Recognition of Poly(methacrylic acids) by a Monolayer of a Poly(oxyethylene)-based Amphiphile at the Air–Water Interface

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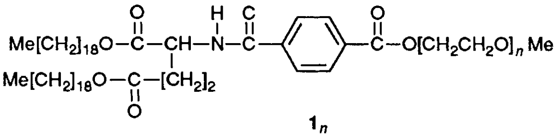
Formation of monolayers of a poly(oxyethylene) segment containing amphiphiles on water and their chain-length recognition of a guest poly(methacrylic acid) in the subphase are described.

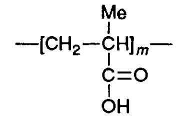
The interaction between two different macromolecules plays an important role in living systems since biological phenomena such as enzymatic processes and molecular recognition on biomembrane surfaces depend primarily on specific intermacromolecular interactions. Our current interest has focused on the development of novel macromolecular interaction systems by using monolayer assemblies, whose component molecules possess a well-defined polymer segment in their hydrophilic portion.[1] In this communication we describe the preparation of monolayers of a poly(oxyethylene) (POE) segment containing double-chain amphiphile $\mathbf{1}_n$ at the air–water interface and their interpolymer interactions with poly(methacrylic acids) [PMAA(m)] having different chain lengths examined by surface pressure–area isotherm measurements. Interactions of POE-based amphiphiles with ions such as Li^+ in monolayers and multilayers have been investigated particularly by anisotropic ion conduction in their ordered films.[2] Interpolymer complexations of POE and PMAA through hydrogen bonding have been extensively investigated in aqueous media.[3,4]

The amphiphiles $\mathbf{1}_n$ (n = 23 and 46) were synthesized by the method described previously.[2] PMAAs with different chain lengths as the guest polymer in the subphase were prepared by photopolymerization of methacrylic acid with bis(isopropylxanthogen) disulphide [$Pr^iO-C(=S)-S-S-C(=S)-OPr^i$; BX] as an initiator–chain transfer agent–primary radical terminator in ethanol.[5] The chain-length (m) of the PMAA could be controlled over a wide range (m = 6–96) by the changing feed ratios ([methacrylic acid]/[BX]) and conversions of the monomer. The chain length was estimated from the number-average molecular weight of the polymers, measured by vapour pressure osmometry. The monolayers were obtained by spreading benzene–ethanol (8 : 2 in v/v) solutions of $\mathbf{1}_n$ on purified water (Milli-Q system, Millipore Ltd.) or on aqueous PMAA (5×10^{-4} unit mol dm^{-3}). The concentration of the spreading solution was about 1.0 mg cm^{-3}. Surface pressure (π)–area (A) curves were measured as described previously.[1]

The amphiphiles ($\mathbf{1}_{23}$ and $\mathbf{1}_{46}$) were found to form stable monolayers from their π–A isotherms on pure water (not shown here). The molecular area of $\mathbf{1}_{46}$ was larger than that of $\mathbf{1}_{23}$, probably owing to the difference in steric bulk of the polymer (POE) segment between them. The pH dependence of these monolayers was examined with and without PMAA in the subphase. Fig. 1 gives plots of the limiting molecular area (A_0), estimated by extrapolating the steepest region to zero pressure on the basis of π–A curves of $\mathbf{1}_{23}$, a typical monolayer, against pH in the subphase. On pure water, the A_0 value was not affected at all by varying pH in the range pH 2.5–9.5, as was expected. When PMAA (m = 24) was added to the subphase, the A_0 values were always larger than those



$\mathbf{1}_n$



$-[CH_2-\underset{\underset{OH}{C=O}}{\overset{Me}{C}}H]_m-$ PMAA (m)

