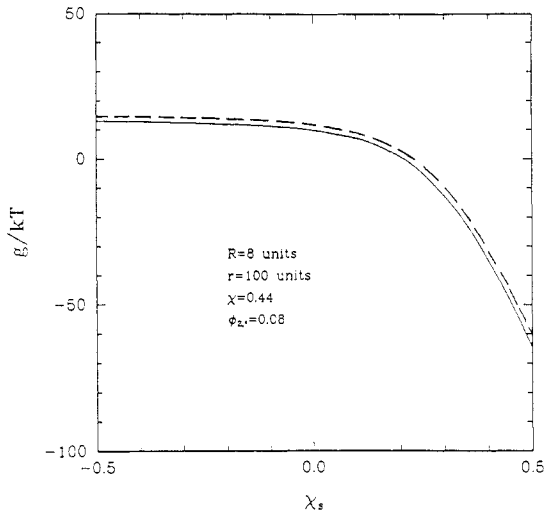

Figure 1. Gibbs energy per particle as a function of the polymer–particle interaction parameter χ_s; the solid line shows the results obtained with our definition of the directional weight factors λ_i (ref 1), the dashed line represents values obtained with the formulas of Leermakers, van der Schoot, Scheutjens, and Lyklema (ref 4 and 5).

formulations, are the major influences on the observed partitioning behavior.

Clearly, Leermakers et al.'s choice of function for λ_i is formally superior to the one we made, based on a physically intuitive appeal, and should be chosen for curved lattices without a solid particle at the center where the molecules can reach the origin. For the case where a particle blocks the center of the lattice, such as the one addressed in our paper,[1] the choice of formulas makes very little difference, and is essentially aesthetic: ours has, in our view, a more satisfying physical meaning, that of Leermakers et al. leads to a more consistent lattice model.

Erratum to the Original Paper. We would like to take this opportunity to correct an embarrassing set of mistakes in the original text. These mistakes are completely editorial in nature and have no bearing on the final equations or results but make for confusing reading.

Appendix III in the original text is blatantly incorrect, and eq 8 is ambiguous. The correct expression for the Helmholtz energy (eq III-1) for the phase containing the particle should be[7]

$$a = -kT \ln \Xi + n_1^{\mathrm{T}}\mu_1 + n_2^{\mathrm{T}}\mu_2 \qquad \text{(i)}$$

where n_1^{T}, n_2^{T} are the numbers of solvent molecules and polymer chains in the system and μ_1 and μ_2 are their respective chemical potentials. In a lattice of constant volume and pressure, changes in the Helmholtz energy will be equal to changes in the Gibbs energy. Since here both are referenced to the pure bulk components, $g^{\mathrm{phase+particle}}$, the Gibbs energy for the phase with the particle, is also given by eq i. The derivation presented in Appendix III should read as follows.

The Gibbs energy of the "unperturbed" phase, i.e., the phase without the particle, is given by

$$g^* = n_1^{\mathrm{T}}\mu_1 + n_2^{\mathrm{T}}\mu_2 \qquad \text{(ii)}$$

The Gibbs energy of the system *with* the particle is given by eq i above, so that the change in the Gibbs energy of the system upon addition of the particle, g^{excess}, may be written

$$g^{\mathrm{excess}} = g^{\mathrm{phase+particle}} - g^* = -kT \ln \Xi \qquad \text{(iii)}$$

(g^{excess} here is the same as g in the main body of the text of the original paper.) Substituting eq 9 from the original paper

$$\Xi = \sum_{\{n_c\}} Q_{\{n_c\}} \exp[\textstyle\sum_i (L_i\phi_{1,i}\mu_1)/kT] \exp[\sum_i (L_i\phi_{2,i}\mu_2/rkT)] \qquad (9)$$

for Ξ in eq iii above gives

$$g^{\mathrm{excess}} = -kT \ln Q - \textstyle\sum_i (L_i\phi_{1,i}\mu_1) - \sum_i (L_i\phi_{2,i}\mu_2/r) \qquad \text{(iv)}$$

