terminal groups and found to be $\bar{M}_n = 1900$. ^{1}H NMR characterization of 4 was performed in CD_2Cl_2, at −20 °C, on a WM 250 Bruker spectrometer. ^{1}H and ^{13}C NMR spectra of oligomer samples were run on an AM 200 Bruker spectrometer at 120 °C in a solution of $CDCl_2CDCl_2$. Hexamethyldisiloxane (HMDS) was used as an internal reference (δ ^{13}C 2.0 ppm and δ ^{1}H 0.06 ppm), and the chemical shifts were converted to the TMS scale. For selection of the ^{13}C resonances, the sequence DEPT with a pulse angle $\theta = 135°$ was used. Minor ^{13}C resonances appear as follows: quaternary carbons downfield 140 ppm; methinic resonances at 48.29 and 37.06 ppm; methylenic resonances at 113.66, 44.91, 44.12, and 42.05 ppm; a methyl resonance at 21.07 ppm. The *J*-correlated 2D ^{1}H spectrum was obtained with the pulse sequence COSY, using a 90° mixing pulse.

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Registry No. 1, 78002-90-1; PCy_3, 2622-14-2; $C_6H_5CH{=}CH_2$, 100-42-5.

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José R. Ascenso, Alberto R. Dias,* Pedro T. Gomes, and Carlos C. Romão

Centro de Química Estrutural, Complexo I
Instituto Superior Técnico, Avenida Rovisco Pais
1096 Lisboa Codex, Portugal

Quang-Tho Pham*

Service Central d' analyse du CNRS
B.P. 24, 69390 Vernaison, France

Denis Neibecker and Igor Tkatchenko*

Laboratoire de Chimie de Coordination du CNRS
205 route de Narbonne
31077 Toulouse Cêdex, France

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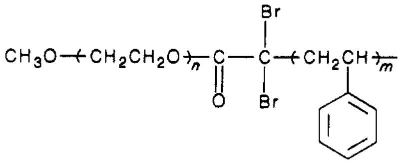
Reversible Interpolymer Complexation between Poly(oxyethylene)-Based Amphiphilic Block Polymer and Poly(acrylic acid) at the Air–Water Interface

The present paper describes the results of a study on surface monolayer properties and reversible interpolymer complexation at the air–water interface for the amphiphilic block polymer 1, poly(oxyethylene-*block*-styrene). The interpolymer complexation between 1 and poly(acrylic acid) in the subphase is reversibly controllable by varying pH in the subphase; at the lower pH (<5) the formation of an interpolymer complex is observed, whereas such a complex is deformed at pH >5.



1: *n* = 10; *m* = 14, 20, 113

We have reported that amphiphilic block polymers consisting of poly(acrylic acid) (PAA) and poly(styrene) (PSt), prepared by using the catalytic system[1,2] of halo-terminated polymer and manganese carbonyl ($Mn_2(CO)_{10}$), can form stable monolayers at the air–water interface and that they are readily transferred on a quartz plate at each downward and upward dip (Y-type deposition)[3] by using the Langmuir–Blodgett method.[4]

In the present study, we prepared amphiphilic block polymers composed of poly(oxyethylene) (POE) and PSt and studied the effect of addition of PAA in the subphase on the monolayer behavior by using surface pressure (Π)–area (*A*) isotherm measurements at various pHs in order to obtain information regarding the polymer–polymer interaction at the air–water interface. Polyion complexations from bilayer-forming amphiphiles and oppositely charged polyions at the air–water interface have been reported to be useful for stabilization and facilitated deposition of surface monolayers.[5,6] It is well-known that an interpolymer complex is formed between PAA and POE through hydrogen bonding in an aqueous medium.[7–9] However, the polymer–polymer interaction at the air–water interface has not yet been established.