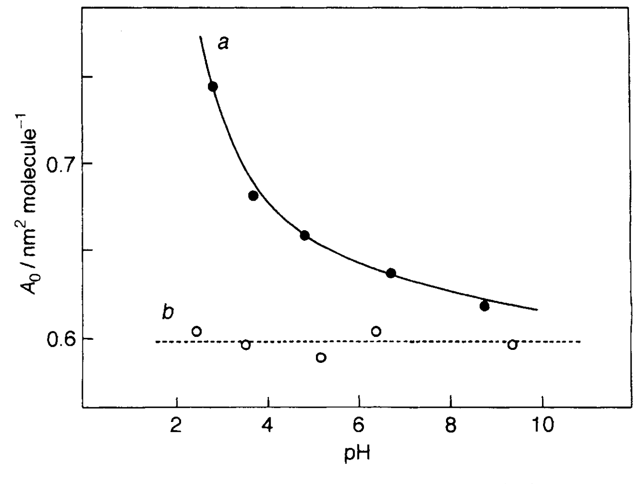


Fig. 1 pH Dependence of the limiting molecular area (A_0), estimated by extrapolating the steepest region to zero pressure on the basis of π–A curves in Fig. 1, of $\mathbf{1}_{23}$ monolayer: (a) on aqueous PMAA (m = 24) (5×10^{-4} unit mol dm^{-3}) and (b) on pure water

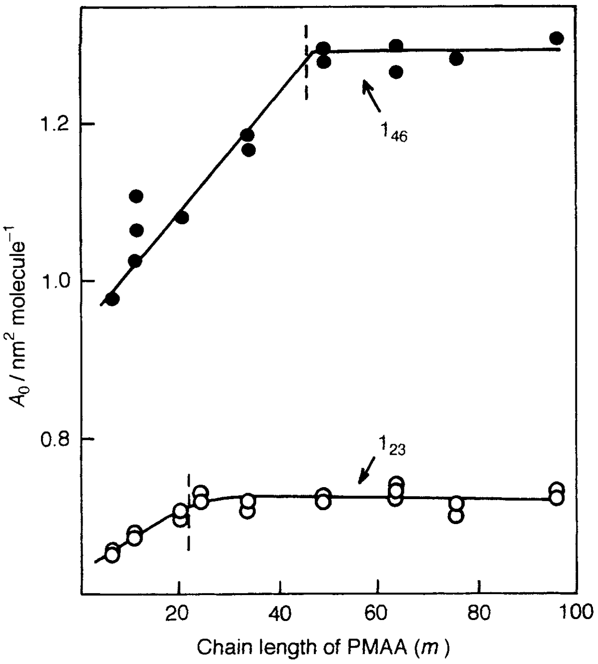


Fig. 2 Limiting area (A_0) changes of $\mathbf{1}_{23}$ and $\mathbf{1}_{46}$ monolayers at pH 3.0, responding to the chain length (m) of PMAA in the subphase

on pure water over the whole pH region, suggesting formation of a surface interpolymer complex between the POE segment of the monolayer former and the guest PMAA upon binding of PMAA *via* hydrogen bonding from the bulk aqueous phase. It is also clear from Fig. 1 that the A_0 value depends markedly upon pH in the subphase: with decreasing pH, the A_0 value increases gradually, and below pH *ca.* 5, in particular, a steep increase in A_0 is observed. At higher pH, the POE segment–PMAA interaction may be weak since the carboxylic acid groups of PMAA are ionized. The A_0 value is relatively close to that on pure water. Upon decreasing the pH, the POE segment interacts with PMAA through hydrogen bonding since the carboxylate groups are protonated, which caused expansion of the monolayer. Similar observations were made for the $\mathbf{1}_{46}$ monolayer.

Fig. 2 displays the area (A_0) changes of the $\mathbf{1}_{23}$ and $\mathbf{1}_{46}$ monolayers at pH 3.0, responding to the chain length (m) of PMAA in the subphase. It is clear from Fig. 2 that the A_0 value increases systematically with increasing m up to around m = 25 (for $\mathbf{1}_{23}$ monolayer) and m = 50 (for $\mathbf{1}_{46}$ monolayer), beyond which the A_0 value is independent of m for each monolayer. Interestingly, the chain length of PMAA (m) at each inflection point as observed in Fig. 2 is in agreement with the chain length of the POE segment of $\mathbf{1}_n$ (n). These results seem to suggest that a cooperative interaction between the POE segment of $\mathbf{1}_n$ and the PMAA chain is enhanced with increasing m up to $m = n$. The interesting match between n of the amphiphile and m of the PMAA in the subphase we consider may be due to the formation of the most expanded conformation of surface polymer complexes at $m \geqslant n$.

In conclusion, monolayers of amphiphilic molecules bearing POE segments with a controlled chain length recognized the chain length of PMAA in the subphase *via* specific polymer–polymer interactions, which can be detected by changes in the molecular area.

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