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Langmuir and Langmuir–Blodgett films of derivatives of α-olefin–maleic anhydride alternating copolymers prepared from olefins containing hydrophilic groups

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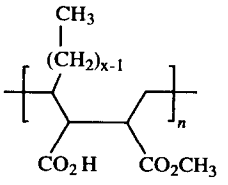
A range of long chain α-olefins were prepared which contained amide (four examples) or ester (five examples) linkages. The olefins were copolymerized with maleic anhydride and the alternating copolymers produced were subjected to ring-opening reactions at the anhydride residues to give polymers containing acid–ester, acid–acid or acid–amide head groups. Monolayers of these polymers on water were studied and, in favourable cases, thick Langmuir–Blodgett multilayers were prepared. The latter were studied by X-ray reflectivity. The results obtained were compared with those obtained from analogous polymers prepared starting from the simple α-olefins undecene, octadecene and tricosene. The polymers prepared from the α-olefins containing amide linkages generally gave poor monolayers and in only one case could a Langmuir–Blodgett multilayer be prepared. The polymers prepared from the α-olefins containing ester linkages generally gave better monolayers, especially if the ester group was shielded from solvation either by being surrounded with lipophilic chains or by virtue of being a t-butyl ester or an ester of an aromatic acid, or because the ester was linked to a mesogenic group. Several of the latter polymers gave excellent Langmuir–Blodgett films. In general polymers with acid–acid head groups gave better films than the analogues with acid–methyl ester head groups.

(Keywords: Langmuir–Blodgett films; α-olefins; maleic anhydride)

INTRODUCTION

Langmuir–Blodgett (LB) films, being ordered at the molecular level, have numerous potential applications in, for example, molecular electronics and optoelectronics[1,2]. Most LB films prepared from low-molecular-weight amphiphiles are, however, not sufficiently stable mechanically and/or sufficiently stable to molecular reorganization for commercial applications[3,4]. This has prompted an interest in polymeric LB films[5–10], especially films prepared from pre-formed polymers[7,8]. The advantage of using pre-formed polymers to prepare LB films rather than amphiphilic monomers that can subsequently be polymerized is that no processing is needed either on the water surface or after deposition. Recently we reported that various derivatives prepared from alternating copolymers of simple straight chain α-olefins and maleic anhydride form excellent LB films, especially when the α-olefin contains 13–16 carbon atoms[9]. Examples are polymers **1**–**3**. For most applications using polymers of this general type, however, more complex olefins will be required and these are likely to contain various chemical moieties depending on the properties the LB films are required to display. The presence of certain chemical moieties could well result in monolayers on water and LB films which are much less organized than those prepared from polymers **1**–**3**. Hydrophilic moieties in the pendent groups on the polymer derived from the α-olefin are likely to be particularly disruptive of film order. In this paper we report results obtained for some polymers prepared starting from α-olefins containing amide or ester moieties. As expected, the presence of these moieties causes the derived polymers to give less satisfactory films than those of polymers **1**–**3**. However, we have shown that in certain circumstances excellent films can still be obtained.



1: x = 9
2: x = 16
3: x = 21

(Note, a proportion of the structural units will have the acid and ester groups in the positions shown. Others will have the positions of these groups reversed.)

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EXPERIMENTAL

General experimental details are as given previously[9].

Synthesis of α-olefins

The amides **4a**–**4d** and esters **4f**–**4h** were prepared from commercial acid chlorides and amines or alcohols using standard methods[11]. All these products had satisfactory i.r. and ^1H n.m.r. spectra. Amide **4a** had m.p. 83–83.5°C and C 77.2, H 12.6 and N 5.5%; $C_{19}H_{37}NO$ requires C 77.3, H 12.5 and N 4.75%. Amide **4b** was a clear oil which decomposed on vacuum distillation. Amide **4c** had m.p. 68–68.5°C and C 77.8, H 12.6 and N 4.4%; $C_{21}H_{41}NO$ requires C 78.0, H 12.7 and N 4.3%. Amide **4d** had m.p. 75.5–76.5°C and C 79.7, H 13.0 and N 3.3%; $C_{27}H_{53}NO$ requires C 79.6, H 13.0 and N 3.4%. Ester **4f** had b.p. 246°C at 265 mm (lit.[12] 248°C at 270 mm). Esters **4g** and **4h** were obtained as clear oils which suffered decomposition on distillation.

Ester **4e** was prepared by reacting polymer-supported (Amberlyst A26) undec-10-enoate with 1-bromohexadecane[13]. Ester **4e** had m.p. 63°C and C 79.3 and H 12.4%; $C_{27}H_{52}O_2$ requires C 79.4 and H 12.5%.

Ester **4i** was a commercial sample.