Substituting eq 19, III-7, and III-8 from the original paper

$$-(\ln Q) = n_2 \ln \phi_{2,*} + \textstyle\sum_i n_{1,i} \ln \phi_{1,i} + \sum_i n_{2,i} \ln p_i + \Delta U/kT \qquad (19)$$

$$\mu_2/kT = 1 - \phi_{2,*} - r\phi_{1,*} + \ln \phi_{2,*} + r\chi\phi_{1,*}(1 - \phi_{2,*}) \qquad \text{(III-7)}$$

$$\mu_1/kT = 1 - \phi_{1,*} - \phi_{2,*}/r + \ln \phi_{1,*} + \chi\phi_{2,*}(1 - \phi_{1,*}) \qquad \text{(III-8)}$$

for Q, μ_1, and μ_2 in eq iv above gives eq 20 in the original paper. Note that g^{excess} here is equal to the total surface tension $\gamma A/kT$ as defined by Roe[8] and by Scheutjens and Fleer.[2]

Acknowledgment. We thank Dr. J. M. H. M. Scheutjens for providing us with a preprint of ref 5.

References and Notes

(1) Baskir, J. N.; Hatton, T. A.; Suter, U. W. *Macromolecules* **1987**, *20*, 1300–1311.
(2) Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1979**, *83*, 1619–1635.
(3) Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1980**, *84*, 178–190.
(4) van der Schoot, P. P. A. M.; Leermakers, F. A. M., preceding article in this issue.
(5) Leermakers, F. A. M.; van der Schoot, P. P. A. M.; Scheutjens, J. M. H. M.; Lyklema, J. In *Surfactants in Solution, Modern Applications*; Mittal, K. L., Ed., in press.
(6) If we assume a sphere of radius $R = 0$ at the core of the lattice, the formulas of Leermakers et al. can be directly compared to ours. For the purpose of illustration we note that for values of $i = 3$, 5, and 10, respectively, their formulas yield values for $\lambda_i(+1)$ of 0.36, 0.31, and 0.28, respectively, while ours give 0.49, 0.37, and 0.31, respectively.
(7) Reed, T. M.; Gubbins, K. E. *Applied Statistical Mechanics*; McGraw-Hill: New York, 1973.
(8) Roe, R. J. *J. Chem. Phys.* **1974**, *60*, 4192.

* To whom correspondence should be addressed at the Institut für Polymere, ETH-Zentrum, CNB E92, CH-8092 Zürich, Switzerland.

Jesse N. Baskir, T. Alan Hatton, and Ulrich W. Suter*

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received February 19, 1988

Formation of a Surface Monolayer and a Built-Up Multilayer from a Well-Defined Amphiphilic Block Copolymer

In this report we show that a well-defined amphiphilic block copolymer (**3**), derived from poly(ethyl acrylate)-*block*-poly(styrene) (**2**), can be prepared by using the catalytic system of halo-containing macroinitiator **1** and manganese carbonyl ($Mn_2(CO)_{10}$) and that such an amphiphilic block copolymer readily forms a surface monolayer, which is strongly affected by poly(styrene) (PSt) chain length and by varying pH in subphase, and forms a built-up multilayer.

Langmuir–Blodgett (LB) films have received much attention in recent years due to the fact that the control of

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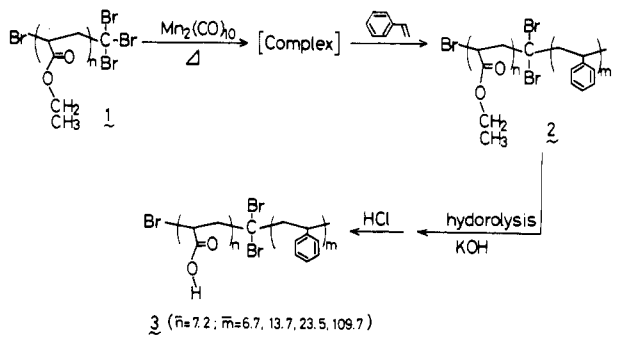
Scheme I



3 ($\bar{n}$=7.2; $\bar{m}$=6.7, 13.7, 23.5, 109.7)

the molecular aggregation state is readily achieved by the preparation technique of thin films developed by Langmuir[1] and Blodgett.[2]

