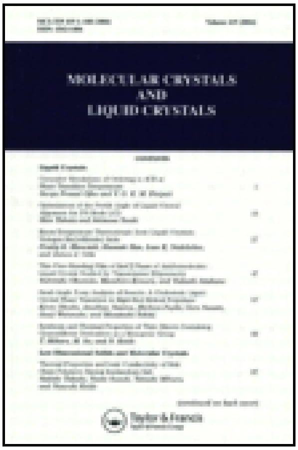

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A Mechanical Control Over Orientation of Pendent Oligoetheres of Amphiphilic Polymers at the Air-Water Interface

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A MECHANICAL CONTROL OVER ORIENTATION OF PENDENT OLIGOETHERES OF AMPHIPHILIC POLYMERS AT THE AIR-WATER INTERFACE

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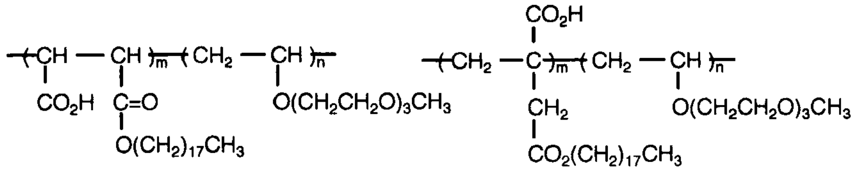
Abstract Monooctadecyl maleate and monooctadecyl itaconate copolymers containing pendent oligoethers and carboxyls were synthesized and spread on pure water, on the aqueous poly(allylamine), and on saturated aqueous NaCl. Examination of the monolayer properties of the polymers by surface pressure-area isotherms reveals that their pendent oligoethers lie at the air-water interface at low surface pressures and are forced down into the subphase when the film is compressed. This orientation switching by compression-expansion cycle of monolayers is reproducible. Another pendant of carboxyls makes these polymers possible to form the polyion-complexed monolayers with the subphase polymer poly(allylamine) at the air-water interface. The polyion-complexation at the air-water interface and in resulting Langmuir-Blodgett film was confirmed by the surface pressure-area isotherm and FT-IR spectroscopy, respectively. SEM observation of these films on a porous membrane filter showed that the six-layer film was sufficiently stable to cover the filter pore(0.1 μm).

INTRODUCTION

Recently, the preformed polymers have been employed in order for the Langmuir-Blodgett(LB) film to have the improved mechanical stability and to become their technological applications possible.[1] Since the copolymers of maleic anhydride and their derivatives were spread to monolayers[2], polyacrylates[3], polymethacrylates[4], polymers of aromatic backbones[5] or with aromatic side chains[6], condensation polymers[7], water-soluble polymers[8], rod-like polymers[9], and poly(vinyl alkylals)[10] were used to



$$-\!\left(\mathrm{CH(CO_2H)}-\mathrm{CH(C(=O)O(CH_2)_{17}CH_3)}\right)_m\!\left(\mathrm{CH_2}-\mathrm{CH(O(CH_2CH_2O)_3CH_3)}\right)_n\!-$$

C18MA-VE3

$$-\!\left(\mathrm{CH_2}-\mathrm{C(CO_2H)(CH_2CO_2(CH_2)_{17}CH_3)}\right)_m\!\left(\mathrm{CH_2}-\mathrm{CH(O(CH_2CH_2O)_3CH_3)}\right)_n\!-$$

C18ITA-VE3

fabricate stable monolayers and LB films. Specifically, Kunitake et al. have reported stabilization of monolayers and LB films by electrostatic interaction of ionic polymers with oppositely-charged amphiphiles[11] and by covalent cross-linking of ionically interacting polymers.[12] Very recently, concurrent removal of alkyl tails along with a cross-linking of LB films was achieved by heat treatment.[13]

On the other hand, we have become interested in the monolayer behavior of poly(ethylene oxide) (PEO). PEO forms stable monolayers at the air-water interface up to a surface pressure of ca. 10 dyn/cm.[14] And then, when the film is compressed beyond its collapse point, the segments of PEO are forced down into the aqueous subphase.[15] Thus, one might expect that by coupling polyether groups to one side of hydrophobic compounds showing low compressible monolayers, the resulting surfactant should yield isotherms showing both an expanded and a condensed phase; i.e., the polyether groups are forced down into the subphase by compression, while expansion brings them back toward the surface of water. This phenomenum means that by adjusting the orientation of its polyether groups, one might be able to fine-tune the interaction of the surfactants with a guest ion or molecule in unique manner. Recently, Regen et al. demonstrated excellently this monolayer behavior with calix[6]arene-based "octopus molecules" containing polyether groups.[16]

