Langmuir and Langmuir–Blodgett Films of Derivatives of Alternating Copolymers of Straight-Chain α-Olefins and Maleic Anhydride

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ABSTRACT: A series of alternating copolymers of straight-chain α-olefins and maleic anhydride were synthesized ($\bar{M}_n$ = 2500–37 000) and derivatives prepared by reaction of the anhydride residues with methanol and, in some cases, other alcohols, water, ammonia, and dimethylamine. Isotherms were measured for monolayers of the various polymer derivatives on water, and Langmuir–Blodgett (LB) multilayers were prepared. The majority of the polymers gave excellent isotherms (steep, high-collapse pressures) and, as determined by the detection of Bragg peaks by X-ray diffraction, Y-type LB films with a regular layer structure. Best results were obtained for polymers with a lipophilic side chain (derived from the α-olefin) containing 13–16 carbon atoms and with the two head groups as a carboxylic acid plus either carbomethoxy (or other small carboalkoxy group), carboxylic acid, or carboxamide. The LB films of these polymers were close packed, and, as judged from layer thicknesses and an infrared study, the lipophilic side chains were on average tilted at an angle of ca. 40°. The in situ hydrolysis of one anhydride polymer on the water surface was investigated.

Introduction

Langmuir–Blodgett (LB) films have been known since 1935,[1] but it is only in recent years that it has been recognized that such films, being ordered at the molecular level, might have applications in microelectronic and optoelectronic devices.[2] Unfortunately, most LB films are not sufficiently stable or robust for use in commercial devices. This has prompted an interest in polymeric LB films, though such films are, of course, also of considerable fundamental interest in themselves because they are one of the simplest types of ordered polymeric materials.

Two approaches may be used for the preparation of polymeric LB films. One, extensively studied in recent years, uses amphiphiles that are also monomers.[3–7] Once the multilayer has been formed, polymerization is initiated by irradiation, most commonly by UV light. The polymerization process may be facilitated by the molecular order in the film.[4,5] Not surprisingly, since polymerization generally results in a contraction in volume, the polymeric films produced using this approach tend to crack and craze,[5] though this is not always the case.[6,7] The second approach, and the one with which this paper is concerned, is to prepare the LB films directly from preformed polymers.[8,9] This has the attraction that virtually no processing of the LB film is needed once it is formed and that certain types of polymers may prove to be suitable vehicles for moieties that by themselves will not form good films, for example, cholesterol.[9,10] It is recognized that the films obtained from preformed polymers may not be so highly ordered as the films prepared from low molecular weight amphiphiles, but for many applications this is quite acceptable.

If regular LB multilayers are to be obtained from preformed amphiphilic polymers, it would be expected that the hydrophilic and lipophilic parts should be frequently and regularly placed along the polymer chain. Polymers that have structures of this type and that have been studied as monolayers on water[11] (Langmuir films) include polyacrylates,[12] polymethacrylates,[12–16] poly(vinyl ester)s,[16] poly(vinyl ether)s,[17] acetals prepared from poly(vinyl alcohol),[18] and poly(alkyl L-glutamate)s.[15] However, in all of these polymers, the hydrophilic groups are relatively weakly hydrophilic and the preparation of ordered LB multilayers is not always easy.[12,15] Polymers that meet the structural requirement, that are readily available, and that have more strongly hydrophilic head groups are derivatives of alternating vinyl–maleic anhydride copolymers **1** obtained by reacting the polymers with water, alcohols, ammonia, or amines: see Scheme I. Our early work in this area was concerned mainly with derivatives of copolymers of styrene and maleic anhydride.[8] Although these polymers form monolayers on water that display "good" isotherms, the LB films prepared from them are not in general highly ordered unless the anhydride residues have been reacted with a long-chain alcohol. Even then, when studied by low-angle X-ray scattering, they showed just one Bragg peak.[19] Derivatives of octadec-1-ene–maleic anhydride copolymers were, however, much more satisfactory.[19,20]

In this paper we present the results of more detailed studies of Langmuir films and LB films formed from derivatives of α-olefin–maleic anhydride copolymers. The studies include the effect of varying the length of the lipophilic olefin side chain, the effect of varying the hydrophilic head groups, an infrared spectral study of a typical LB film, and a brief study of the in situ hydrolysis of one of the anhydride polymers on the Langmuir trough.

Experimental Section

Unless indicated otherwise tetrahydrofuran (THF) and methanol were used a purchased, petroleum ether refers to the fraction bp 40–60 °C, and polymer samples were dried in the presence of P_2O_5 in a vacuum oven (0.2 mmHg) at ambient temperature. Infrared spectra (KBr disks unless indicated otherwise) were measured by using a Nicolet MX-1 FTIR. ^1H and ^{13}C nuclear magnetic resonance (MNR) spectra were measured on a Jeol 100 FT instrument equipped with a multinuclear probe. Gel permeation chromatography (GPC) was carried out on a Waters Associates Model 440 instrument using high molecular weight polystyrene columns, THF as the eluent, and polystyrene standards.

