An n.m.r. study of a polymeric Langmuir–Blodgett multilayer film

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The properties of a Langmuir–Blodgett polymeric multilayer film formed from the octadecyl ester of a pentadec-1-ene–maleic anhydride copolymer have been investigated using ^1H wideline and ^{13}C cross-polarization/magic angle spinning n.m.r. spectroscopy. The spectra indicate that in the multilayer, the polymer chains are disorganized, but are significantly more rigid than in the bulk polymer.

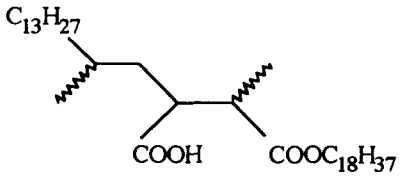
(Keywords: Langmuir–Blodgett films; polymeric multilayers; nuclear magnetic resonance)

Introduction

Langmuir–Blodgett (LB) films have numerous potential applications in micro-, opto- and molecular electronics[1–3] and in recent years this has prompted great interest in such films[4–7]. While the LB multilayer films prepared from many non-polymeric amphiphiles are highly ordered, such films are, unfortunately, generally mechanically fragile and prone to reorganization both during[8] and after[9–11] deposition. LB multilayers prepared from preformed polymers, though they may not be so highly organized, can be expected to be more robust and less prone to reorganization. Recently we described the Langmuir and LB multilayers prepared from various derivatives of a series of terminal alkene–maleic anhydride copolymers[12]. In this paper we describe a study of the LB multilayer of one of these polymers using ^1H wideline and ^{13}C cross-polarization/magic angle spinning (CP/MAS) solid-state n.m.r. techniques. Such techniques have been widely used in studies of bulk polymers to characterize phase structure and dynamics[13,14] but have not to our knowledge been applied to LB multilayers.

Experimental

The polymer studied had structure **I**. As described previously, it was prepared by reacting an octadecanol with a pentadec-1-ene–maleic anhydride copolymer[12] of $\bar{M}_n = 10000$ and $\bar{M}_w = 19000$. For comparison, an amorphous film of the polymer was prepared by evaporating a 5% chloroform solution on a flat Pyrex glass plate. After drying, the film peeled from the glass.



I

Preparation of LB films. LB multilayer films containing 1000 layers were prepared from polymer **I** using the procedures described previously[12], except that in each case the substrate was a piece of flexible polycarbonate film, 2 μm in thickness, held taughtly over a Pyrex glass microscope slide. After deposition, the LB film was allowed to dry in a desiccator overnight, then the composite film was detached from the microscope slide. Assuming that the bilayer thickness of the deposited polymer was the same as determined previously[12], the LB multilayer had a total thickness of about 2.2 μm. It covered 60–70% of the polycarbonate film.

N.m.r. spectroscopy. ^1H wideline (static) and ^{13}C CP/MAS n.m.r. spectra were obtained using a Varian Associates Unity 300 spectrometer operating at 300 MHz for protons and equipped with Doty Scientific Industries probe. All spectra were run at ambient temperature (23°C). Samples for ^1H spectra consisted of a crumpled film packed into a short length of a 5 mm o.d. Pyrex glass high-resolution n.m.r. tube. Samples for ^{13}C CP/MAS spectra were prepared from a rectangular sheet of film approximately 50 mm × 75 mm in size. The sheet was tripled in thickness by folding twice lengthwise, and then carefully rolled around a thin glass rod former. On insertion into the 7 mm zirconia MAS rotor, the rolled film sprang open, distributing itself uniformly around the inner surface. The glass former was then removed. It proved possible to spin samples prepared in this way at 5 kHz without difficulty. CP/MAS spectra were obtained with a contact time of 1 ms and a recycle time of 5 s. About 8000 transients were required for the LB multilayer sample.

^1H longitudinal relaxation times (T_1) were measured using the inversion recovery technique. ^1H relaxation times in the rotating frame ($T_{1\rho}$) were measured using the phase-shift spin-locking technique with a B_1 field corresponding to a precession frequency of 53 kHz.

Results and discussion

Although the polymer studied forms relatively good LB multilayers, it was not the best of those studied previously[12]. It was selected because it was also available in deuterated forms, but in the event no satisfactory ^2H n.m.r. spectra were obtained with the facilities available. Accordingly, all the n.m.r. spectra discussed here were for the non-deuterated form.