We describe, in this paper, i) monolayer properties of polymers C18MA-VE3 and C18ITA-VE3 which are designed to have pendent polyethers and carboxyls. The pendent polyethers are expected to give a flexibility to the polymer backbone, and their orientations to be mechanically controlled. The carboxyls can also interact with guest ions or moecules. ii) a formation of self-supporting LB films over pores of a membrane filter, as a indirect method to measure the mechanical stability of the LB film, in which polymers C18MA-VE3 and C18ITA-VE3 are polyion-complexed with subphase polymer poly(allylamine) through carboxylate/ammonium salt formation.

EXPERIMENTALS

Materials

The monomers, octadecyl maleic acid monoester and octadecyl itaconic acid monoester, and the comonomer, 2-[2-(2-methoxyethoxy)ethoxy]ethyl vinyl ether, were synthesized according to the known procedures.[13,17] The copolymerization of the monoalkyl maleate and the monoalkyl itaconate monomer was carried out in a pressure bottle at 60 °C for 24 h by using the vinyl ether as comonomer. AIBN was used as initiator. The structures of the monomers and the resulting copolymers were confirmed by IR and NMR spectra. The composition of the copolymers were estimated to be 1:1 by elemental analysis. Poly(allylamine) hydrochloride was purchased from Nitto Boseki Co. and treated with a strong anion exchange resin (Amberlite IRA-402) to obtain free poly(allylamine) (PAA). The concentration of the amino group in aqueous solution was determined by colloid titration with standard poly(vinyl sulfate) solution using Toluidine Blue O as indicator.

π-A isotherm and LB deposition of monolayer

A film balance system HBM-SS(Kyowa Interface Science) was used for measuring surface pressure as a function of molecular area(trough size, 150 X 600 mm). Isotherms were taken at a compression rate of 0.5 mm/s. Chloroform was employed as spreading solvent. Monolayers were spread on pure water, on aqueous poly(allylamine) (2×10^{-4} mol/-NH_2), and on saturated aqueous NaCl, and incubated for 10 min before starting the compression.

The deposition of the monolayer was performed in the vertical mode. The employed substrates were fluorocarbon membrane filters (FP-010, Sumitomo Electric Co.) for scanning electron microscopy (SEM) observations and CaF_2 plates (GL Sciences) for FT-IR measurements. The transfer onto the substrates was carried out at a surface pressure of 30.0 ± 0.2 dyne/cm and a deposition rate of 5 mm/min except for 50 mm/min at downward stroke in the case of CaF_2 plates.

Measurements

FT-IR measurements were carried out on a Bomem MB-102 FT-IR spectrometer by the transmission method. In order to minimize the influence of water vapor and CO_2 on the spectra, the system was purged by

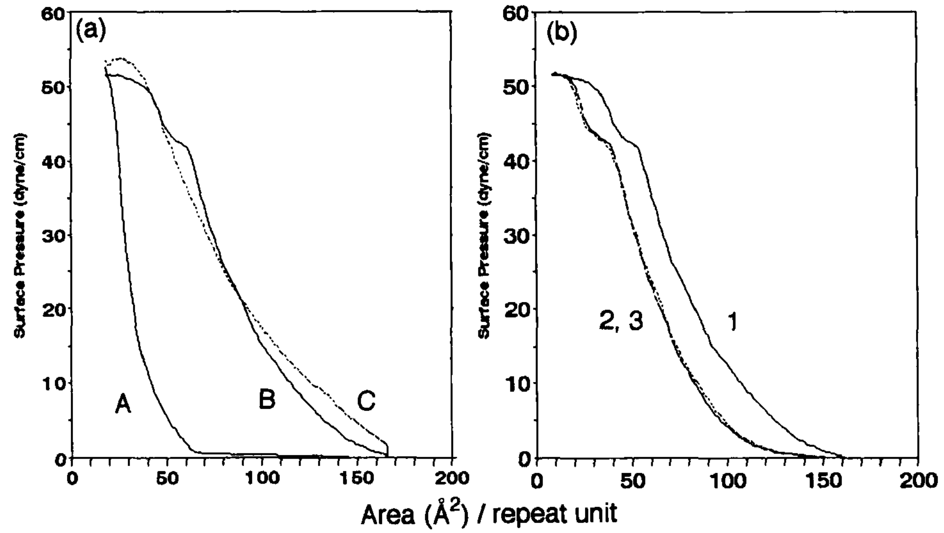


FIGURE 1. (a) Surface pressure-area (π-A) isotherms of C18MA-VE3. A; on pure water. B; on aqueous poly(allylamine) (PAA). C; on saturated Aqueous NaCl. (b) π-A isotherms by multiple compression. The concentration of the amino group of PAA is 2 X 10^{-4} M.

