Langmuir and Langmuir−Blodgett Films of Schiff Base Modified Styrene−Maleic Anhydride Copolymers

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Introduction

Monolayers of amphiphiles ordered at the air/water interface (Langmuir films) are one of the simplest type of organized molecular system.[1] Such films transferred onto solid substrates by the Langmuir−Blodgett (LB) technique have numerous potential applications in molecular electronics and optoelectronics.[2−4] Most LB films prepared from low molecular weight amphiphiles are, however, not sufficiently stable mechanically and also not sufficiently stable to molecular reorganization for commercial applications.[5,6] This has prompted an interest in polymeric LB films, [6−15] especially films formed from preformed polymers.[8,9] Recently, it was reported that various derivatives prepared from alternating copolymers of simple straight chain α-olefins and maleic anhydride form excellent LB films, especially when the olefin contains[13−16] carbon atoms.[11] In order to improve the heat stability and mechanical strength, the introduction of polar groups, aromatics, and heterocycles is very effective. Such heat stable aromatic polymer precursors have been synthesized and their properties studied.[16]

In this work, styrene−maleic anhydride copolymer has been modified by reacting with Schiff base formed between thiosemicarbazide and salicylaldehyde by the known procedure.[17] Multilayers of aromatic Schiff base oligomers,[18] poly(benzimidazole),[19] and polyimides from poly(amic acid) alkylamine salts[20] have been reported by the earlier studies. Our study consists of three steps: (1) synthesis of the Schiff base and subsequent reaction of the anhydride groups in the copolymer to give the acid−amide and diimide "head groups" (Scheme (1), (2) formation of the Langmuir films and their characterization, and (3) deposition of the LB films on various substrates for characterization by FTIR, X-ray diffraction, and DSC.

Experimental Details

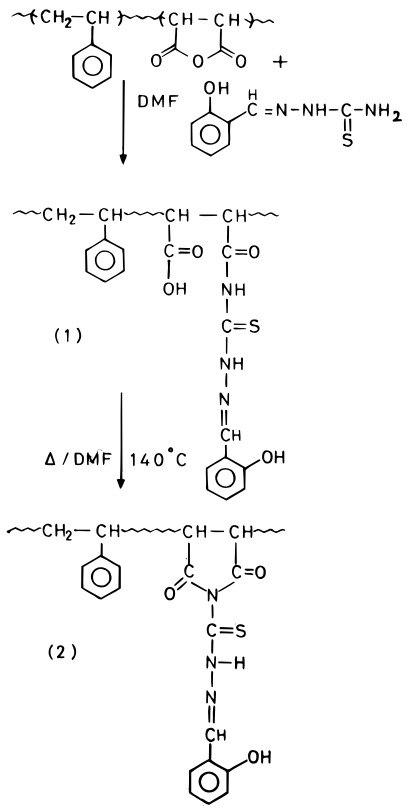
The Schiff base modified styrene−maleic anhydride copolymer **1** was synthesized by the reaction of the copolymer (mol wt M_n = 1600, Aldrich Chemie) with the Schiff base which was itself formed by reacting thiosemicarbazide with salicylaldehyde. After the reaction a white solid precipitated. Repeated precipitation of the crude product from THF into methanol and subsequent drying in vacuo gave the pure compound. The corresponding alkylamine salt of **1** was prepared by mixing a solution of the copolymer with Me_2NR prior to use. The diimide with the Schiff base (Scheme 1) was formed by heating polymer **1**, resulting in a yellow solid. All materials were characterized by NMR and IR spectroscopy and were found to be satisfactory. The characteristic absorption bands due to the carbonyl, ester, and amide appeared at 1764, 1740, and 1430 cm^{-1}, respectively, in the IR (and on heating the ester bands disappeared and the characteristic bands due to imide formation appeared at 1772 and 1382 cm^{-1}, respectively), while the NMR spectra (measured with a Bruker MSL 300, 300 MHz) for ^{13}C (DMSO-d_6) showed three distinct regions for polymer **1** corresponding to carbonyl carbons at δ (ppm) 177.72, C−N at δ 162.5, and C═S at δ 156.45; aromatic carbons between δ 140.51 and 126.87; CH at δ 52.31 and 44.24; and CH_2 between δ 33 and 37 for polymer **2**: δ 166.45, carbonyl carbons attached to imide N; δ 131.26 and 126.29, C's ortho to carbonyl C's; CH ranging between δ 44.06 and 38.67; CH_2 at δ 35.8). The molecular weights of the polymers were estimated by GPC by direct measurement on the anhydride copolymers. The results indicate that the products have average molecular weights M_w in the range 5000−7000 and polydispersity values between 1.1 and 1.6. The monolayers were spread from 1 mmol L^{-1} solutions prepared from a mixture of *N*,*N*-dimethylacetamide and chloroform (1:1) on double distilled deionized water at a subphase temperature of T = 22 °C and in some cases on KBr or KI (2.5×10^{-4} M). A NIMA trough model 601 was used for measuring the $\pi-A$ isotherms. Deposition of the LB films on quartz and silicon wafers was carried at a constant pressure of 25 mN/m at a rate of 5 mm/min. The films showed Y-type transfer on hydrophobic substrates with transfer ratios of about 0.8−0.9. The Brewster angle micrographs were obtained using the trough in the same condition as associated with a commercial apparatus from Nanofilm Technology, Gottingen, FRG.