Copolymerizations of α-olefins with maleic anhydride

The copolymerizations were carried out using the general procedure given previously[9]. The yields of the copolymers **5** and their molecular weights are summarized in *Table 1*. Elemental analyses were satisfactory for the products being 1:1 copolymers.

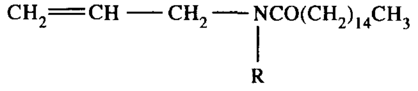
Derivatives of α-olefin–maleic anhydride copolymers

Derivatives of types **6**–**9** were prepared from the copolymers **5** using the typical procedures given previously[9]. Particular care was taken in preparing polymer derivatives of types **8** and **9** that the reaction conditions used were not so severe that the side chain ester groups reacted. I.r. spectra of the products indicated that acid, ester and amide carbonyl groups were present in essentially the expected proportions.

Measurement of isotherms and film deposition

Monolayers of the various polymers were prepared and the isotherms measured using the equipment and general procedures described previously[9]. The isotherms are shown in *Figures 1–4*. The areas at specific pressures (A_0 and A_{30}) and collapse pressure (π_c) are summarized in *Table 2*.

LB multilayers were also prepared using the equipment and general procedures described previously[9]. The LB



$CH_2{=}CH{-}CH_2{-}\underset{R}{\underset{|}{N}}CO(CH_2)_{14}CH_3$

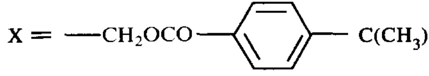
4a R = H
4b X = CH_3

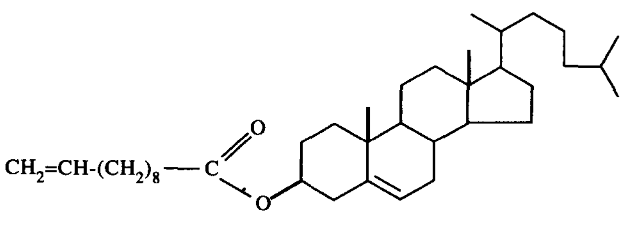
$CH_2{=}CH{-}(CH_2)_nCONH(CH_2)_{15}CH_3$

4c n = 2
4d n = 8

$CH_2{=}CH{-}(CH_2)_8{-}X$

4e X = $-CO_2(CH_2)_{15}CH_3$
4f X = $-CO_2CH_3$
4g X = $-CO_2C(CH_3)_3$
4h





4i

Table 1 Synthesis and molecular weight data for the α-olefin–maleic anhydride copolymers

Copolymer designation	α-Olefin(s) used	Yield of copolymer (%)	Polymer used for mol.wt estimation[a]	$\bar{M}_n$ ($\times 10^{-3}$)	$\bar{M}_w$ ($\times 10^{-3}$)	$\bar{M}_w/\bar{M}_n$
5a	**4a**	60	A	5.0	6.0	1.2
5b	**4b**	10	A	9.0	18.0	2.0
5c	**4c**	67	A	5.0	6.0	1.2
5d	**4d**	71	A	7.0	9.0	1.3
5e	**4e**	44	A	8.0	10.0	1.3
5f	**4f**	54	B	5.9	9.8	1.7
5g	**4g**	46	B	5.3	8.5	1.6
5h	**4h**	45	B	4.7	8.1	1.7
5i	**4i**	83	A	4.0	5.0	1.3
5j	**4f** and octadec-1-ene[b]	60	B	5.3	6.6	1.3
5k	**4f** and octadec-1-ene[c]	70	B	3.9	6.0	1.5

[a] Determined by g.p.c. using polystyrene standards: A, measurement made on olefin–maleic anhydride copolymers **5**; B, measurement made on dimethyl esters of type **7**
[b] Molar ratio 1:4
[c] Molar ratio 1:1

