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Structural study of monolayers of alkyl side chain substituted polyimides

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Monolayers of alkyl side chain substituted preformed polyimides (BACBP/BPDA) exhibit behaviour different from that of other 'hairy-rod' polymers which were studied previously. This behaviour is thought to arise from the extreme rigidity of the backbone as well as the particular way in which the alkyl side chains extend from the biphenyl unit. These soluble polyimides can form metastable monolayers for which the pressure-area isotherms vary markedly with side chain length. This side chain length dependence suggests that the side chains can not readily project away from the water surface, but rather occupy considerable space at the interface at lower temperatures. For the polyimide with octadecyl side chains, a sharp reduction in zero pressure area occurs between 20 and 24°C, suggesting an important change in side chain mobility, while the polyimide with heptyl side chains shows no strong dependence of zero pressure area on temperature. These materials are promising for creating robust molecularly thin layers. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polyimide; monolayer; pressure–area isotherm)

INTRODUCTION

Hairy-rod polymers were studied recently for the deposition of robust and useful ultrathin films using the Langmuir–Blodgett deposition technique[1–5]. As a result of the exceptional physical properties of polyimides, attempts to prepare polyimide LB films were also reported. In these studies, polyimide precursor monolayers were transferred and thermal imidization used to create the polyimides after transfer[6–8]. This approach requires a complex process and is accompanied by shrinkage, since van der Waals interactions are replaced by chemical bonds during the imide-ring closure in the thermal treatment. A by-product, usually water, is also released during the imidization. It is much preferable to prepare LB films from preformed polyimide molecules that contain side chains. These side chains provide two functions. They help render the polyimide soluble in common organic solvents and also allow one to form stable monolayers from the materials on the surface of an aqueous subphase.

In our previous article[9] we reported that multilayer films of preformed polyimide molecules were obtained for the first time by the Langmuir–Blodgett technique. To our knowledge, no study of the behaviour of preformed polyimide monolayers on the water subphase has yet been published. Monolayer behaviour was reported for some other 'hairy-rod' polymers including substituted polyglutamates[5,10,11]. The isotherms of several of the various of polyglutamate homopolymers and copolymers show qualitatively similar features. Often, a plateau at a pressure of 25–35 mN m^{-1} is observed. Its presence was ascribed by Takeda *et al*.[12,13] and Malcom[14,15] to the formation of a bilayer on the water surface. This plateau becomes more apparent at higher temperatures and the plateau pressure rises with side chain length of the longer substituent for copolymers. In Menzel's work[10], the conformation of side chains containing an isomerizable azobenzene moiety is seen to have a strong influence on the monolayer behaviour, including the character of the plateau. In particular, when the side chain is in the *cis* conformation, the monolayers pack much less efficiently. The monolayer behaviour of polyamic acids with long alkyl side chains was also studied[6,7,16] and no plateau was seen for that material.

In this article, monolayer pressure-area isotherms for preformed polyimides were studied while varying side chain length, temperature and compression speed. The results are discussed with a view to understanding how the molecules arrange at the surface, and particularly how this is influenced by the way in which the alkyl side chains extend form the backbones.

EXPERIMENTAL

The BACBP/BPDA polyimides substituted with different lengths of aliphatic side chains, shown in *Figure 1*, were prepared by polymerizing 3,3',4,4'-biphenyltetracarboxylicdianhydride and n-alkyl 4,4'-diamino-6,6'-dibromodiphenate in refluxing *m*-cresol[17]. The polymers are designated by the names C_n–BACBP, where 'n' is the number of carbon atoms in the alkyl chain.