dry air for 1-2 h before measurement. Scanning electron microscopy (SEM; JSM 35CH) was used to observe the surface morphology of the FT-010 membrane filter (pore diameter, 0.1 μm). An acceleration voltage of 15 kV was employed. The samples were sputtered with Au before observation.

RESULTS AND DISCUSSION

Chloroform solution of polymer C18MA-VE3 was spread on pure water, on aqueous PAA, and on saturated aqueous NaCl. Surface pressure-area (π-A) isotherms of Figure 1a show that the polymer forms stable monolayers. The monolayer on pure water gives condensed phase, while the monolayers on aqueous PAA and on saturated aqueous NaCl show expanded phases. The condensed phase of the monolayer on pure water was unexpected, but it is supposed to be understood from the polyether hydration, i.e., the extensively hydrated polyethers on pure water are already placed not on the water surface but toward into the subphase in this polymeric monolayer. The expanded area on the saturated aqueous NaCl seems to be due to the reduction of polyether hydration and the resulting increase of hydrophobicity in high concentrations of NaCl as suggested by Regen.[16] In

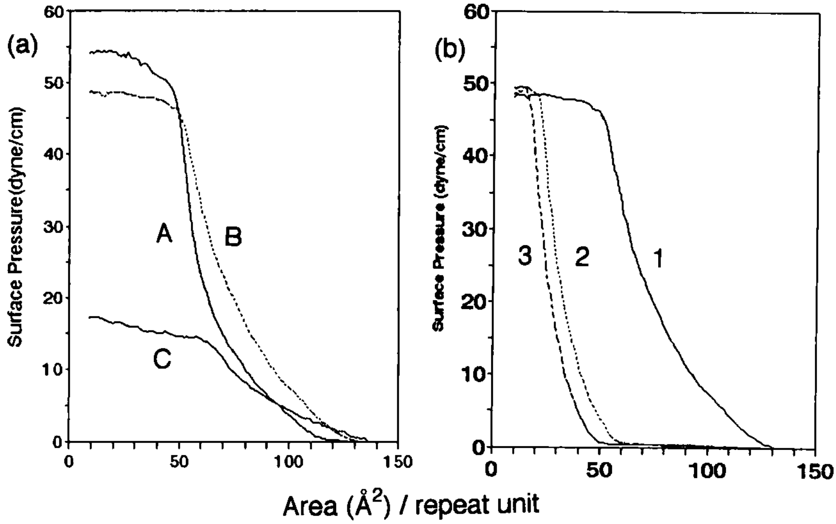
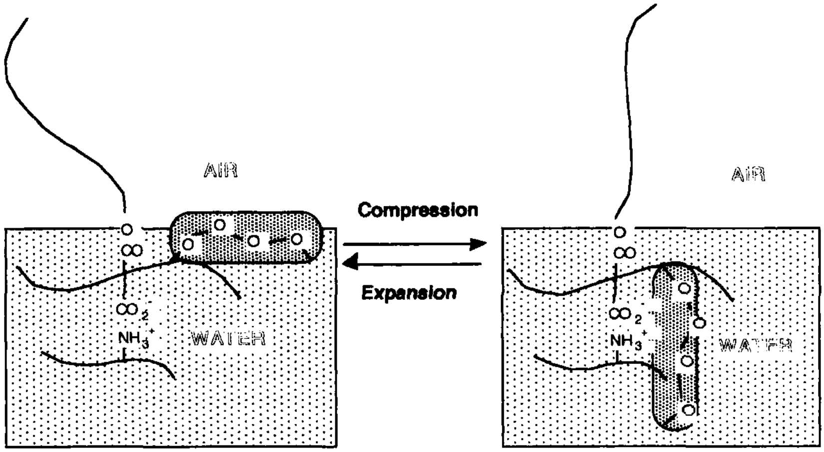


FIGURE 2. (a) Surface pressure-area (π-A) isotherms of C18ITA-VE3. A; on pure water. B; on aqueous poly(allylamine) (PAA). C; on saturated Aqueous NaCl. (b) π-A isotherms by multiple compression. The concentration of the amino group of PAA is 2 X 10^{-4} M.