Amphiphilic block polymers 1 with different hydrophobic chain length were prepared according to Scheme I. Macroinitiator 2 was prepared by the reaction of sodium ω-methoxypoly(oxyethylene) ($M_n = 480$; Japan Catalytic Chemical Industry Co., Ltd.) with tribromoacetyl chloride.[10] Block polymerizations of styrene (St) as a second monomer with macroinitiator 2 were carried out in bulk with $Mn_2(CO)_{10}$. We have already established that well-defined block copolymers with controlled chain length of blocking are prepared by varying the conversion of the second monomer and the feed composition of macroinitiator and second monomer in such catalytic system.[1–3] Resulting amphiphilic block copolymers were characterized to consist of a POE chain ($n = 9.7$) as the hydrophilic part and a PSt chain (m = 14, 20, and 113) as the hydrophobic part on the basis of the structural analyses.[11]

Spreading experiments of 1 were performed on a microprocessor-controlled film balance (San-esu Keisoku Co., Ltd.). A series of 1 was spread from benzene. The concentrations of the spreading solutions were about 1.5 mg/mL. The surface pressure (Π)–area (*A*) isotherm measurements for 1 on pure water showed that well-behaved monolayers were formed and the limiting area trended toward expanding with increasing *m* similar to the case of PAA-*block*-PSt as described before:[3] i.e., when *m*

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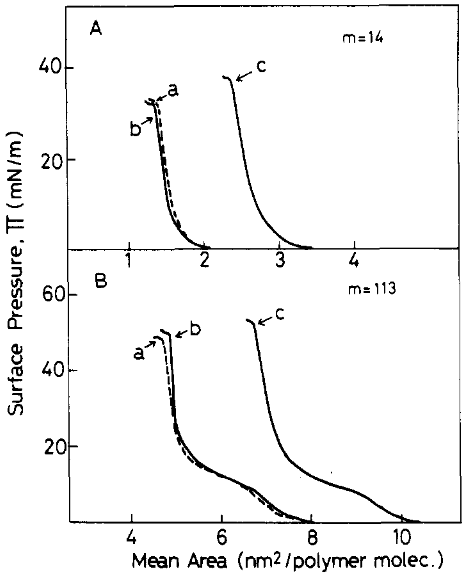


Figure 1. Π–*A* isotherms of 1 (A, $m = 14$; B, $m = 113$) at 20 °C: (a) on pure water (pH 6,5); (b) on aqueous PAA (pH 8.2); (c) on aqueous PAA (pH 2.0).

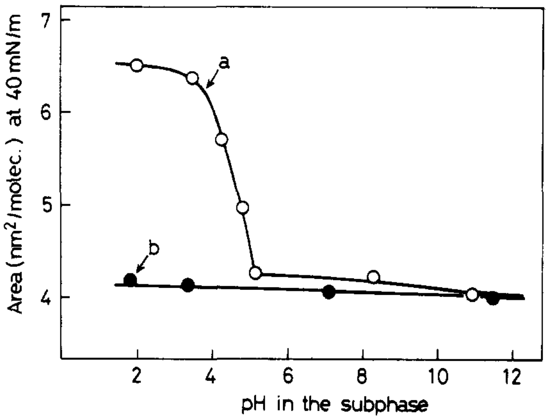
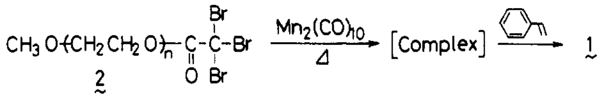


Figure 2. pH dependence of the mean area on aqueous PAA (a) and on pure water (b) at a constant surface pressure of 40 mN/m on the basis of Π–*A* curves of 1 at 20 °C.

Scheme I



$$CH_3O(CH_2CH_2O)_n-\overset{\displaystyle O}{\underset{}{C}}-CBr_3 \xrightarrow[\Delta]{Mn_2(CO)_{10}} [\text{Complex}] \longrightarrow 1$$

2

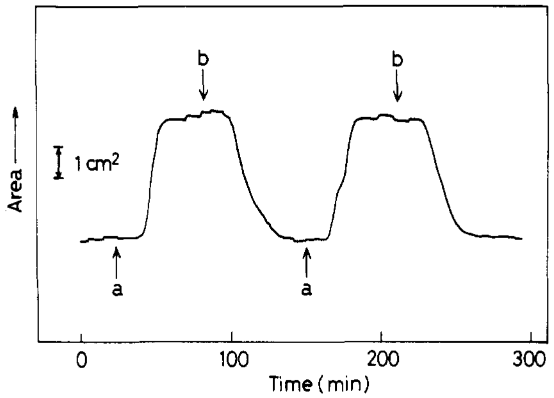


Figure 3. Mean area changes of a monolayer of 1 ($m = 113$) on aqueous PAA at a constant surface pressure of 10 mN/m responding to the pH at 20 °C. Aqueous HCl was added to the subphase at arrow a, giving pH ca. 3.0; aqueous NaOH was charged to the subphase at arrow b, giving pH ca. 6.5.