Relaxation temperatures and solution viscosities in chloroform are summarized in *Table 1*. Substitution of the biphenyl with two bromine atoms and the two alkyl side chains renders all three polymers soluble in THF, chloroform, and a few other common organic solvents. This makes it possible to readily spread the polyimides to form monolayers. Two relaxations were identified for each polymer in the bulk state using dynamic mechanical spectroscopy. One occurs at a temperature markedly below room temperature and another occurs at a temperature considerably above room temperature. The higher temperature relaxation was associated with movement

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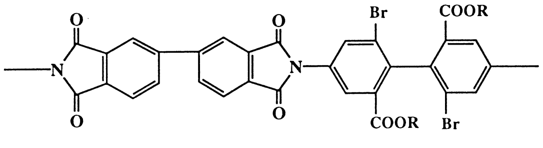
Table 1 Properties of polyimides

Polymer	$T_{\text{transition}}$ (°C)^a side chains	backbone	[η] (g dL^{-1}) CHCl$_3$ at 25°C
C18–BACBP	− 34	81	0.75
C16–BACBP	− 36	86	1.69
C7–BACBP	< − 42	145	0.68

^{a} As measured by dynamical mechanical spectroscopy



R : -CH$_2$(CH$_2$)$_{n-2}$CH$_3$

n=7, 16, 18

Figure 1 Chemical structure of the polyimide molecules (BACBP/BPDA)

within the backbone and the temperature of that transition decreases with increasing side chain length. The lower temperature transition is thought to arise from the behaviour of the side chains.

Monolayers were prepared by spreading 0.2 mg mL^{-1} solutions in chloroform onto a Millipore-quality water subphase in a Nima 611 trough (300 × 200 mm). Pressure-area isotherms were measured at various compression speeds (20–100 cm^2 min^{-1}) and various temperatures (15–32°C). Polarization Modulated Infrared Reflection Absorption Spectroscopy (PM–IRRAS) spectra of the covered $S(d)$ and uncovered $S(0)$ water surface were recorded with a Nicolet 850 FTIR spectrometer at 4 cm^{-1} resolution[18]. A total of 500 scans were collected for each measurement at an angle of incidence of 76° with respect to the surface normal. Normalized difference spectra, $\Delta S/S$, were considered, where $\Delta S/S = (S(d) - (S(0))/S(0)$.

RESULTS AND DISCUSSION

The first characteristic of the pressure-area isotherms to note is that they are strongly compression rate dependent—much more so than for polyglutamate hairy-rods. *Figure 2* shows the 'isotherms' of the octadecyl substituted (C18) polyimide collected at these different compression speeds at a temperature of 32°C. The largest compression rate of 100 cm^2 min^{-1} corresponds to a barrier speed of 50 mm min^{-1}. The curves for 40 and 100 cm^2 min^{-1} are not true isotherms, as it is clear they are kinetically controlled. However, information can be deduced about the nature of monolayers from the effect of compression speed on the shape of the isotherms. At 100 cm^2 min^{-1} the pressure-area curve shows a single transition from a dilute to condensed phase with a collapse pressure of about 17 mN m^{-1}. This collapse pressure is lower than those found in polyimide precursors monolayers or polyglutamate monolayers. Thus these monolayers are not as stable as those formed from some other hairy-rod molecules. The zero pressure area is about 135 Å^2/repeat unit. This is much larger than the area which would be required by the backbone of the repeat unit alone, suggesting that the side chains occupy considerable area at the water surface as discussed below. As the compression rate is decreased from 100 to 40 cm^2 min^{-1}, a marked change is seen in the behaviour. The zero pressure area associated with the condensed phase appearing first is about the same as before, but the compressibility of the layer is considerably larger. The second change is the appearance of a shoulder at a pressure of about 6 mN m^{-1}. Without other observations of the structure of the monolayer it is not possible to state with certainty what structural change occurs here. However, it was suggested that similar behaviour in polyglutamate systems is associated with bilayer formation. The collapse pressure for this lower barrier speed is lower, about 12 mN m^{-1}. These changes are consistent with the presence of slow relaxations characteristic of stiff polymers[19]. Under fast compression the monolayer is stiffer and less compact than when compressed slowly. Further reduction in compression rate to 20 cm^2 min^{-1} changes the details of the pressure-area curve, but not the qualitative features. Thus we have chosen to focus on the behaviour seen at 20 cm^2 min^{-1}.