the case of the monolayer on aqueous PAA subphase, besides the dehydration effect and the steric effect by polyamines, the change between the two isotherms (on pure water and on aqueous PAA) should be attributed to the formation of a polyion complex at the interface, as already described for other systems.[12,13] And, in the case of the monolayer on aqueous PAA subphase, two component isotherm is observed. Although we have no experimental means to clarify the two-component isotherms, it is supposed that the polyether groups still lying on the surface are forced down into the subphase when the surface pressure is increased up to ca. 42 dyn/cm to the monolayer, as illustrated in Scheme 1. Fig. 1b shows that the π-A isotherms of monolayer compression are reproducible from the second run, i.e., when the compressed monolayer is expanded, the polyether groups are supposed to be placed back on the surface. And, the two-component isotherm was not observed on saturated aqueous NaCl. No noticeable expansion of the isotherms are observed with increasing incubation times from 10 min to 1 h.

The π-A isotherms of the polymer C18ITA-VE3 are shown in Fig.2. When spread on pure water, in this time, the monolayer reveals the expanded phase at low surface pressure and a limiting area of ca. 50



SCHEME 1. Schematic illustration of orientation switching of the pendent oligoether by compression and expansion.

Å^2/repeat unit. The hydrated polyether pendants seem to be extended on water surface. The isotherms of the monolayers on aqueous PAA and on saturated aqueous NaCl show also the expanded phase at low surface pressure. The monolayer on saturated aqueous NaCl shows relatively low collapse pressure of ca. 15 dyn/cm. Another difference in the isotherms between the polymers C18MA-VE3 and C18ITA-VE3 is that the two-component isotherms are not observed in the C18ITA-VE3 monolayers. And when the pendent polyethers are once forced down into the subphase, the pendants are not placed back along with the expansion of the monolayer, as shown the isotherms in Fig. 2b. The polymer C18ITA-VE3 has same functional groups as the C18MA-VE3 has, but only the attachment of the pandants on the backbone carbons and one methylene unit in the ester pendant are different. The C18ITA-VE3 has the structure of carboxyls and long alkyl ester chains attached on the same backbone carbon, while the C18MA-VE3 on the different backbone carbons. Why such a structural difference between the two kinds of polymers causes the different monolayer behaviors is not clear yet.

The monolayers on aqueous PAA were transferred onto solid substrates such as a porous fluorocarbon membrane filter (FP-010) and a CaF$_2$ plate in order to measure indirectly the mechanical stability of the LB films by observing the self-supported films over the pores of the filters by SEM and to confirm the polyion complexes formed from the carboxyls of the copolymers and the amino groups of PAA by FT-IR, respectively. The Y-type deposition on FP-010 was performed at a surface pressure of 30 dyn/cm at a transfer rate of 10 mm/min. In the case of the CaF_2 substrate, a rapid downward stroke of 50 mm/min was necessary to obtain the Y-type deposition in C18MA-VE3 monolayers, because, when the speed of the downward stroke was slowed down, the already deposited layers were peeled off from the substrate during the downward stroke. The transfer ratios were 1.2 to 0.8 on both substrates for 6 layer depositions. The monolayers were so stable that no spontaneous area decrease was observed up to 2 h at 30 dyn/cm which the transfer was carried out.