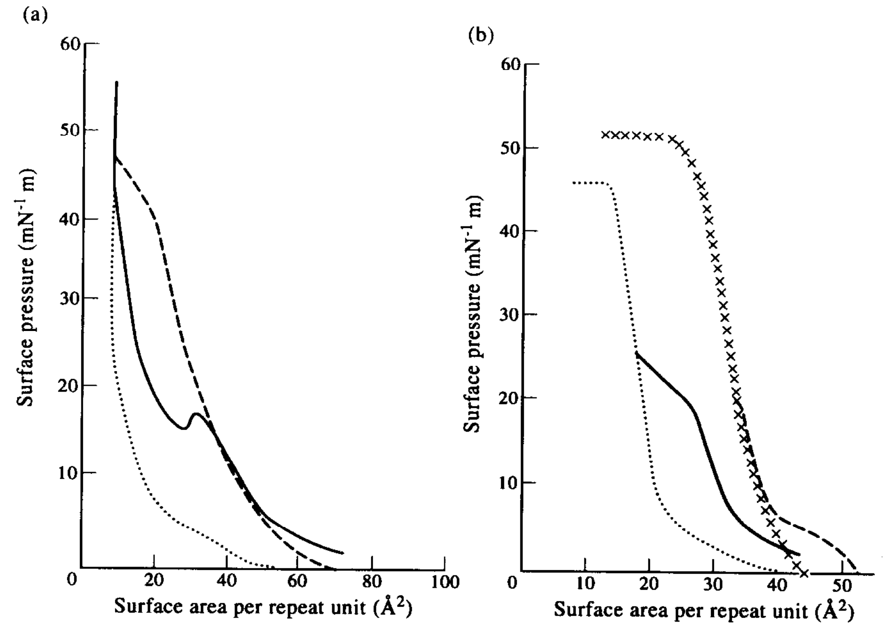


Figure 1 Isotherms of amide-containing polymers on a subphase of water at 20°C and pH 5.3–5.6. (a) Polymer **6a**, first compression (——); polymer **6a**, second and subsequent compressions (····); polymer **6b** (– – –). (b) Polymer **6c**, first compression (——); polymer **6c**, second and subsequent compressions (····); polymer **6d**, first compression (– – –); polymer **6d**, second and subsequent compressions (× × ×)

Table 2 Properties of Langmuir and Langmuir–Blodgett films of polymers

	Langmuir film			X-ray data			
	Area per repeat unit (Å^2)						
Polymer	at 0 mN m^{-1}[a]	at 30 mN m^{-1}	Collapse pressure (mN m^{-1})	Number of layers in LB film[b]	Substrate[c]	Number of Bragg peaks	*d*-spacing (Å)
1[d]	48	39.5	~42	332	S	2	26.4
2[e]	39	33.1	~50	500	S	3	38.2
3[f]	34	24.2	45	400	S	1	45.0
6a	10	8.1	~45	350[g]	S	1	~27
6b	42	24.6	~42	–	–	–	–
6c	23	16.5	~45	–	–	–	–
6d	38	31.5	52	–	–	–	–
6f	67	40.0	~30	100	G	1 (v. broad)	~32
6g	68	45.3	>42	150[h]	G	2	31.7
6h	43	34.0	~32	150[i]	G	2	32.7
6j	21	16.6	~41	150	G	2	35.6
6k	20	16.0	32	–	–	–	–
8f	55	30.0	~37	150	G	2	33.7
8g	33	27.0	~47	150[h]	G	2	30.8
8h	41	34.0	>44	150[h]	G	3	37.1
8i	55	–	>28	–	–	–	–
8j	17	14.2	>45	150	G	2	35.5
8k	16	13.4	44	150[h]	G	3	36.8
9i	60	49.0	>34	350	S	2	34.4

[a] By extrapolation of the 'solid' section of the isotherm to zero pressure
[b] All films were, from deposition, Y-type. Unless indicated otherwise deposition pressure was 30 mN m^{-1}
[c] S, hydrophobic silicon wafer; G, hydrophobic glass microscope slide
[d] Data from ref. 9: $\bar{M}_n = 12\,000$ and $\bar{M}_w = 25\,000$
[e] Data from ref. 9: $\bar{M}_n = 8000$ and $\bar{M}_w = 17\,000$
[f] Data from ref. 9: $\bar{M}_n = 8000$ and $\bar{M}_w = 13\,600$
[g] Deposition pressure = 20 mN m^{-1}
[h] Deposition pressure = 40 mN m^{-1}
[i] Deposition pressure = 25 mN m^{-1}