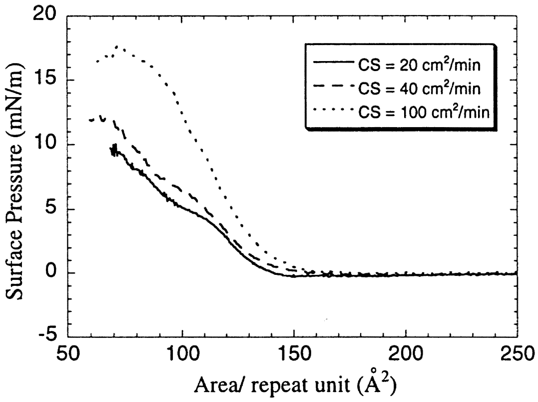


Figure 2 Pressure–area curves for C18–BACBP with different compression speeds at a temperature of 32°C

Having established a standard compression rate for measuring the isotherms, it is of interest next to consider how varying the side chain length affects the monolayer behaviour. *Figure 3* presents isotherms for all three molecules at 20°C, a temperature considerably below that for the data in *Figure 1*. At this temperature no plateau in the isotherm is seen before the collapse is reached for any of the materials. The zero pressure area for C18, 180 Å^2/repeat unit, is much higher than that at 32°C. We also note once again that the zero pressure areas are all much larger than that (*ca.* 100 Å^2) which would be necessary simply to accommodate the backbone of the repeat unit. Of importance here are the observations that both zero pressure area and collapse pressure decrease with decreasing side chain length. The decrease in zero pressure area with decreasing side chain length is consistent with the idea that the side chains may project away from the water subphase at some small angle rather than standing up perpendicular to the water surface as shown in the cartoon of *Figure 4*. If the

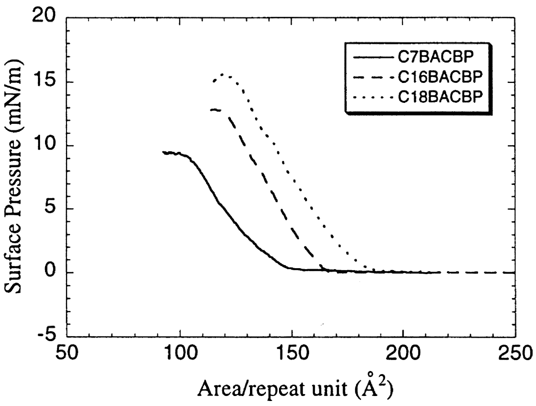


Figure 3 Pressure–area curves for polyimides with different side chain lengths at a temperature of 20°C and compression speed of 20 cm^2 min^{-1}

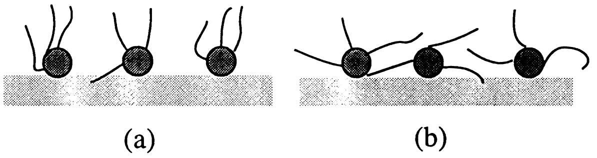


Figure 4 Schematic drawings of the polyimide molecules on the water subphase. The backbone is represented very crudely by a cylindrical cross-section to emphasize that it is not fully planar. In (a) the side chains are envisioned as extending nearly perpendicular to the water. If the side chains can not do this (b), then each repeat unit will require much more space at the interface

side chains were oriented primarily perpendicular to the water surface, the three molecules would have almost the same zero-pressure areas, irrespective of side chain length. The failure of the side chains to orient perpendicular to the water is reasonable in light of the molecules' structures. Steric hindrance between the substituents on the biphenyl will lead to a tendency for the two aliphatic chains to project away from the backbone in opposing directions, though this is not favourable for keeping the aliphatic chains away from the water surface.

