4650 *Macromolecules* **1989**, *22*, 4650-4652

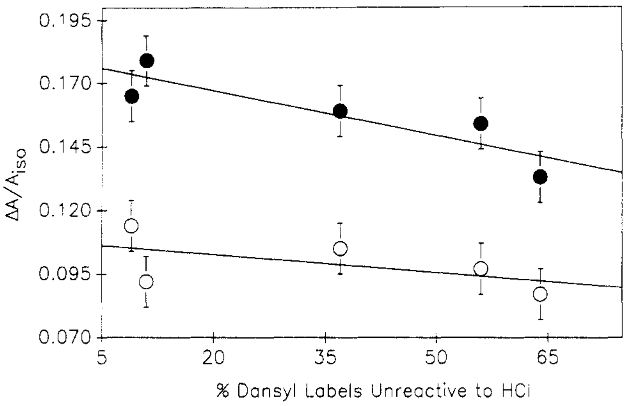

Figure 2. Extent of isomerization of PE/1 after 50 min (○) and after 500 min (●) as determined by the change in absorbance at 428 nm in various solvents suspensions plotted versus the extent of reaction of the dansyl labels of PE/3 with HCl in the same solvent suspensions.

cases is quite small (ca. 0.002 absorbance unit). Nonetheless, the data are good enough to show that isomerization is about 4 times faster in the presence of solvent than for dry films.

In summary, photoisomerization of azo dyes entrapped in polyethylene shows a modest dependence on the nature of the solvent in contact with the functionalized polymer. Good correlations are obtained between the initial amount of isomerization and prior ESR and fluorescence studies of functional group behavior for functionalized polymers suspended in these same solvents. Similar kinetic behavior are seen with both etched polyethylenes and entrapment-functionalized polyethylene films though the low loading of the former films frustrates quantitative analysis in that case.

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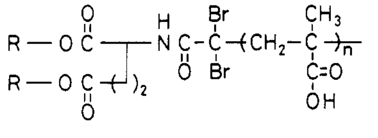
Chain-Length Effects of Poly(ethylene glycol) on a Monolayer of a Poly(methacrylic acid)-Based Amphiphile at the Air-Water Interface

In this report we show that the newly prepared amphiphile 1 composed of two long alkyl chains and a poly(methacrylic acid) segment forms a stable surface monolayer which is significantly affected by variation of the pH in the subphase and by the addition of poly(ethylene glycol) (PEG) to the subphase and that such a monolayer responds to the chain length of PEG in the subphase as a result of a polymer-polymer interaction based on hydrogen bonding at the air-water interface.



1 ; $R = C_{18}H_{37}-$
$n = 55$

$HO\!\left(CH_2CH_2O\right)_m\!H$ PEG
$m = 4 - 191$

We have reported that amphiphilic block polymers of poly(acrylic acid-*block*-styrene) (PAA-PSt) and poly(oxyethylene-*block*-styrene) (POE-PSt), prepared by using the catalytic system of halo-terminated polymer and manganese carbonyl ($Mn_2(CO)_{10}$), 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.[1,2] 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] Interpolymer complexations of PMAA and PEG through hydrogen bonding have been extensively investigated in an aqueous medium.[3,4] However, the polymer-polymer interaction at the air-water interface has not yet been established. The π-A isotherm measurement is a useful tool for detecting molecular interactions at the air-water interface due to its high sensitivity to the monolayer state. In the present study, we employ PMAA-containing amphiphile 1 as a molecular recognizable monolayer component and studied the effects of chain length of PEG as an additive in the subphase on the surface monolayer of 1 by using surface pressure (π)-area (A) isotherm measurements.

