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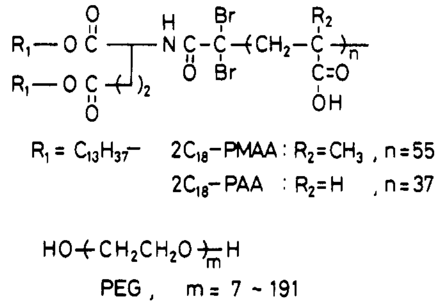
Chain-Length Effects of a Guest Polymer (PEG) on the Thermal Behavior of Interpolymer-Complexed Monolayers at the Air-Water Interface

The interaction between two different macromolecules is very important in living systems because biological phenomena such as enzymatic processes, muscle contraction, and molecular recognition on the biomembrane surfaces owe their functionalities mainly to specific intermolecular interactions. In general, macromolecular chains undergo drastic changes in conformation simultaneously with the process of mutual interaction. We have reported that amphiphilic block polymers of poly(acrylic acid-*block*-styrene) (PAA-PSt) and poly(oxyethylene-*block*-styrene) (POE-PSt) can form stable surface monolayers, which are affected by the chain length of the PSt segment, by variation of the pH in the subphase and by addition of a water-soluble polymer to the subphase.[1-3] In particular, POE-PSt monolayers formed an interpolymer complex with PAA in the subphase through hydrogen bonding, and such complexation was reversibly controlled by pH change.[2,3] Recently, we have also found that a monolayer of a poly(methacrylic acid) (PMAA) based amphiphile containing two long alkyl chains (host monolayer) recognizes the chain length of poly(ethylene glycol) (PEG; guest polymer) as an additive in the subphase based on a specific polymer-polymer interaction at the air-water interface.[4] This phenomenon resulted from a combination of the amphiphilic character and the chain-length responsive character of the host monolayer former.

In this paper, we show chain-length effects of PEG as a guest polymer on the thermal behavior of host monolayers from $2C_{18}$–PMAA and $2C_{18}$–PAA, which consist of PMAA and PAA segments, respectively, and two long alkyl chains, at the air-water interface.



Osada et al.[5] have shown a mechanochemical system that works by thermoreversible polymer-polymer complexation between PEG and PMAA. However, the thermal properties of such an interpolymer complex at the air-water interface have not yet been established. Since our amphiphiles ($2C_{18}$–PMAA and $2C_{18}$–PAA) have PMAA or PAA segments at the hydrophobic portion, they should be favorable for clarifying polymer-polymer interactions between monolayer components and PEG in the subphase. We employ an isobar technique[6] (temperature-induced area variation at a constant pressure) to reveal the thermal behavior of complexed monolayers.

The preparation of $2C_{18}$–PMAA (n = 55) was described in the previous paper.[4] Amphiphile $2C_{18}$–PAA was prepared in the same manner as that of $2C_{18}$–PMAA. The resulting amphiphile was confirmed to consist of two long alkyl chains ($C_{18}H_{37}$–) as the hydrophobic part and a PAA chain (n = 37) as the hydrophilic part, on the basis of structural analyses.[7]

The monolayers were obtained by spreading of benzene-ethanol (8:2 in volume) solutions of the amphiphiles on purified water (Milli-Q system, Millipore Ltd.) or on aqueous PEG. The concentration of the spreading solution was about 1.5 mg/mL. A total of 10 min after spreading, the gaseous monolayer was continuously compressed. The compressional velocity was 1.20 cm^2/s. The Wilhelmy pressure pick-up system and a Teflon-coated trough with a microprocessor-controlled film balance (FSD-50, San-Esu Keisoku Ltd., Fukuoka, Japan), with a precision of 0.01 mN/m, were used for surface pressure measurements. The isobars were also recorded on a film balance (FSD-50). The monolayers were spread at low-subphase temperature (7 °C). At a constant pressure, the temperature of subphase was gradually increased. The dependence of area on temperature at constant pressure was recorded. Commercial PEG[8] with different chain lengths (7-191) was used as the subphase additive.