The temperature effect on the isotherm for each molecule is shown in *Figure 5*. For C18, a plateau appears as temperature is increased. The shape of isotherms at low temperature resembles that with higher compression rate. Also, the zero pressure area per repeat unit decreases abruptly with temperature between 20 and 24°C and remains nearly constant for still higher temperatures. We attribute this to the rotation of the oxygen linkage of the ester group or conformational change of the alkyl side chains[20,21]. Measurements of the monolayers were made with PM–IRRAS at four different temperatures (21, 22, 26, and 28°C) and four different pressures (3, 5, 7, and 9 mN m^{-1}) in order to probe directly the side chain orientation. These measurements show no bands for the CH_2 symmetric and antisymmetric stretches at any temperature or pressure. Two aspects of the monolayer structure dictate the intensities of these bands. One is the surface density of side chains and the second is the orientation of those chains. Since the density of the side chains is very low, it is possible that they could be oriented somewhat and that the degree of orientation changes with temperature, but this orientation would still not be observed with PM–IRRAS. However, we believe that it is unlikely that they are highly oriented perpendicular to the surface.

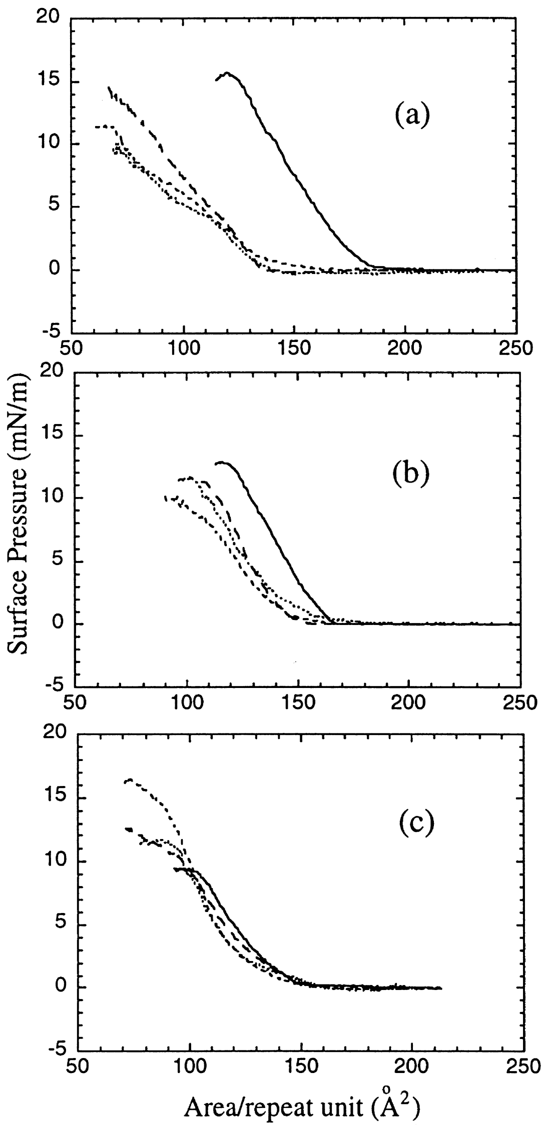


Figure 5 Pressure–area isotherms of the polyimide molecules (a) C18–BACBP, (b) C16–BACBP, and (c) C7–BACBP at 20°C (————————), 24°C (— — —), 28°C (- - -), and 32°C (…). All were collected at a compression rate of 20 cm^2 min^{-1}

A strong argument for an important change in the molecules behaviour with temperature is the fact that it is hard to obtain consistent isotherms below a temperature of 20°C. It seems the monolayer is unstable at this low temperature and hence easily collapsed when the molecules are compressed. With decreasing the side chain length through C16 to C7, the change in the zero pressure area with temperature becomes smaller. As the side chains become shorter they do not play a role in the monolayer behaviour.