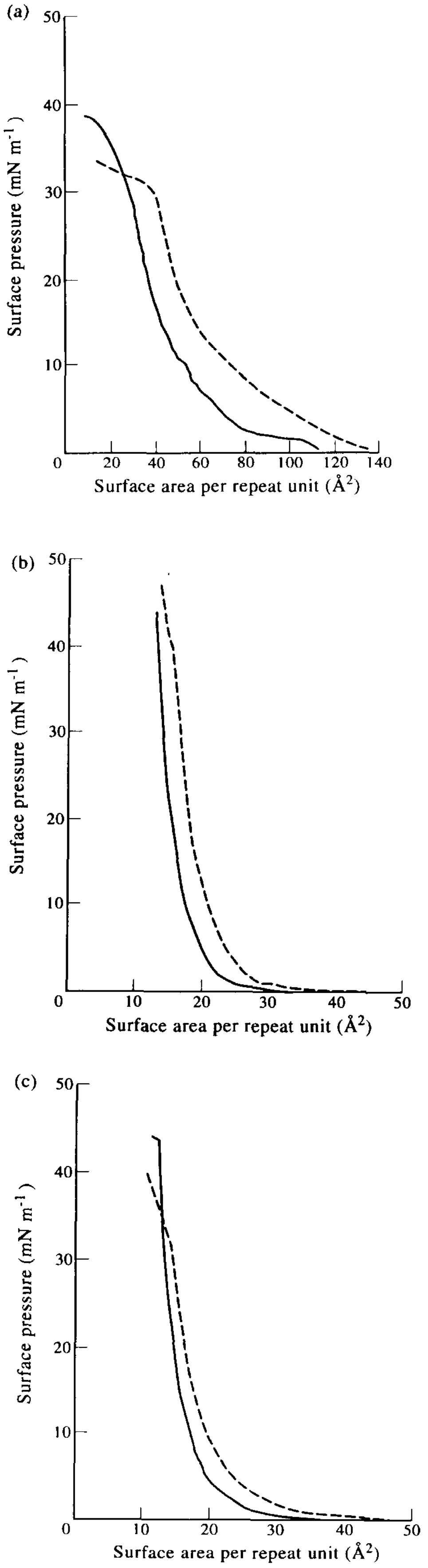


Figure 2 Isotherms of polymers with side chains containing a carbomethoxy moiety. Measured on water at 20°C and pH 5.3–5.6. (a) Polymer **6f** (– – –); polymer **8f** (——). (b) Polymer **6j** (– – –); polymer **8j** (——). (c) Polymer **6k** (– – –); polymer **8k** (——)

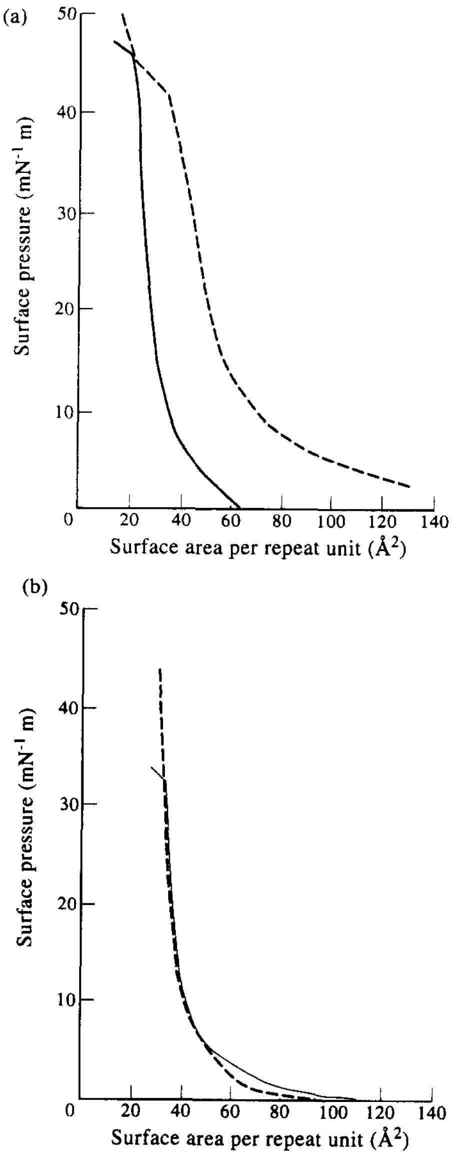


Figure 3 Isotherms of polymers on a subphase of water at 20°C and pH 5.3–5.6. (a) Polymer **6g** (– – –); polymer **8g** (——). (b) Polymer **6h** (– – –); polymer **8h** (——)

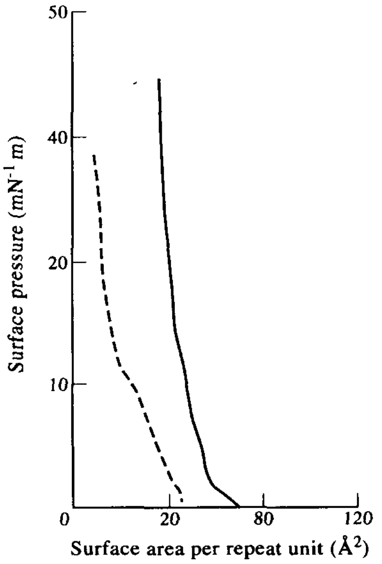


Figure 4 Isotherms of polymer **8i** (– – –) and polymer **9i** (——) on a subphase of water at 20°C and pH 5.3–5.6

films were deposited onto silicon wafers or Pyrex glass microscope slides (*Table 2*) that had been treated with hexamethyldisilazane[14]. When films were deposited successfully the transfer ratios were 1.00 ± 0.05. X-ray reflectivity measurements were carried out using either a Raymax RX3D or a Phillips type PW1050 diffractometer using nickel-filtered CuKα radiation. *Table 2* summarizes the properties of the LB films.