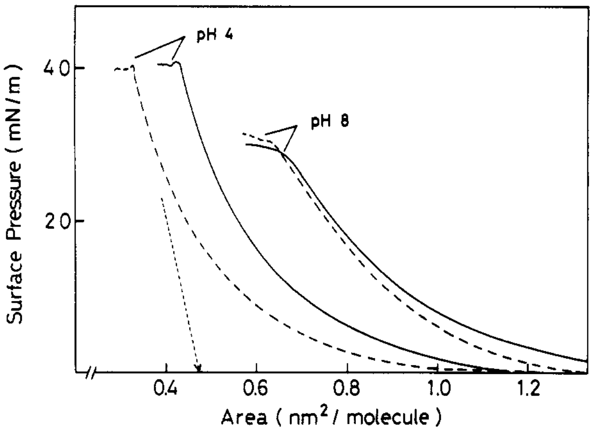
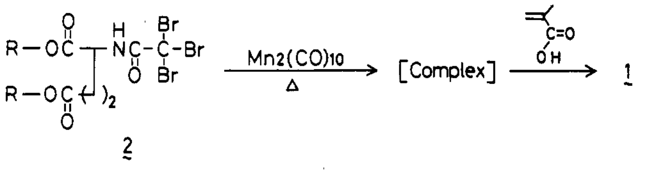


Figure 1. Surface pressure–area isotherms of 1 at 20 °C, pHs 4.0 and 8.0: solid lines, on water; dashed lines, on aqueous PEG (m = 191).

Scheme I



Amphiphile 1 was prepared according to Scheme I. A tribromomethane derivative, 2, was prepared by reaction of dioctadecyl-L-glutamate with tribromoacetyl chloride. Polymerization of methacrylic acid with 2 was carried out in ethanol with $Mn_2(CO)_{10}$ according to the method as described in the previous reports.[5,6] The resulting amphiphile consists of two long alkyl chains ($C_{18}H_{37}$–) as the hydrophobic part and a PMAA chain (n = 55) as the hydrophilic part, on the basis of structural analyses.[7]

The monolayer was obtained by spreading of a benzene–ethanol (8:2 in volume) solution of 1. 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^{-1}. The Wilhelmy plate method and a Teflon-coated trough with a microprocessor-controlled film balance (San-Esu Keisoku Ltd., Fukuoka, Japan), with a precision of 0.01 mN/m, were used for surface pressure measurements. The measurements of π–A curves were repeated several times to check their reproducibility. Commercial PEG with different chain lengths (m = 4–191)[8] were used as the subphase additives.

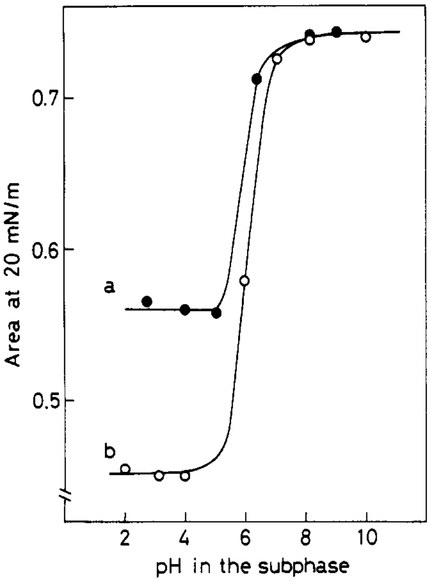


Figure 2. pH dependence of the area on water (a) and on aqueous PEG (m = 191) (b) at a constant surface pressure of 20 mN/m on the basis of 1 π–A curves at 20 °C.

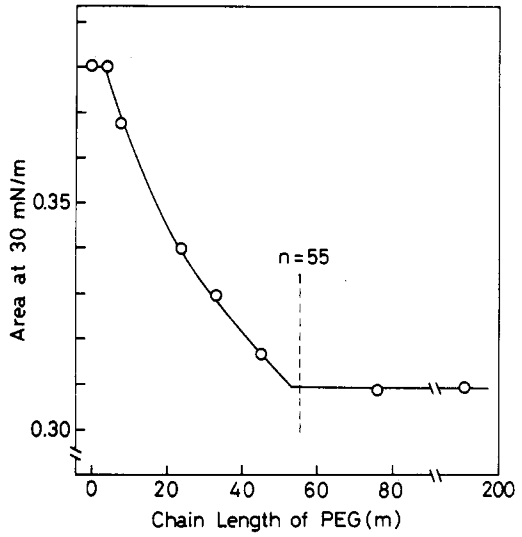


Figure 3. Area changes of the 1 monolayer on aqueous PEG at a constant surface pressure of 30 mN/m responding to the chain length (m) of PEG at 20 °C. The dashed line indicates the chain length (n) of PMAA of 1.