The stability of the monolayer structure present at 20°C was addressed with two experiments. First, the monolayer was subjected to several cycles of compression and expansion at 20°C. The pressure area curves for this experiment are shown in *Figure 6*. For cycles two through five, some hysteresis is observed, but the cycles essentially reproduce one another. That is, all of the changes which occur during the cycle are reversible. However, some irreversible change does occur on the first cycle. The monolayer is changed upon initial compression in a way from which the monolayer does not fully recover upon expansion. At present we have no evidence as to what that change may be.

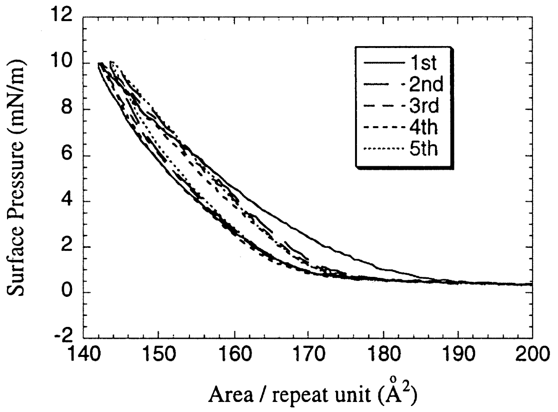


Figure 6 Pressure–area curves at 20°C for five cycles of compression and expansion of C18–BACBP monolayer

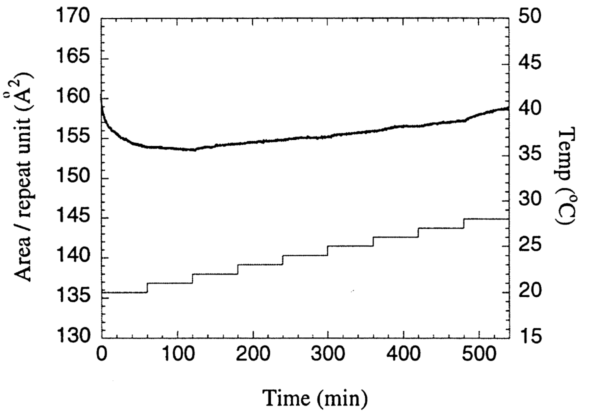


Figure 7 Plot of change in area per repeat unit with time for a monolayer of C18–BACBP compressed initially at 20°C to a target pressure of 5 mN m^{-1}. The pressure was held constant as the temperature was stepped up as indicated in the plot

In a second experiment, the monolayer was compressed at 20°C to a target pressure of 5 mN m^{-1} and the area per repeat unit monitored over the time as the temperature was very slowly increased from 20 to 28°C in 1°C steps, as shown in *Figure 7*. The temperature setpoint was kept at each temperature for 60 min. Initially, the monolayer relaxes slightly while at 20°C. With the gradual increase in temperature one expects to see a decrease in area reflecting the behaviour seen in *Figure 5*. However, the area only increases with increasing temperature due to thermal expansion of the layer and not any gross change in structure. The monolayer does not readily escape from the structure induced by compression at 20°C even after the temperature is increased to 28°C. The existence of such metastable structures has important implications for the proper transfer of these polyimide ultrathin films to substrates for various applications.

CONCLUSIONS

The monolayer behavior of preformed polyimides on a water subphase was studied systematically for the first time. For the octadecyl substituted repeat unit no transition among condensed phases is seen at high compression rates or sufficiently low temperatures, indicating that the monolayer relaxes very slowly. As compression rate is dropped or temperature increased, a shoulder or plateau appears, as was seen as well in monolayers of hairy-rod polyglutamates. A strong increase in area per repeat unit with side chain length, as well as the magnitude of the occupied area, indicate that the side chains do not readily project away from the water surface. This is consistent with the steric hindrances expected for the substituted biphenyl unit. The monolayers are therefore not very efficiently packed at low temperatures. Increasing temperature causes a strong change in the side chain mobility, providing better packing. This effect becomes negligible, however, when the number of carbon atoms in the side chain drops to seven.

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