The ATR-IR spectrum was measured using a Nicolet 20Dx FTIR instrument, while the X-ray measurements were carried out on a Philips type PW 1050 diffractometer using nickel-filtered CuKα radiation. Thermal analysis (thermogravimetry-differential thermal analysis) was carried out using a DuPont model 2910 instrument.

Table 1

band (cm^{-1})	LB band intensities ATR-IR	T-IR
1764	33	208
1710	21	114
1446	16	48
1430	13	46
1200	22	55
1170	20	52

Scheme 1



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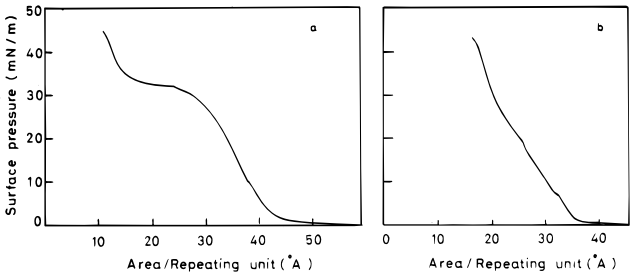

Figure 1. $\pi-A$ isotherms of polymers (a) **1** and (b) **2** on double distilled water at $T = 22$ °C, pH = 5.6.

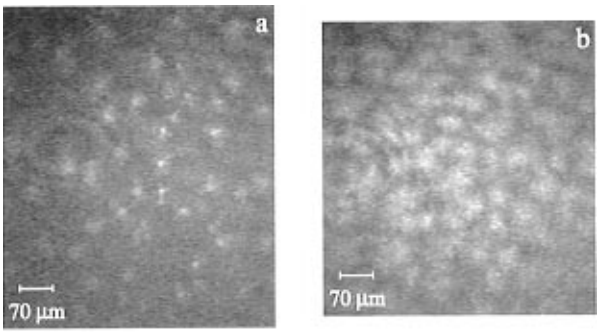

Figure 2. Optical micrographs of Langmuir films of the polymer at (a) $\pi = 5$ mN/m and (b) $\pi = 25$ mN/m (incident light at the Brewster angle).

Results and Discussion

Figure 1 shows the $\pi-A$ isotherms of polymers **1** and **2**. In each case the monolayer was successively compressed without exceeding the collapse pressure of the monolayer and then relaxed through several cycles until reproducible isotherms were obtained. Usually, two or three cycles were sufficient. All the monolayers formed stable monolayers and displayed good isotherms which included significant "solid" regions and collapse pressures >35 mN/m (Figure 1). In the isotherm of compound **1** (Figure 1a) it is observed that there are two distinct regions in which π rises linearly with reduction in surface area. The linear rise in the less condensed region is possibly due to the backbone of the polymer being forced into a closely packed quasi 2D structure against considerable steric hindrance. The second and steeper rise of surface pressure apparent upon reducing the area is attributed to interactions between the side chains of the polymer. It is seen that the smallest stable area/repeating unit (copolymer with the modified side chain) is 32 Å^2, which is slightly in excess of the optimum packing area (cross-sectional) of the side chain, indicating that a completely ordered crystalline packing may not be possible. In the case of the polyimide compound **2** (Figure 1b) the isotherm is fairly condensed, indicating that there is less steric hindrance, with the area/repeating unit being 27 Å^2. Given that the cross-sectional area of the side chain is 25 Å^2, this is reasonable. The monolyers of **1** could be transferred onto solid substrates with transfer ratios of 0.8−0.9 while **2** could be transferred onto only hydrophobic substrates.

Figure 2 shows the optical micrographs of the Langmuir films of **1** seen using the Brewster angle setup for $\pi = 5$ and $\pi = 25$ mN/m, respectively. The films show initially small domains with no particular shape which seem to fuse together at higher surface pressures. Under the high pressure value conditions, the monolayer appears homogeneous with fairly uniform orientation with respect to the incident light, as is seen from the uniform intensity in the micrograph. The IR spectra of the LB films carried out using ATR-FTIR and normal transmission are shown in Figure 3. For the T-IR 20 layers of polymer **1** were deposited on silicon wafers, while for ATR a quartz slide was used. A common feature of the spectra is the strong C═O stretching occurring at 1764 cm^{-1}. The spectra with T-IR (upper spectrum of Figure 2) and ATR show similar band intensity variations, especially the 1764 cm^{-1} band, indicating that the orientation of C═O does not change very much. A comparison of normal transmission with the ATR-FTIR spectra indicates that the order found in a single layer is maintained in each of the repeating units and the ratio of the integrated intensity of any band in the monolayer to that of the multilayer spectra is the same for all absorption bands. Also, as seen in the case of compound **2**, the intensities of principal bands in the IR, as given below, show that the ratio of integrated intensity of any band in the monolayer to that of the multilayer spectrum is 1:6. This indicates that the side chains are close to the vertical. The X-ray diffraction studies (Figure 4) showed three Bragg peaks for **1** and two for **2**, indicating layer structure. This allows an estimate of the layer spacings to be obtained.