For most practical applications the LB film will need to be mechanically and thermally stable. From this point, research efforts on LB films consisting of monolayers of synthetic polymers are rapidly expanding. Most of those polymeric materials are, however, homopolymers[3] or copolymers[4-6] with hydrophilic comonomers prepared from long alkyl chain containing vinyl monomers which are attached along the resulting polymer backbone, and they are mainly discussed by virtue of lateral fixation. On the other hand, there has been little study of the surface monolayer of synthetic amphiphilic block polymers composed of hydrophilic and hydrophobic segments. Roberts et al.[7] reported the preparation and dielectric properties of a quaternary ammonium salt terminated polybutadiene. Ikada et al.[8] reported the surface monolayers of graft and block copolymers consisting of poly(styrene) (PSt) and poly(vinyl acetate) or poly(vinyl alcohol), which were prepared by a radiation-induced copolymerization. Unfortunately, the chain length of each segment in those copolymers seemed to be uncontrollable and too long to discuss the monolayer behavior precisely.

We have reported that a well-defined block copolymer can be easily prepared by making use of the catalytic system[9,10] of halo-containing macroinitiator 1 and $Mn_2(CO)_{10}$ as shown in Scheme I.[11] The block copolymer 2 will be transformed readily into the amphiphilic form by hydrolysis of ethyl acrylate units with ethanolic KOH.

In this paper, we report the preparation of amphiphilic block copolymers 3 with systematically different chain lengths and properties of those peculiar monolayers at the air–water interface. Macroinitiator 1 was prepared by polymerization of ethyl acrylate initiated with α,α'-azobis(isobutylonitrile) (AIBN) in the presence of carbon tetrabromide (chain transfer agent) as described before.[12] The number-average degree of polymerization ($\bar{n}$) of the macroinitiator thus obtained was estimated to be 7.2 on the basis of vapor-pressure osmometry.[13] Block polymerization of styrene (St) as a second monomer with macroinitiator 1 was carried out in bulk with $Mn_2(CO)_{10}$ at 80 °C (Table I). Blocking efficiencies were almost 100% for any block polymer with different conversions, resulting from Soxhlet extraction. M_g values, which denote the molecular weights at peak tops of gel permeation chromatography (GPC) curves[14] calibrated with polystyrene standard, were consistent with the number-average molecular weight ($\bar{M}_n$) calculated from the peak intensities assigned to each blocking unit in the ^1H NMR spectra.[15] $\bar{M}_n$ (calcd) values, estimated by using the feed composition of St and macroinitiator and the conversion (X_w) (see Table I), were very close to the values of M_g (GPC). These indicate that well-defined block copolymers with controlled chain length of blocking were able to be prepared by varying the conversion of the second monomer and the feed composition of macroinitiator and the second monomer.

Table I
Block Polymerization of St with TBE–$Mn_2(CO)_{10}$ in Bulk at 80 °C[a]

macroinitiator [TBE], mol/L	[St], mol/L	conversion X_w, %	M_g[b] (GPC)	$\bar{n}$[c]	$\bar{m}$[d]	$\bar{M}_n$[e] (calcd)
0.30	6.56	27.4	1750	7.2	6.7	1670
0.20	7.59	31.6	2480	7.2	13.7	2298
0.10	7.91	28.1	3500	7.2	23.5	3368
0.05	8.92	52.9	12480	7.2	109.7	10958

[a] Concentration of manganese carbonyl, 5.0 mmol/L. [b] Molecular weight calibrated with polystyrene standard at the peak top of the GPC curve. [c] Number-average degree of polymerization of the macroinitiator. [d] Number-average chain length of blocked PSt. [e] Molecular weight calculated, $\bar{M}_n$ = 1050 + (104-[St]X_w/[TBE]).

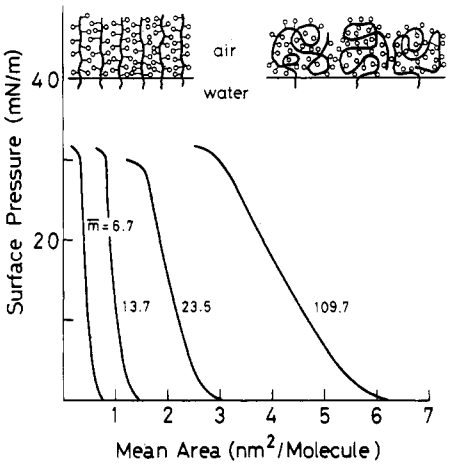


Figure 1. π–A isotherms of 3 containing different chain length ($\bar{m}$) on pure water at 20 °C. Inset shows a schematic illustration of surface monolayer; —○, PSt chain.