RESULTS AND DISCUSSION

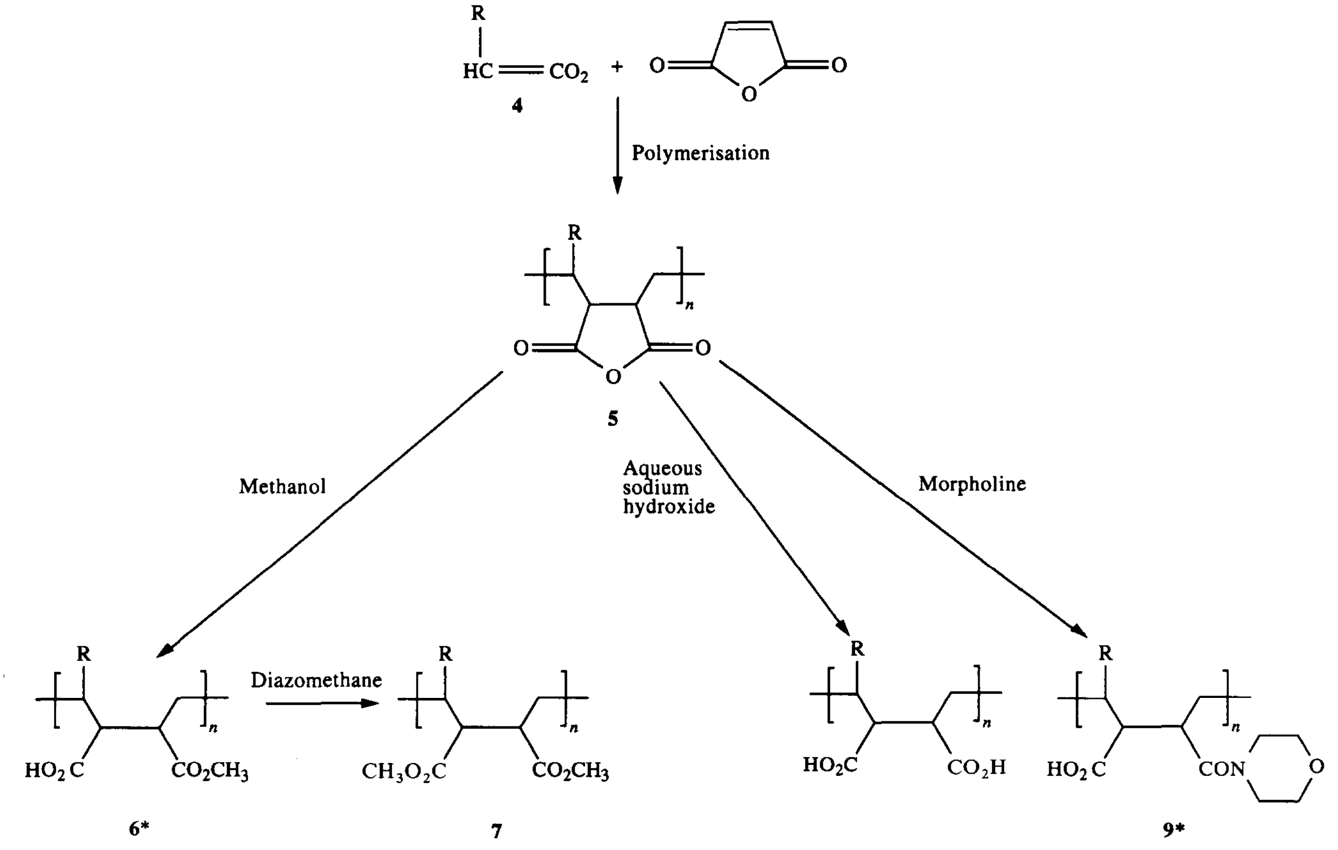
Polymer synthesis

The reactions used to synthesize the various polymers are shown in *Scheme 1*. The α-olefins **4a**–**4h** were prepared by standard methods. Olefin **4i** was a commercial sample. The olefins were copolymerized with maleic anhydride to give alternating copolymers **5a**–**5k** (*Table 1*). The anhydride groups in the copolymers were reacted with appropriate chemical species (*Scheme 1*) to give polymers with acid–ester (polymers **6**), diester (polymers **7**), diacid (polymers **8**) or acid–amide (polymer **9**) 'head groups'. It is convenient to refer to the hydrophilic groups derived from the anhydride residues of polymers **5** as the 'head groups' by analogy with the polymers **1**–**3** studied previously[9], though in the present work the additional hydrophilic groups in the side chain may behave in a similar manner. The molecular weights of the copolymers were estimated by g.p.c. either by direct measurement on the anhydride copolymers **5** or by measurement on the dimethyl ester derivatives (polymers **7**). The results indicate that the products had number-average molecular weights ($\bar{M}_n$) in the range 4000–13 000 and polydispersity ($\bar{M}_w/\bar{M}_n$) values in the range 1.2–2.0.