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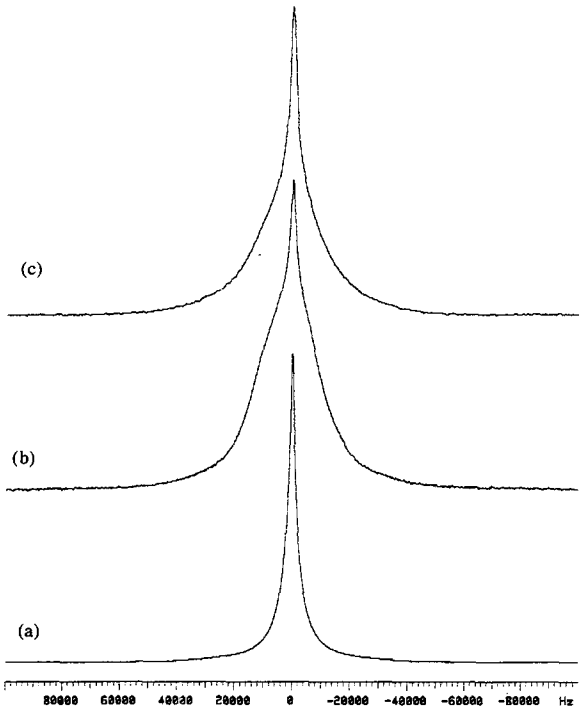


Figure 1 Wideline ^1H spectra at ambient temperature: (a) bulk polymer I; (b) the polycarbonate substrate; (c) substrate + LB multilayer

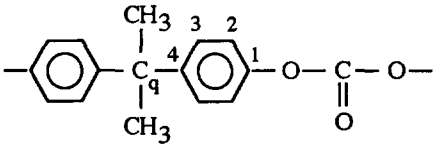
^1H wideline spectra. The ^1H wideline spectra at ambient temperature of polymer I, the polycarbonate substrate and the substrate with LB multilayer are compared in *Figures 1a, b* and *c*, respectively. The spectrum of I consisted of a relatively narrow single component lineshape with a linewidth of 3.3 kHz. The substrate spectrum consisted of a broad envelope with a linewidth of 25.5 kHz superimposed on which was a small narrow component amounting to 3% of the total intensity as determined by comparing the integral of the full spectrum with that of a 5 kHz expansion around the peak centre. The origin of the narrow component was not identified, but possible sources could have been mobile end-groups or absorbed water. The spectrum of the LB multilayer sample was comparable in form to that of the substrate alone, except that the intensity of the narrow component was greater, amounting to 8% of the total. From the dimensions of the substrate/multilayer sample, assuming equal densities for I and the substrate, it was calculated that 56% of the protons were located in the LB multilayer. Clearly, a component of this magnitude with the same linewidth as bulk I is not observed in the composite spectrum, indicating that molecular mobility in the multilayer is significantly reduced compared to the bulk polymer. The small increase in the relative intensity of the narrow component could have arisen either from additional absorbed water in the multilayer, or from mobile methyl groups at the termini of the alkyl chains in I. From the composite dimensions, and assuming equal densities, it was calculated that in the composite sample, the fraction of protons existing as methyl protons in the multilayer was about 0.05. This proportion is consistent with the observed increase in relative intensity of the narrow peak.

In order to further investigate the multilayer structure, we have examined the second moments, M_2, of the broad component. Measured over a spectral width of 200 kHz, the values of M_2 for the broad component in the substrate and the substrate + multilayer were, respectively, 2.8×10^8 and 3.2×10^8 Hz^2. From the composite dimensions and assuming equal densities, a value of 0.53 was calculated for the fraction of immobile protons located in the multilayer, yielding a value for M_2 of the isolated multilayer of 3.6×10^8 Hz^2. This is less than one-half of the value of 7.8×10^8 Hz^2 which we have measured for M_2 of solid (crystalline) tetracosane ($C_{24}H_{50}$), suggesting a disorganized structure in the multilayer. This is consistent with X-ray studies[15], which also indicate the absence of long-range order of the alkyl side chains.

^1H relaxation times. For the substrate and composite samples, attention was directed to the relaxation properties of the broad component, since this constituted by far the majority of the protons. Its intensity was isolated by subtracting the integral of the central 5 kHz region from the integral of a 200 kHz spectrum display. The T_1 relaxation curve of I was closely fitted by an exponential whereas the T_1 curves of the substrate and composite samples were better fitted by a biexponential function. The $T_{1\rho}$ relaxation curves of all three samples were biexponential. The time constants and fractions of fast and slow relaxation components, obtained using data analysis facilities provided in the spectrometer software, are given in *Table 1*.

There is a general similarity in the values of the relaxation times for the substrate and composite samples. However, the fraction of the fast T_1 component is much larger in the composite than in the substrate, presumably indicating somewhat more efficient T_1 relaxation in the multilayer constituent. The smaller value of T_1 for the polymer in the multilayer compared to the bulk is consistent with the larger value of the second moment described above.