After hydrolysis of these block copolymers with ethanolic KOH in dioxane and neutralization with aqueous HCl, they were transformed completely to the amphiphilic form containing a poly(acrylic acid) (PAA) chain instead of a poly(ethyl acrylate) chain. These transformations were confirmed on the basis of ^{13}C NMR spectroscopy.[15] Resulting amphiphilic block copolymers consist of a PAA chain ($\bar{n}$ = 7.2) as the hydrophilic part and a PSt chain ($\bar{m}$ = 6.7–109.7) as the hydrophobic part.

Spreading experiments of 3 were performed on a microprocessor-controlled film balance (San-esu Keisoku Co. Ltd.). A series of 3 were spread from a benzene–chloroform mixture (8/2 in vol) or benzene. The concentrations of the spreading solutions were about 1.5 mg/mL.

Figure 1 shows the surface pressure (π)–area (A) isotherm of 3 containing different chain length ($\bar{m}$) on pure water (pH 6.5) at 20 °C. Mean areas were computed by using the number-average molecular weight of the block copolymers. The π–A curves depend strongly on the hydrophobic chain length ($\bar{m}$), and the limiting area, estimated by extrapolating the steepest region to zero surface pressure, tends clearly toward expanding with increasing $\bar{m}$. When $\bar{m}$ becomes longer, the hydrophobic polymer chain may be unable to stand up perpendicularly to the interface due to the formation of a random-coil structure on the water surface as shown in the schematic illustration inserted in Figure 1.

On the other hand, in the shorter case ($\bar{m}$ = 6.7) the polymer chains seem to be oriented perpendicularly and

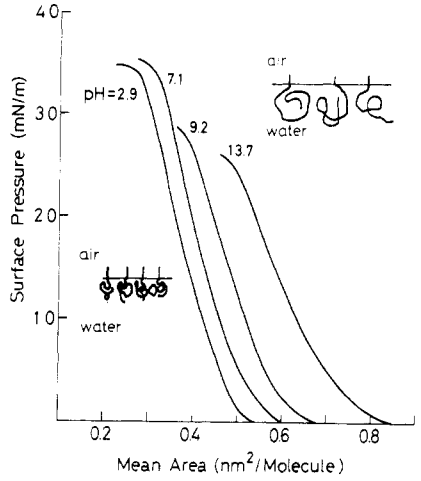


Figure 2. π–A isotherms of 3 ($\bar{m}$ = 6.7) at different pH values at 20 °C. Inset shows a conformational model of PAA in subphase; —, PAA chain.

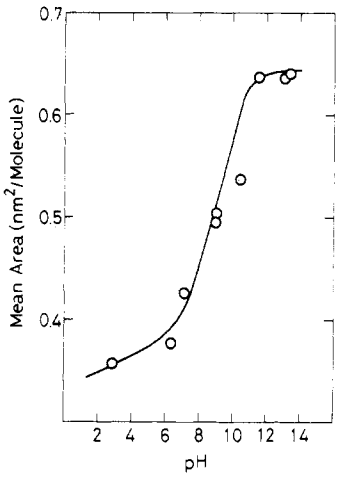


Figure 3. pH dependence of the mean area at zero pressure.

packed more tightly. Since the area did not change for several hours when we checked the time course of area at a constant pressure (20 mN/m), dissolution of amphiphilic molecules into the subphase might be negligible.

Figure 2 shows the π–A isotherms of **3** ($\bar{m}$ = 6.7), a typical polymer, at different pH values. The π–A curves have a tendency to expand with pH. Figure 3 shows the pH dependence of the area at zero pressure. The pK_a of the carboxylic acid group of a PAA chain is probably about 5.0, so the fraction of ionized carboxyl groups will vary considerably in the range of pH investigated. It is, in general, expected that ionization of the carboxyl groups will introduce ionic repulsion, which caused a conformational change of the PAA chain from a globular coil in acidic solution to an expanded conformation at high pH in the subphase. This probably explains the pH sensitivity of π–A curves as shown schematically in the Figure 2 inset.