Studies of the film properties

General aspects. For all the polymers discussed below, isotherms were measured for monolayers on water at 20°C and pH 5.3–5.6. The isotherms are shown in *Figures 1–4*. The areas per repeat unit at 0 mN m^{-1}, A_0, obtained by extrapolation of the 'solid' section of the isotherm to zero pressure, and at 30 mN m^{-1}, A_{30}, and the collapse pressure, π_c, for the various polymers are summarized in *Table 2*. In every case attempts were made to transfer the monolayers from water containing cadmium chloride onto silicon wafers or Pyrex microscope slides made hydrophobic by treatment with hexamethyldisilazane[13]. In successful cases thick multilayers were prepared and X-ray diffraction experiments carried out to seek Bragg peaks. The observation of Bragg peaks indicates the presence of a layer structure and allows the layer spacings, i.e. the spacing between the layers of cadmium ions associated with the hydrophilic head groups, to be estimated. The results are summarized in *Table 2*.

Since the main purpose of the present project was to determine whether the polymers of the types **6**, **8** and **9** prepared in the present work could form Langmuir and LB films with a similar degree of order to those of polymers **1**–**3**, it is helpful to include here the relevant data for the latter polymers. The isotherms are shown in *Figure 5*. *Table 2* gives the corresponding data for these



Scheme 1 Polymer synthesis. (*See note below formulae 1–3)

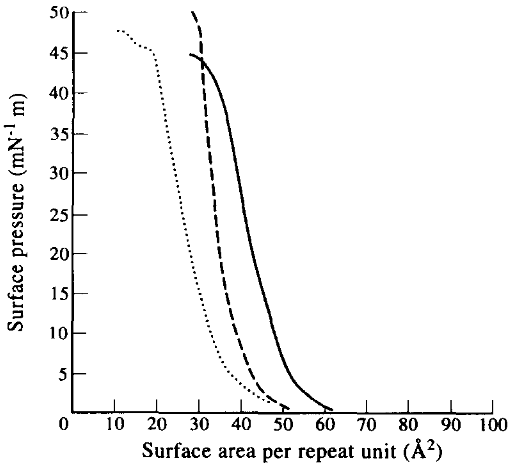


Figure 5 Isotherms of polymer **1** (——), polymer **2** (– – –) and polymer **3** (····) on a subphase of water at 20°C and pH 5.3–5.6. Measurements made on polymers described in reference 9

polymers as is given for the polymers studied in the present work.

Before discussing the results obtained with individual polymers, it is helpful to indicate the criteria we have taken as evidence of order in both the monolayers and the LB films. An isotherm is considered to indicate that the monolayer on water is well ordered when the isotherm has a steep 'solid' section over a substantial pressure range and a high collapse pressure, typically $>35\,\mathrm{mN\,m^{-1}}$. The LB multilayers are considered to be well ordered when the monolayers on water from which they were prepared were well ordered, when they transferred from the water surface onto the solid support with essentially no change in the area per repeat unit (i.e. deposition ratios were 1.00 ± 0.05), and when the multilayers so formed showed Bragg peaks, preferably sharp Bragg peaks, when studied using X-rays. Films which showed several Bragg peaks were considered to be particularly well ordered. It should be noted here that LB films prepared from pre-formed polymers cannot be expected to be as well ordered as LB films prepared, for example, from stearic acid. As far as we are aware the highest number of Bragg peaks so far observed for a multilayer prepared from a pre-formed polymer is five[10].

Polymers prepared from α-olefins containing amide linkages. Initially polymer **6a** was investigated. This polymer was prepared by copolymerizing olefin **4a** with maleic anhydride, followed by ring-opening of the anhydride residues in the product with methanol. Polymer **6a** contains a secondary amide group very close to the hydrophilic acid–ester 'head group'. Comparison of the isotherm obtained for this polymer (*Figure 1a*) With that obtained for polymer **2** (*Figure 5*) shows clearly that the presence of the amide group results in a film with considerably less order than that of polymer **2**.

Our usual procedure when measuring isotherms is to successively compress (not exceeding π_c) and relax the monolayers until a reproducible ($\pm 5\%$) isotherm is obtained. Typically this requires two or three cycles. In the case of polymer **6a**, however, it was found that the initial compression gave an isotherm with a pronounced 'hump' at a surface area per repeat unit of 32 Å^2. The 'hump' was not apparent on subsequent compressions or on the initial one if the monolayer was first allowed to stand for 14 h (shorter periods were not investigated). The 'hump' is clearly the result of a major reorganization of the monolayer and appears to be associated with the hydrogen-bonding properties of the secondary amide group because the isotherm of the corresponding N-methyl derivative (polymer **6b**) (*Figure 1a*) shows no 'hump' and resembles more closely that of polymer **2** than that of polymer **6a**. In monolayers of polymer **2** both the acid and ester groups are at the water surface[9,15,16]. The secondary amide group is strongly hydrophilic and in polymer **6a** there will be a strong tendency for this group also to be at the water surface. Indeed, at surface areas per repeat unit of >32 Å^2 it may be that all three hydrophilic groups are at the surface. The 'hump' may well correspond to a reorganization in which one of the groups leaves the surface and/or the monolayer begins to stack into a multilayer. In support of the latter the surface area per repeat unit in the 'solid' part of the isotherm is only 8 Å^2. If left at surface pressures $>45\,\mathrm{mN\,m^{-1}}$ the film can be visually seen to collapse.