Figure 1 shows the π–A isotherms of 1 on pure water and on aqueous PEG (m = 191, 1 × 10^{-3} unit mol/L) at different pH values at 20 °C. The pH was adjusted with either NaOH or HCl as required. With addition of PEG to the subphase at pH 4.0, the π–A curve was considerably compressed compared with that on pure water. In contrast, when the pH of the subphase increased up to 8.0, the π–A curve becomes fitted to that on pure water. These imply that there is an interaction between the hydrophilic moiety (PMAA segment) of 1 and PEG in the subphase at the air–water interface in the lower pH region. Figure 2 shows the pH dependence of the mean area at a constant surface pressure of 20 mN/m on the basis of π–A curves of 1. The area on pure water increased drastically at around pH 6 due to expansion of the monolayer when the pH of the subphase increased. This pH-induced expansion of the monolayer may be ascribable to ionization of carboxylic acid groups of the PMAA chain from a globular coil in acidic solution to an expanded conformation at high pH. On the other hand, the pH dependence on aqueous PEG was different from that on pure water: at the lower pH region (<pH 6) the area was remarkably compressed compared with that on pure water as described above although the limiting area (at pH 4), estimated by extrapolating the solidlike regions to zero pressure, 0.47 nm^2 is relatively close to the cross section (0.40 nm^2) of the vertically oriented hydrocarbon chains. The observed monolayer compression may be produced by the formation of an interpolymer complex between the PMAA segment of 1 and the PEG through hydrogen bonding. When the pH increased, the area expanded drastically at around pH 6 similar to the case of monolayer on pure water and then became close to that on pure water upon further increase of pH because of weakening of the hydrogen bonding due to ionization of carboxylic acid groups of PMAA. Thus, the interpolymer complexation was suppressed in such a pH region.

The monolayer of 1 "responds" to the chain length of PEG in the subphase below pH 6 where the monolayer can form an interpolymer complex with PEG. Figure 3 displays the area changes of the 1 monolayer at a constant pressure of 30 mN/m, pH 4.0, responding to the chain length (m) of PEG in the subphase. It is clearly seen from Figure 3 that, except for the case of PEG ($m = 4$), the area decreases systematically with increasing m up to around $m = 50$, beyond which the area is independent of m. Furthermore, the chain length of PEG, $m = 50$, at the inflection point in Figure 3 is in agreement with the chain length of the PMAA segment of 1. These results imply that a cooperative interaction between the PMAA chain of 1 and the PEG chain is enhanced with increasing m up to $m = 50$. The interesting match between n of the amphiphile 1 and m of the PEG in the subphase is considered due to the formation of the most compact coil conformation of polymer complexes at $m \geq n$. Such a compactness of the polymer complex reduced the molecular area at the air–water interface.

In conclusion, the present paper provides the first example of the chain-length relation for interpolymer complexation by a PMAA-based amphiphile at the air–water interface. This phenomenon was attained due to a combination of the amphiphilic character and the chain-length responsive character of 1. Attempts to reveal the chain-length relationships in a multilayer state are now in progress.

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(7) The structure of 1 was confirmed by ^{1}H and ^{13}C NMR spectroscopy. Average chain length of PMAA segment in 1 was estimated by a potentiometric titration with aqueous NaOH solution.
(8) The PEGs with average molecular weights ($\bar{M}_n$) of 200, 300, 1000, 1500, 2000, 3400, and 8400 were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Polydispersities of these PEGs ($\bar{M}_w/\bar{M}_n$) were in the range from 1.1 to 1.3.