Deposition of the surface monolayer of **3** ($\bar{m}$ = 6.7) was examined by using a quartz plate at 20 °C under a surface pressure of 20 mN/m. In the first downward stroke the monolayers could not be deposited, but in further strokes the monolayer was readily transferred in both the upward and downward strokes. The formation of the Y-type multilayer was assured, because decreases in the surface area were the same in the downward and upward strokes. The UV absorption spectra also supported the formation of a multilayer. Figure 4 shows the absorbance at 262 nm, which corresponds to PSt, plotted against the number of layers (N) deposited. The absorbance was proportional

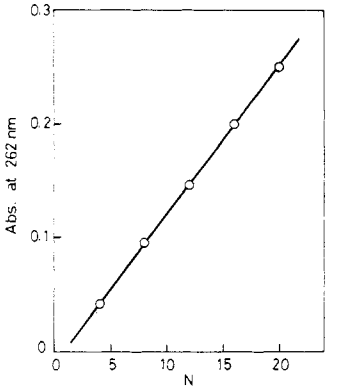


Figure 4. Absorbance at 262 nm of a built-up film as a function of the number of deposited layers (N).

to N at least up to 20 depositions.

We conclude that the monolayer properties of the well-defined amphiphilic block polymers are quite sensitive to the chain length of PSt as the hydrophobic segment and also to pH in the subphase resulting from the conformational change of PSt and/or PAA chains. The monolayers could be transferred on a quartz plate in the Y-type deposition. Attempts to reveal the structural characteristics of such multilayers are now in progress.

Acknowledgment. We are grateful to T. Matsumoto for valuable technical assistance.

References and Notes

(1) Langmuir, I. *J. Am. Chem. Soc.* **1917**, *39*, 1848.
(2) Blodgett, K. *J. Am. Chem. Soc.* **1935**, *57*, 1007.
(3) Mumby, S. J.; Swalen, J. D.; Rabolt, J. F. *Macromolecules* **1986**, *19*, 1054.
(4) Winter, C. S.; Tredgold, R. H.; Vickers, A. J. *Thin Solid Films* **1985**, *134*, 49.
(5) Laschewsky, A.; Ringsdorf, H.; Schmidt, G.; Schneider, J. *J. Am. Chem. Soc.* **1987**, *109*, 788.
(6) Watanabe, M.; Kosaka, Y.; Sanui, K.; Ogata, N. *Macromolecules* **1987**, *20*, 452.
(7) Christie, P.; Petty, M. C.; Roberts, G. G.; Richards, D. H.; Service, D.; Stewart, M. J. *Thin Solid Films* **1985**, *134*, 75.
(8) Ikada, Y.; Iwata, H.; Nagaoka, S.; Horii, F.; Hatada, M. *J. Macromol. Sci.—Phys.* **1980**, *B17*, (2), 191.
(9) Bamford, C.; Finch, C. *Trans. Faraday Soc.* **1963**, *59*, 540.
(10) Bamford, C.; Xiao-zu Han. *Polymer* **1981**, *22*, 1299.
(11) Niwa, M.; Katsurada, N.; Matsumoto, T.; Okamoto, M. submitted for publication in *J. Macromol. Sci.—Chem.*
(12) Niwa, M.; Hayashi, T.; Matsumoto, T. *J. Macromol. Sci.—Chem.* **1986**, *A23* (4), 433.
(13) Number-average molecular weights were measured by a Knauer vapor-pressure osmometer from acetone solutions at 37 °C.
(14) GPC curves were recorded on a Shimadzu high-performance liquid chromatograph (LC-3A) from THF solutions at 40 °C.
(15) ^{1}H NMR and ^{13}C NMR spectra were measured by a JOEL JNM-GX400 FT-NMR spectrometer with TMS as internal standard from $CDCl_3$ solutions at 400 and 100 MHz, respectively.

Masazo Niwa,* Naoki Katsurada, and Nobuyuki Higashi
Department of Applied Chemistry
Faculty of Engineering, Doshisha University
Karasuma-Imadegawa, Kamikyo-ku, Kyoto 602, Japan
Received January 4, 1988

Mechanisms of Ring-Opening Polymerization of 2-(Perfluoroalkyl)-2-oxazolines Initiated by Sulfonates: A Novel Covalent-Type Electrophilic Polymerization

The present paper describes the results of study on the ring-opening polymerization of 2-(perfluoroalkyl)-2-oxa-

0024-9297/88/2221-1880$01.50/0