A thick LB multilayer of polymer **6a** was prepared successfully from a monolayer at a surface area per repeat unit of 20 Å^2 (surface pressure $20\,\mathrm{mN\,m^{-1}}$). The Y-type film obtained showed just one Bragg peak at a *d*-spacing of 27 Å, substantially thinner than that (38 Å) for polymer **2**. Attempts to form an LB multilayer from polymer **6b** were unsuccessful. A monolayer could be transferred successfully on the down stroke but on the up stroke it returned to the water surface.

Polymers **6c** and **6d** were structurally similar to polymer **6a**, but the 'spacer chains' between the amide groups and the acid and ester 'head group' were longer. The isotherms obtained (*Figure 1b*) for the initial compression of monolayers of polymers **6c** and **6d** showed, like that of polymer **6a**, clear evidence for a phase change and as before this was not repeated on subsequent compressions. Comparison of the isotherms for the three polymers shows that as the 'spacer chain' becomes longer the phase change on the initial compression becomes less pronounced and at a given pressure the area repeat unit becomes greater. The isotherm for polymer **6d** is similar to that of polymer **2**. In monolayers of polymer **6d** hydrogen bonding between the side chains (*Figure 6*) may assist the formation of a stable monolayer[17]. The situation is similar to that found in extended nylon 66 fibres. In support of this it was found that polymer **6e**, the ester analogue of polymer **6d**, would not form stable monolayers even though the ester linkage is less hydrophilic than the amide linkage.

Polymers **6c** and **6d** both failed to form LB multilayers.

The generally poor results obtained with the amide series of polymers prompted us to turn our attention

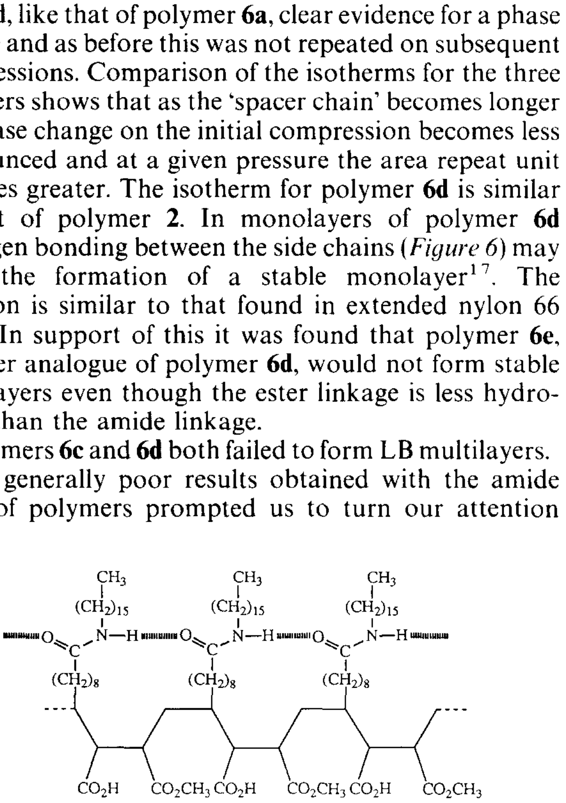


Figure 6 Possible arrangement of polymer **6d** with hydrogen bonding between side chains

instead to a series where the hydrophilic linkage in the side chain was an ester linkage. It was anticipated that the latter was less likely to be disruptive of film order because the ester moiety is considerably less hydrophilic than the secondary amide moiety.

Polymers prepared from α-olefins containing ester moieties. The first polymer of this type to be investigated was polymer **6f**. This contains a C_8 side chain with a terminal carbomethoxy group and an acid–methyl ester 'head group'. The isotherm for this polymer was reasonable (*Figure 2a*) but not as good as that of polymer **1** (*Figure 5*) which contains a side chain with similar number of atoms. Thus, the isotherm of polymer **6f** was less steep, had a larger surface area per repeat unit and a lower collapse pressure. This is probably because the monolayer is disorganized due to a significant fraction of the carbomethoxy groups being at the water surface. Nevertheless thick LB multilayers (Y-type) could be prepared. They showed just one very broad Bragg peak corresponding to a bilayer spacing of ~32 Å. The corresponding polymer with the acid–acid head group (polymer **8f**) gave a substantially better isotherm (*Figure 2a*), though still not as good as that from polymer **1**. A thick LB multilayer could be prepared. It displayed two sharp Bragg peaks corresponding to a bilayer spacing of 33.7 Å. Thus, the polymer with the diacid 'head group' gave better films than the analogue with the acid–methyl ester 'head group'.