Figure 3a shows IR spectra of C18MA-VE3 and C18MA-VE3/PAA

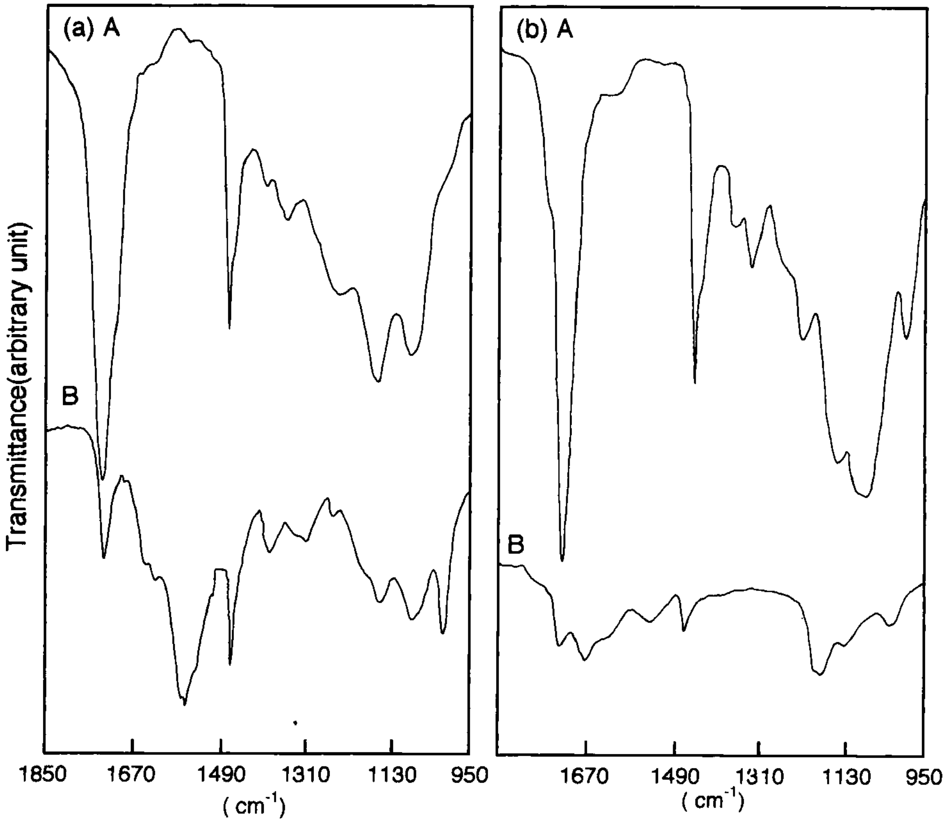


FIGURE 3. (a) C18MA-VE3 system. (b) C18ITA-VE3 system. A; IR spectra (KBr disc) of copolymers B; Transmission FT-IR spectra of copolymer/PAA LB films (15 X 2 layers) on a CaF_2 plate.

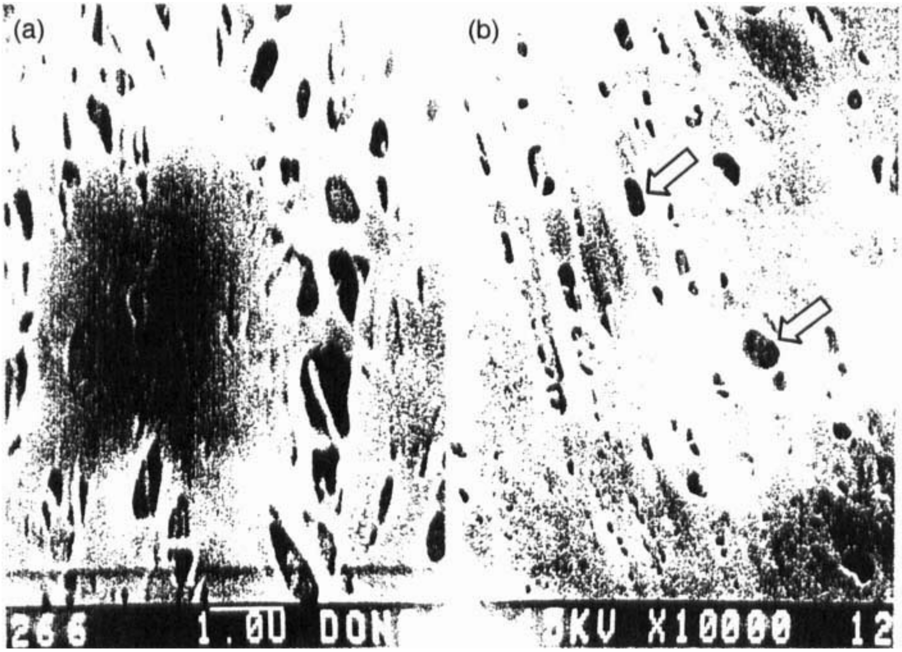


FIGURE 4. Scanning electron micrographs of C18MA-VE3/PAA LB films deposited on fluorocarbon membrane filters (FP-010). (a) 2-layer film. (b) 6-layer film. The samples were sputtered with Au and observed at 15 kV. Typical defects are indicated with arrows.

complex. The strong carbonyl peak at 1740 cm^{-1} on Fig. 3a A is decreased on Fig. 3a B. Instead, the two characteristic peaks at around 1635 cm^{-1} and 1561 cm^{-1} on Fig. 3a B occurred, which are attributed to carboxylate salt stretching and the N-H bending modes, showing incorporation of PAA into the film. Similar peak patterns of the IR spectra are seen on Fig. 3b A and B of C18ITA-VE3 and C18ITA-VE3/PAA complex, respectively.