Figure 1 shows the surface pressure (π)-area (A) isotherms of $2C_{18}$–PMAA and $2C_{18}$–PAA on aqueous PEG (m = 191, 1×10^{-3} unit·mol/L) at pH 4, 20 °C. We have shown that the $2C_{18}$–PMAA monolayer forms an interpolymer complex with PEG in the subphase through hydrogen bonding in such a pH region.[4] The $2C_{18}$–PAA monolayer on aqueous PEG exhibited a pH dependence similar to that of the $2C_{18}$–PMAA monolayer (not shown in Figure 1). With addition of PEG into the subphase at pH 4, the π–A curve was considerably compressed compared with that on pure water. In contrast, when the pH of the subphase increased up to 8, the π–A curve became fitted to that on pure water because of weakening or breaking of the hydrogen bonding due to the ionization of carboxylic acid groups of PAA. Thus, the following isobar measurements were performed at pH 4, at which both monolayers form interpolymer complexes with PEG in the subphase.

Figure 2 shows typical isobars for $2C_{18}$–PMAA and $2C_{18}$–PAA on aqueous PEG (m = 191) at 25 mN/m. At the melting point the isobar of a three-dimensional system (crystal) shows an increase in volume. Similarly an increase in area is displayed in the two-dimensional monolayer system when an increase in temperature causes a phase change of the monolayer from the solid analogue to the liquid analogue orientation. As is seen from Figure 2 the monolayer of $2C_{18}$–PAA gives such a transition temperature of 12 °C. This phase transition for $2C_{18}$–PAA monolayer was also observed when the other PEGs with different chain length were added into the subphase, although the transition temperature varied slightly dependent upon the chain length of PEG. On the other hand, the $2C_{18}$–PMAA monolayer has no transition in this temperature region. The structural distinction between $2C_{18}$–PAA and $2C_{18}$–PMAA exists only in their hydrophilic polymer segment. Therefore, the results obtained above are considered due to the difference of an interaction mode between the PMAA-PEG complex and the PAA-PEG complex at the air-water interface. Upon further elevating temperature, a decrease in area for both monolayers appeared at around 35 °C. Since the area did not change for several hours when we examined the change in area at a constant temperaure of 40 °C, 25 mN/m, dissolution of monolayer components into the subphase might be negligible. Thus, such a decrease of area in isobars should be ascribable to the contraction of monolayer-PEG surface complexes. In order to elucidate the chain-length effects of PEG on the temperature-induced contraction of complexed monolayers, isobars of $2C_{18}$–PMAA and $2C_{18}$–PAA were measured in the presence of PEGs with various

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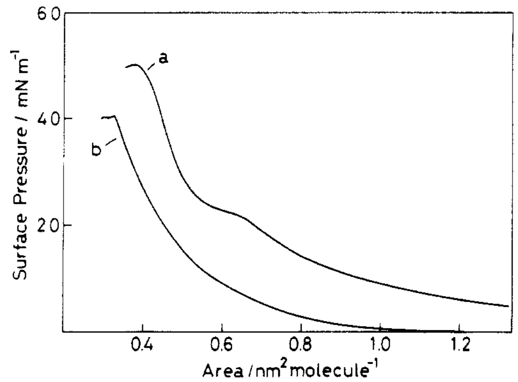

Figure 1. Surface pressure–area isotherms for $2C_{18}$–PAA (a) and $2C_{18}$–PMAA (b) on aqueous PEG (m = 191) at 20 °C.

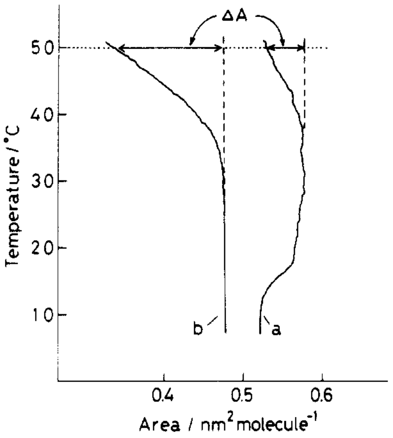

Figure 2. Typical isobars for $2C_{18}$–PAA (a) and $2C_{18}$–PMMA (b) on aqueous PEG (m = 191) at a constant pressure of 25 mN/m. ΔA denotes the difference between the area at 50 °C and the area at an inflection temperature.