It was expected that the disordering effect of the side chain carbomethoxy group could be reduced by diluting these side chains with simple straight hydrocarbon chains. Accordingly polymer **6j** was prepared starting from olefin **4f** and octadec-1-ene in a mole ratio of 1:4. As anticipated the general shape of the isotherm (*Figure 2b*) was now more like that of polymer **2** than that of polymer **6f**, though the area per repeat unit was rather small. Thick LB multilayers could be prepared from both polymers. The latter displayed two Bragg peaks which corresponded to a bilayer spacing of 35.6 Å, a value very similar to that (38.2 Å) found for polymer **2**. In view of the success of this approach polymers **6k** and **8k** were prepared. These were similar to **6j** and **8j**, but the starting α-olefins were now used in equal proportions. Polymers **6k** and **8k** were found to give good isotherms and LB films. Thus, even a dilution of the hydrophilic side chain ester to 50% is helpful in improving film quality. Clearly surrounding the side chain carbomethoxy groups with simple hydrocarbon chains is one way of overcoming the deleterious effect of the side chain hydrophilic groups. However, dilution is not a satisfactory solution to the problem in general as the side chain containing the ester group might well be that which incorporates the desired active moiety into the LB film.

It was thought that having the ester linkage near the middle of the side chain might result in a more ordered multilayer than was obtained with polymer **6f**. However, as noted above, polymer **6e** failed even to give stable monolayers. This prompted us to prepare polymers **6g** and **6h** in which the side chain ester linkages were more hindered. It was thought that this would reduce the interaction of the ester group with the water surface and hence, in effect, make it less hydrophilic. In the event both polymers showed better isotherms (*Figure 3*) than polymer **6f**. That of polymer **6g** was a little steeper and had a somewhat higher collapse pressure, whilst that of polymer **6h** was much steeper and closely resembled that of polymer **2**. As with the other systems discussed above, a further improvement in the isotherms was obtained by changing to an acid–acid 'head group'. Thus, polymers **8g** and **8h** both had steep isotherms with high collapse pressures and were very similar to that of polymer **2** or the analogue with an acid–acid head group. Thick LB multilayers could be prepared from all these polymers and they each showed at least two Bragg peaks.

Finally, we investigated polymer **6i**. This has a cholesteryl moiety, i.e. a mesogen, in the side chain and an acid–acid 'head group'. The isotherm obtained for this polymer (*Figure 4*) showed a possible phase change at a surface area per repeat unit of 35 Å^2 (surface pressure 10 mN m^{-1}). Before this point the isotherm was moderately steep with $A_0 = 55$ Å^2, a reasonable value given that the isotherm of cholesterol itself has $A_0 = 50$ Å^2 (ref. 18). Above the phase change the isotherm was steeper with $A_0 = 25$ Å^2, a value approximately half the previous one and one too small to accommodate a cholesteryl unit vertically. These data suggest that the phase change might be due to a transition from a monolayer to a bilayer. It was argued that the monolayer might be more stable with a larger more hydrophilic head group and this prompted the preparation of polymer **9i** which has an acid–morpholino amide 'head group'. It was known from previous work that this 'head group' occupies a somewhat larger surface area than the diacid head group[9]. In the event polymer **9i** gave an excellent condensed isotherm (*Figure 4*) with $A_0 = 60$ Å^2. The monolayer transferred well and thick LB multilayers were prepared. These showed two Bragg peaks corresponding to a *d*-spacing of 34.4 Å. This value is very small given the size of the cholesteryl unit and the fact that the steroid nucleus is essentially flat and rigid. It suggests that the mesogenic side chains are probably tilted and partially interdigitated.

CONCLUSIONS

Derivatives of α-olefin–maleic anhydride alternating copolymers such as polymers **1**–**3** form excellent LB films[9]. For many applications utilizing polymers of this general type more complex olefins will need to be used. We have shown in this paper that incorporation of amide linkages into the olefin results in polymers with poor monolayer and LB film-forming properties. Incorporation of ester linkages, however, is less destructive to the film-forming properties and if the ester linkage is 'screened' good polymeric LB films can still be obtained. Good LB films have been prepared from a polymer containing cholesteryl mesogens. Polymer **2** and the analogue with the acid–acid head group had very similar film properties. However, we have found in the present work, where the side chains are partly hydrophilic and less easily ordered, that the polymers with acid–acid 'head groups' generally give better films than the analogues with acid–methyl ester 'head groups'.

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