SEM photographs show the polyion complex films deposited onto porous membranes (FP-010). Figure 4 is the SEM photograph of a porous FP-010 membrane covered by C18MA-VE3/PAA multilayers. We can readily observe the original pores which are long and have a dark appearance. Defects with sizes of 100-300 nm are seen as dark spots even in the six-layer film shown in Fig. 4. Typical defects are indicated with arrows. Good covering of the pores is found in the six-layer film (Fig. 5) of C18ITA-VE3/PAA complex. Satisfactory coverage of the pore by a six-layer film indicates that this LB film has a good self-supporting capability.

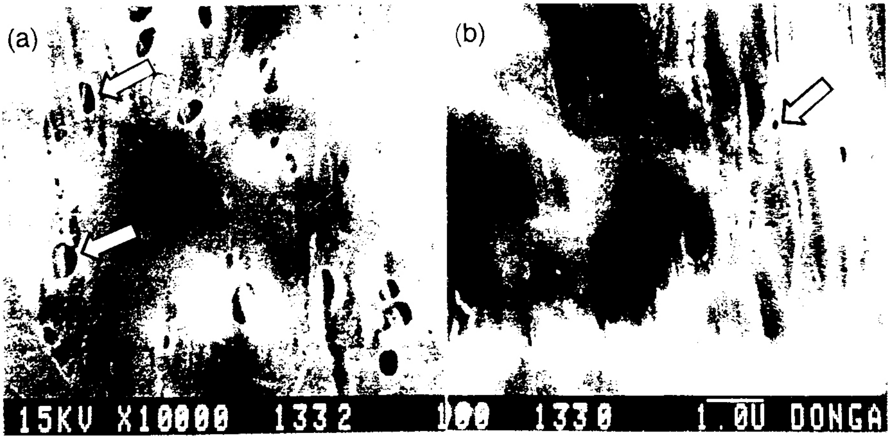


FIGURE 5. Scanning electron micrographs of C18ITA-VE3/PAA LB films deposited on fluorocarbon membrane filters (FP-010). (a) 2-layer film. (b) 6-layer film. The samples were sputtered with Au and observed at 15 kV. Typical defects are indicated with arrows.

REFERENCES

1. H.Baker, K.Dorn, B.Hupfer, and H.Ringsdorf, Adv.Polym.Sci., 69, 1 (1985).
2. R.H. Tredgold and C.S. Winter, J.Phys. D, 15, L55 (1982).
3. S.J.Mumby, J.D.Swalen, and J.F.Rabolt, Macromolecules, 19,1054 (1986).
4. A.Laschewsky, H.Ringsdorf, G.Schmidt, and J.Schneider, J.Am.Chem.Soc., 109, 788 (1987).
5. M.Era, K.Kamiyama, K.Yoshiura, T.Momii, H.Murata, S.Tokito, T.Tsutsui, and S.Saito, Thin Solid Films, 179, 1 (1989).
6. S.Ito, S.Ohmori, and M.Yamamoto, Macromolecules, 25, 185 (1992).
7. D.Lupo, W.Prass, and U.Scheunemann, Thin Solid Films, 178, 403 (1989).
8. K.Nishiyama and M.Fujihara, Chem.Lett., 1257 (1988).
9. S.Schwiegk, T.Vahlenkamp, Y.Xu, and G.Wegner, Macromolecules, 25, (1992) 2513.
10. M.Watanabe, Y.Kosaka, K.Oguchi, K.Sanui, and N.Ogata, Macromolecules, 21, 2997 (1988).
11. M. Shimomura and T. Kunitake, Thin Solid Films, 132, 243 (1985).
12. T. Ueno and T. Kunitake, Chem.Lett., 1927 (1990).
13. B.-J. Lee and T. Kunitake, Langmuir, 8, 2223 (1992).
14. R.L.Shuler and W.A.Zisman, J.Phys.Chem., 74, 1523 (1970).
15. B.B.Sauer, H.Yu, M.Yazdanian, G.Zografi, and M.W.Kim, Macromolecules, 22, 2332 (1989).
16. M.Conner, I.Kudelka, and S.L.Regen, Langmuir, 7, 982 (1991).
17. W.H.Watanabe an L.E. Conlon, J.Am.Chem.Soc., 79, 2828 (1957).