^{13}C CP/MAS spectra. The ^{13}C CP/MAS spectra of the polycarbonate substrate alone and the substrate with multilayer are compared in *Figures 2a* and *b*, respectively. Using the following labelling scheme for the substrate



the assignment of the resonances in the substrate, based on reference chemical shift data[16], is: CH_3, 30 ppm; C_q, 41 ppm; C_1 and C_4, 148 ppm; C_2, 120 ppm; C_3, 126 ppm; C=O, ~152 ppm (shoulder). No distinct peaks arising from the multilayer were detected in *Figure 2b*, the presence of the multilayer being clearly manifest only as an increase in intensity of the peak at 30 ppm. Since the

Table 1 Time constants and fraction of relaxation contributions at 23°C. For the substrate and composite samples, the data apply to the broad spectrum component

	T_1 (s)			$T_{1\rho}$ (ms)		
	Fast	Slow	% Fast	Fast	Slow	% Fast
Polymer I	510		100	3.1	9.5	45
Substrate	74	400	14	1.3	6.1	31
Composite	70	400	50	1.0	5.8	24

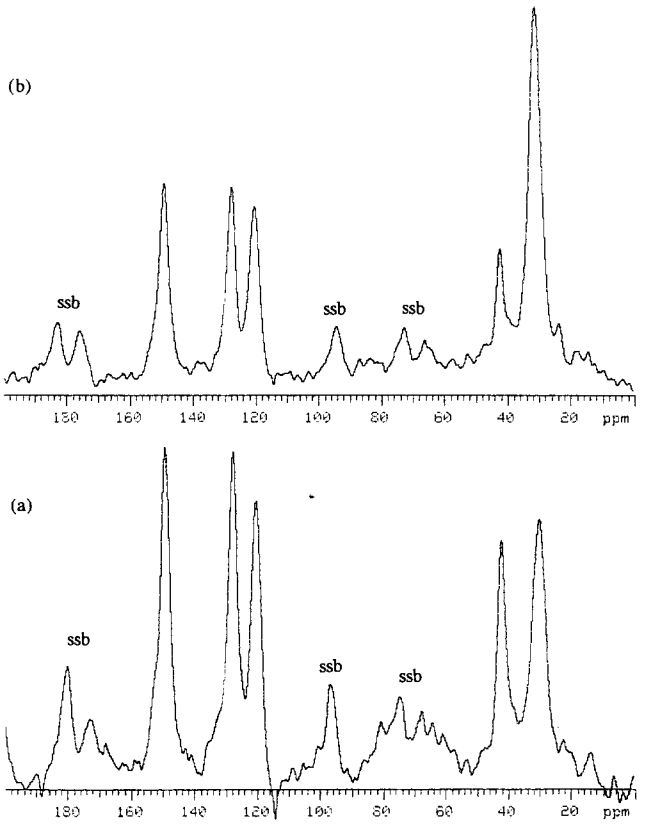


Figure 2 ^{13}C CP/MAS spectra (the label 'ssb' identifies spinning sidebands): (a) the polycarbonate substrate, spin rate 4.0 kHz; (b) the substrate + LB multilayer, spin rate 4.2 kHz

chemical shift of the CH_2 carbons in polyethylene is 30 ppm[17], this effect is presumably due to an overlap of the majority of the CH_2 carbons in the multilayer alkyl chains with the CH_3 peak of the polycarbonate substrate. Because of the high molecular weight of the multilayer repeat unit, individual carbon peaks, such as the acid or ester carbonyl resonances, are too low in intensity to be observed.

Intensities in CP/MAS spectra depend not only on the abundance of the contributing nuclei, but also on the ^1H longitudinal relaxation time, the ^{13}C–^1H CP magnetization transfer relaxation time, and the ^{13}C and ^1H rotating frame relaxation times[13]. For reasonably rigid samples, and short CP contact times of the order of a millisecond, the first two are the most significant. The pulse intervals used for the spectra in *Figure 2* allowed complete ^1H recovery between pulses, so differences in response of the substrate and film resonances will depend principally on the CP relaxation time. This in turn depends on the strength of the C–H dipole–dipole interaction and the rate of molecular motion. In the CP/MAS spectrum of the substrate (*Figure 2a*), the (integrated) intensities of each peak are roughly proportional to their abundance, indicating comparable CP transfer times. Assuming that the substrate and multilayer are equal in thickness, that the film coverage is two-thirds, and that 25 CH_2 in each film repeat unit contribute to the peak at 30 ppm, we calculate that for this peak the ratio of the number of contributing multilayer carbons to the number of contributing substrate carbons is about three, i.e. the increase in intensity in the presence of the LB film should be approximately a factor of four. Using the substrate aliphatic quaternary carbon peak at 43 ppm as an intensity reference, the experimental increase in intensity at 30 ppm is approximately a factor of three. This is somewhat lower than the calculated value, but reasonably consistent with it in view of the number of assumptions made. Thus it appears that in the multilayer, the CP relaxation time is comparable to that in the substrate, indicating a fairly immobile structure.

Conclusions

The data presented in this work demonstrate that solid-state n.m.r. is a practical, powerful method for investigating the molecular dynamic properties of LB multilayer films. For the particular system studied here, the data indicated that in the multilayer, the chains were considerably less mobile than in the bulk polymer. Clearly, more specific information on the film properties could be obtained if it was possible to use substrate and film materials whose molecular structures were such as to avoid spectral overlap, for example by using an entirely aromatic substrate and a multilayer which is at least partly aliphatic.

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