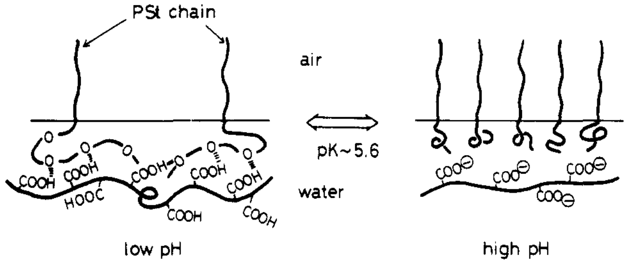


Figure 4. Schematic illustration for the reversible interpolymer complexation at the air–water interface.

becomes longer, the hydrophobic polymer chain may be unable to stand up vertically to the surface due to the formation of a random-coil structure on the water surface.

Figure 1 shows the Π–*A* isotherms of 1 ($m = 14$ and 113) on pure water and on aqueous PAA ($M_v = 10000$, 2×10^{-5} unit mol/L) at different pH value at 20 °C. The pH was adjusted with either NaOH or HCl as required. With addition of PAA to the subphase at pH 2, the Π–*A* curves for both polymers were extremely expanded compared with those on pure water. In contrast, when the pH value increased up to 8.2 the Π–*A* curves almost fitted those on pure water. These suggest that there is an interaction between the POE segment of 1 and PAA at the air–water interface in the lower pH region. Figure 2 displays the pH dependence of the mean area at a constant surface pressure of 40 mN/m on the basis of Π–*A* curves of 1 ($m = 113$). The mean area on pure water did not change by varying pH in the subphase. On the other hand, the pH dependence on aqueous PAA was quite different from that on pure water: at the lower pH region (<5) the area remarkably expanded as described above, suggesting formation of an interpolymer complex between POE segment of 1 and PAA through hydrogen bonding at the air-water interface. When the pH value of the subphase increased, the area decreased drastically at around pH 5, which corresponds to the dissociation constant ($pK_a = 5.6$) of PAA,[12] because of weakening of such polymer–polymer interactions owing to the ionization of carboxylic acid of PAA. Any significant change on the area was not observed upon further increase of pH and the area on aqueous PAA was very close to that on pure water above pH 5. Thus, an interpolymer interaction was suppressed in such a pH region.

Figure 3 shows the area changes of the monolayer of 1 ($m = 113$) on aqueous PAA at a constant pressure of 10 mN/m, responding to the pH adjusted with HCl or NaOH in the subphase. The area rapidly increased within 10 min after addition of aqueous HCl (pH 3) via an induction period (about 20 min), which might be due to the diffusion of H^+ in the subphase, and reverted to the original value on adding aqueous NaOH to the subphase (pH 6). Thus, the formation of the interpolymer complex is reversible at the air–water interface as shown schematically in Figure 4. A similar situation was observed for the other two amphiphilic block polymers.

In conclusion, the poly(oxyethylene)-based amphiphilic block polymer formed a well-behaved surface monolayer and formed an interpolymer complex with poly(acrylic acid) in the subphase at the air–water interface at an appropriate pH value. Also, such complexation is reversibly controlled by pH change. These findings have made it possible for the first time to control a pH-induced interpolymer complexation at the *air–water interface*. Attempts to deposit such complexed monolayers are now in progress.