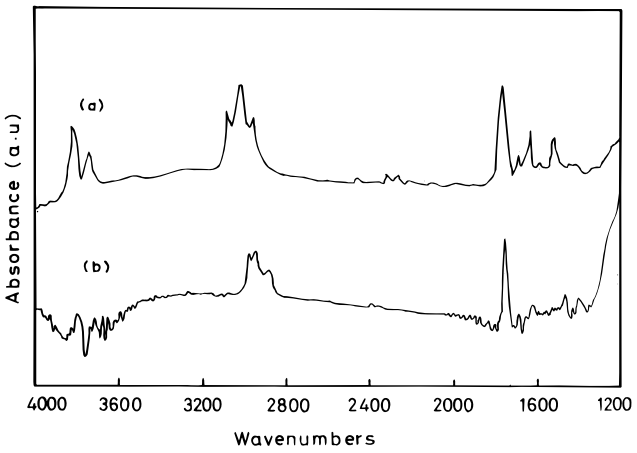

Figure 3. FTIR spectra of polymer **1**: (a) transmission spectrum of multilayers of **1**; (b) ATR-IR (angle of incidence = 60°) for a single LB layer.

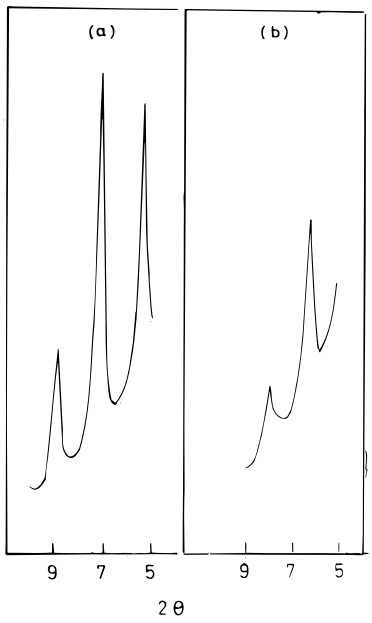

Figure 4. X-ray diffraction intensities as a function of 2θ for polymers **1** and **2**.

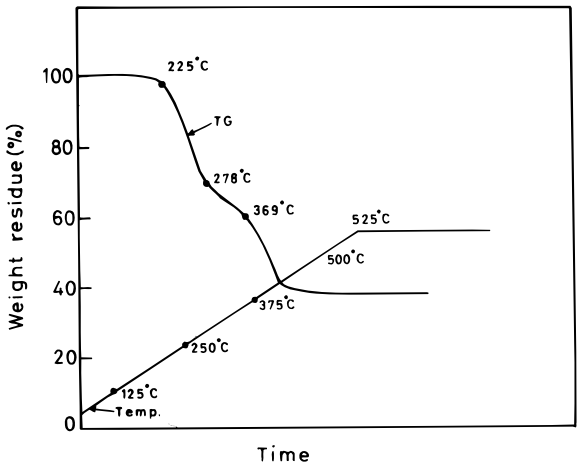

Figure 5. Thermogravimetric analysis of polymer **1** as a function of time.

A particularly interesting feature of the LB film is that the space filling model of the Y-type film with the side chains vertical predicts thicknesses varying between 47 and 75 Å. In practice, they ranged from 34.3 to 49.4 Å. This can be explained by (1) the side chain having a large tilt with respect to the vertical or (2) the side chains interdigitating and tilting only slightly or any combination of these. Anyway, the interdigitation cannot exceed 50%. Otherwise the surface area/repeat unit would need to be larger than the observed experimental value. The results of the thermal analysis of the bulk samples of both the compounds shows that the weight loss starts at about 220 °C for both compounds and ends at about 525 °C, indicating their high thermal stability. Also, the weight loss for both the polymers is in the range of only 60% in this temperature region.

Conclusions

Schiff base modified styrene−maleic anhydride copolymers and the resulting polyimide thereof form stable monolayers, and good LB films may be obtained. These LB films form interdigitated layers and are potentially attractive for several applications on account of their compactness and potentially greater stability both mechanically and thermally. The process is applicable to the formation of a wide range of heat stable polymer LB films and can be used in various fields such as electronics, coatings, and material separation. Work is presently in progress on the study of the optical and mechanical properties of these compounds.

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