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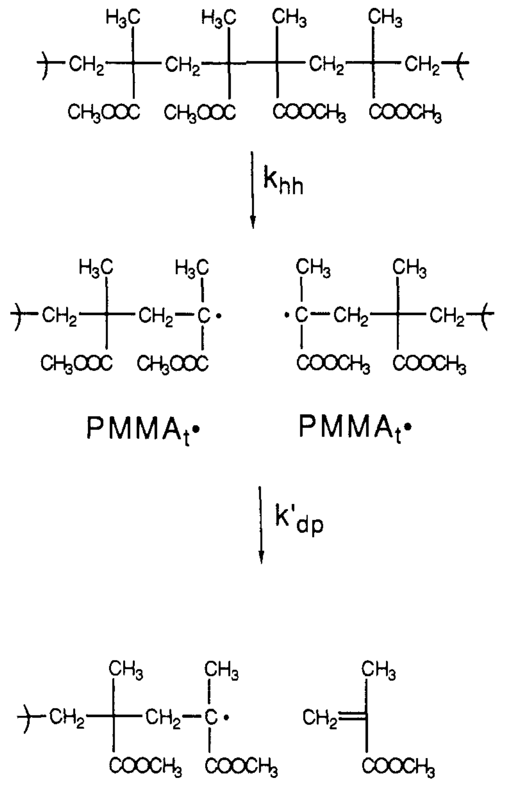
Thermal Degradation of Poly(methyl methacrylate). 3. Polymer with Head-to-Head Linkages[†]

Introduction. We have prepared PMMA in which each chain contains one head-to-head bond (PMMA-HH) using group-transfer polymerization.[1,2] We have compared the thermal degradation of PMMA-HH with PMMA-H (saturated PMMA, which contains no inherent weak links). For polymers with DP > 200 the thermal degradation of PMMA-HH and PMMA-H are similar, indicating that the head-to-head bond is having little effect under the experimental conditions. However, the degradation of DP < 100 PMMA-HH is more facile than the degradation of similar PMMA-H. Our results suggest that a large cage recombination effect, probably due to the high viscosity of the polymer melt, reduces the effective rate of head-to-head bond scission. We believe this is the first direct determination that cage recombination influences the thermal degradation of polymers.

Scheme I



Free radically polymerized PMMA thermally degrades in two or three distinct steps.[3,4] The most stable fraction of free radically polymerized PMMA (PMMA-H) contains no unsaturated end groups or main-chain head-to-head bonds, and the initiation step is a random scission.[3-8] Although it is accepted that random main-chain scission (rather than side-chain scission) initiates degradation, this point is not yet established.

A less stable fraction of free radically polymerized PMMA contains a double bond in the end group.[5,6,9-11] Double bond terminated PMMA (PMMA=) is formed simultaneously with PMMA-H by disproportionation termination of propagating radicals. It is believed that facile homolytic bond cleavage β to the terminal double bond leads to PMMA= degradation. However, we have demonstrated that degradation of PMMA= occurs by an efficient chain-transfer process in which the end group reacts with a radical to form an active chain end, which can depolymerize.[11]

The importance of head-to-head linkages in PMMA thermal degradation has been considered by a number of workers.[4-6] During MMA free-radical polymerization, PMMA chains with head-to-head bonds (PMMA-HH) are formed by coupling termination of the propagating radicals. It has been proposed that up to 28% of PMMA radicals terminate by coupling and that the PMMA-HH formed is less stable than PMMA=.[4] It is assumed the head-to-head bond is an inherently weak link so that PMMA-HH will degrade by the mechanism shown in Scheme I. Initial studies on the thermal degradation of oligomers containing head-to-head linkages indicated that PMMA-HH is less stable than PMMA=;[5] however, recent results have suggested that PMMA-HH is more stable than PMMA=.[6]

Results and Discussion. Figures 1 and 2 compare the rate of MMA appearance as a function of temperature when PMMA-H (DP_0 = 61, 193, and 1250) and PMMA-

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