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Masazo Niwa* and Nobuyuki Higashi

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

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New Mechanism for Craze Toughening of Glassy Polymers

Introduction. Polystyrene and related homopolymers are brittle materials that typically fail in a tensile test at strains of 5% or less. The failure process occurs by the initiation and propagation of a few large crazes which soon fracture under the relatively high levels of stress. These polymers can be toughened by the addition of a rubbery second phase that forms composite particles, which initiate at relatively low stresses a large volume fraction of crazes that produce substantial plastic strain at relatively low stresses, without apparently initiating failure within the crazes. The crazes are believed to initiate as a result of the stress concentrations caused by the rubber particles, so the rubber acts in an essentially mechanical manner, leaving the properties of the surrounding polymer unchanged. Considerable energy is dissipated in the formation of the polystyrene crazes, producing a relatively tough material that shows "craze plasticity" and failure strains of up to 50%.[1]

In this paper we wish to suggest that a rubbery second phase can promote craze plasticity and toughening by a second entirely different process. A few percent of low molecular weight polybutadiene has been found to reduce the stress to craze polystyrene by a large amount and increase the failure strain up to 20%. The polybutadiene is not thermodynamically compatible with the polystyrene and forms a second phase at concentrations above 0.45%. The polybutadiene is believed to act as an environmental crazing agent and plasticizer whose solubility is enhanced along the craze interfaces and at the craze tip by the hydrostatic tensions that exist in these regions. Most crazes initiate from surface imperfections as in unmodified polystyrene though some may initiate from the larger rubber inclusions. These crazes then propagate in the polystyrene with the inclusion helping to supply the polybutadiene to the craze interfaces. The rubber here is believed to act mainly as a strategically placed low-viscosity plasticizer but is only plasticizing the border regions, the so-called active zone, where craze fibril drawing is taking place.

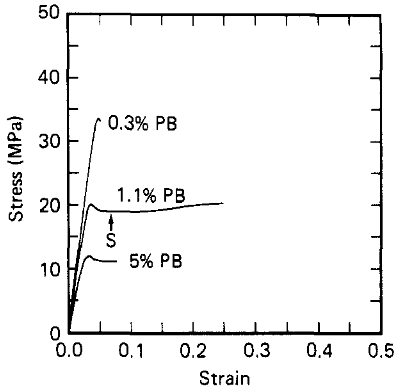

Figure 1. Three representative stress–strain curves of polystyrene containing low M_w PB. The arrow on the 1.1% curve shows where the craze drawing stress, *S*, was measured. A typical HIPS shows a similar stress–strain curve with *S* of about 15 MPa.

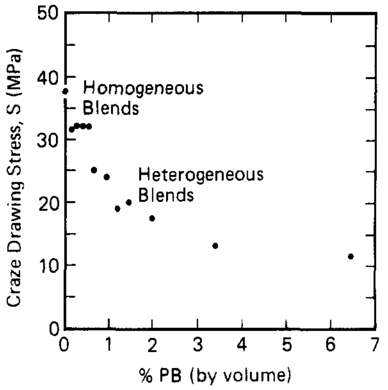

Figure 2. Variation of craze drawing stress with polybutadiene content. For low PB samples the craze yield stress was taken as a good approximation to *S*.

Experimental Techniques. Blends of polystyrene (PS) (2.7×10^5 M_w, $M_w/M_n = 2.4$) with polybutadiene (PB) (cis/trans/vinyl $\simeq$ 45/45/10; 2700 M_w) were made by spin casting from toluene solutions in the manner that has been described in detail earlier.[2] Samples with a polybutadiene content of greater than 0.45% were visibly cloudy. They were found by TEM to contain 0.2-μm mean diameter rubber particles. Strips were cut from these samples for tensile testing in an Instron machine at a strain rate of 1.3×10^{-4} s^{-1} at a temperature of 23 °C. The microstructure of the crazes was examined by using small-angle X-ray scattering (SAXS) using the A1 beam line at the Cornell synchrotron source CHESS. The samples were crazed in three-point bending and the scattering from the crazed region in the bent samples was recorded at a camera length of 351 mm using a EG&G PARC OMA diode array detector. Mean fibril diameters were obtained by a Porod analysis of these data in the manner described before.[3] A fibril volume fraction for the crazes of 0.25 was assumed in the analysis for all the materials.

Results and Discussion. Stress–strain curves for several of the samples with different rubber contents are shown in Figure 1, while Figure 2 shows the effect of PB additions on the craze drawing stress of the materials. SAXS curves for two limiting blends are given in Figure 3. *It is immediately evident from these results that the* addition of a small amount of low molecular weight PB has a strong effect on the crazing properties of the PS