chain lengths (m = 7–191). The extent of contraction was estimated for convenience by the area change, ΔA, which is the difference between the area at 50 °C and the area at an inflection temperature as shown in Figure 2. The relationships between the chain length of PEG (m) and ΔA obtained on the basis of isobars for both monolayers were shown in Figure 3. In the case of $2C_{18}$–PAA monolayer, ΔA *increased* with increasing m up to around m = 40, beyond which ΔA became constant, independent of m. This suggests that the temperature-induced contraction of the PAA segment–PEG surface complex is suppressed upon increasing m and then the m dependence of ΔA disappears at $m \geq n$ (segment length of PAA of $2C_{18}$–PAA). In contrast, $2C_{18}$–PMAA, which possesses a PMAA segment as a hydrophilic portion in place of a PAA segment, gave the reverse m-dependence of ΔA (Figure 3): i.e., ΔA *decreased* with increasing m up to around m = 60, which is close to the PMAA segment length (n = 55) of $2C_{18}$–PMAA. This result implies that the temperature-induced contraction of the PMAA segment–PEG surface complex is enhanced upon increasing m up to $m = n$, contrary to the result of $2C_{18}$–PAA. It has been demonstrated that the contraction with an increase of temperature in PMAA–PEG interpolymer complexed membranes can be related to the hydrophobic interaction between the α-methyl group in PMAA and the methylene group in PEG.[5] Similarly, in a surface monolayer state, the temperature-induced area compression might be caused by $2C_{18}$–PMAA bearing the α-methyl group in a PMAA segment because of stabilization and conformational compactness of the $2C_{18}$–PMAA–PEG surface complex upon elevating the temperature, but it would not be caused by $2C_{18}$–PAA without an α-methyl group. The interesting match between n of $2C_{18}$–PMAA and $2C_{18}$–PAA and m of PEG in the subphase observed in Figure 3 cannot easily be explained, but it could be postulated that cooperative interactions between monolayer formers and PEG are most markedly enhanced at $m \geq n$. The fact that the $2C_{18}$–PMAA monolayer gave the most compact complex with PEG at $m \geq n$, as described elsewhere,[4] supports such a postulate.

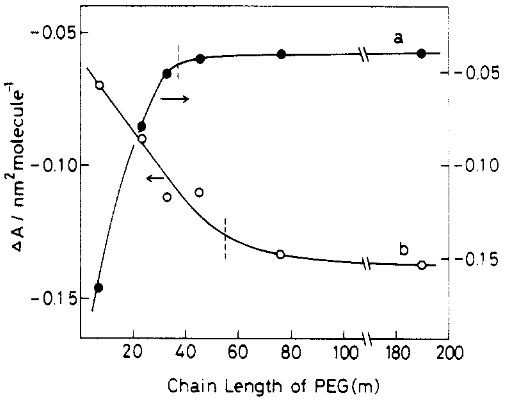

Figure 3. PEG–chain length (m) dependence of the area change (ΔA) for the $2C_{18}$–PAA monolayer (a) and the $2C_{18}$–PMAA monolayer (b). Dashed lines show the PAA or PMAA segment length (n).

In conclusion, the present paper provides the first example of the chain-length effects of interpolymer complexes on temperature-induced contraction at the air–water interface. Spectroscopic studies to reveal the surface interpolymer interactions are now in progress.

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References and Notes

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(7) The structure of $2C_{18}$–PAA was confirmed by ^1H and ^{13}C NMR spectroscopy. Average chain length of PAA segment in $2C_{18}$–PAA was estimated by a potentiometric titration with aqueous NaOH.
(8) The PEGs with average molecular weight (M_n) of 300, 1000, 1500, 2000, 3400, and 8400 were purchased from Nakalai Tesque, Inc. (Kyoto, Japan). Polydispersities of these PEGs (M_w/M_n) were in the range from 1.1 to 1.3.

Nobuyuki Higashi, Hideki Shiba, and Masazo Niwa*

Department of Applied Chemistry, Faculty of Engineering
Doshisha University, Kamikyo-ku, Kyoto 602, Japan

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