Synthesis of the Polymers. Synthesis of α-Olefins. All but three of the required α-olefins were obtained commercially;

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Scheme I
Polymer Synthesis

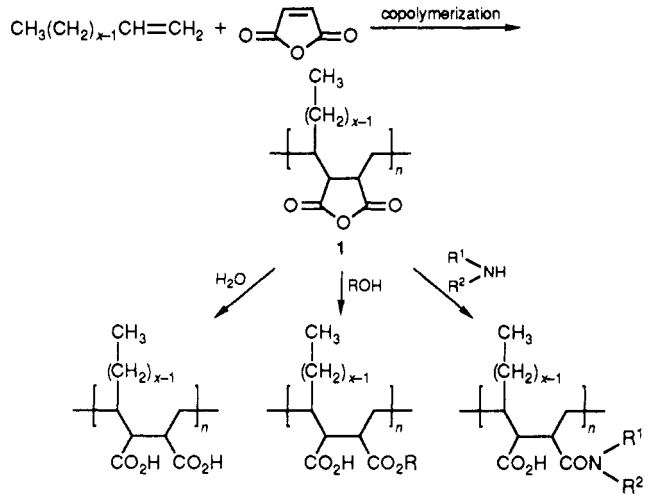


Table I
Synthesis and Molecular Weight Data[a] for the α-Olefin–Maleic Anhydride Copolymers

copolym designatn	olefin monomer CH_3-$(CH_2)_{x-1}CH{=}CH_2$ value of x	yield of copolymer, %	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
1a	4	33	2.5	6.2	2.5
1b	6	17	9.0	14.0	1.6
1c	9	39	12.0	25.0	2.1
1d	13	59	10.0	19.0	1.9
1e	14	55	37.0	56.0	1.5
1f	14	38	15.0	25.0	1.3
1g	14	62	8.0	12.8	1.6
1h	16	52	6.0	20.0	3.3
1i	16	56	8.0	17.0	2.1
1j[b]	16		19.5		
1k	17	60	10.0	20.0	2.0
1l	18	58	10.0	16.0	1.6
1m	21	47	8.0	13.6	1.7

[a] Determined by GPC using polystyrene standards. [b] Commercial sample used in our earlier work.[19,20]

they were purified by fractional distillation. The following procedure, based on that described by Tamura and Kochi,[21] is typical of that used to prepare the other three α-olefins.

Pentadec-1-ene: Bromododecane (6.23 g, 25 mmol), allylmagnesium chloride (30 mmol as a 2.0 M solution in THF), and THF (50 mL, freshly distilled from calcium hydride) were placed under dry nitrogen in a two-necked round-bottomed flask (250 mL) equipped with a magnetic stir bar and a septum inlet. The stirred solution was cooled to 0 °C, and dilithium tetrachlorocuprate (0.10 mmol as a 0.10 M solution in THF) was added with a syringe. The mixture was stirred at 20 °C for 48 h. Aqueous sulfuric acid (100 mL of 0.1 M) was then added and the mixture extracted with petroleum ether (4 × 100 mL). The combined extracts were washed with water and dried ($MgSO_4$), and the solvent was evaporated off. The residue was purified by short-path distillation to give pentadec-1-ene (3.61 g, 69%), bp 145–146 °C (12 mm) [lit.[22] bp 134 °C (10 mm)]. The infrared spectrum (liquid film) and ^1H NMR spectrum were satisfactory.

Nonadec-1-ene, prepared similarly (59% yield), had a bp of 150–151 °C (3 mm) [lit.[22] bp 177 °C (10 mm)] and satisfactory spectra.

Tricos-1-ene, prepared similarly (65% yield), had a bp of 226–228 °C (755 mmHg) [lit.[23] bp 233 °C (760 mmHg)] and satisfactory spectra.

Copolymerizations. The following procedure is typical of that used for the copolymerization of maleic anhydride and α-olefins. The results are summarized in Table I.

Polymer 1e: Maleic anhydride (5.30 g, 53.0 mmol; freshly recrystallized from ethanol-free chloroform) was dissolved in 1,4-dioxane (10 mL; sodium-dried). Hexadec-1-ene (11.77 g, 52.5 mmol) and AIBN (75 mg, 0.46 mmol) were added, and the mixture was placed in a sealable glass pressure vessel (200 mL). A vacuum line capable of <1 mmHg of pressure was used to degas the mixture by the usual freeze–thaw procedure (three or four cycles), and then the vessel was sealed under vacuum and placed in an oil bath at 60 °C. After 14 days the vessel was cooled, the vacuum broken, and THF (20 mL) added to reduce the viscosity of the mixture. The solution was then added dropwise to cold methanol (10 volumes) (in a few other cases the use of cold petroleum ether gave a better product) to precipitate the polymer. The latter was collected, reprecipitated from THF into petroleum ether, and then dried. The final product (9.29 g, 55% yield) had ν_{max} 1850 and 1780 cm^{-1} (carbonyl bands characteristic of a saturated five-ring anhydride); by GPC it had M_n = 37 000, M_w = 56 000; by elemental analysis it had C = 74.1%, H = 11.8%, calculated for a 50:50 copolymer C = 74.5%, H = 10.5%. The ^{13}C NMR spectrum (solution in THF-d_8) was in excellent agreement with that reported for a propene–maleic anhydride copolymer[24] and indicated that in the present polymer 85% of the maleic anhydride residues were incorporated by trans addition and 15% by cis addition.

The vinyl–maleic anhydride copolymer samples tended to deteriorate on storage due to reaction of the anhydride residues with adventitious moisture. The process could be reversed by heating a solution of the polymer in acetic anhydride under reflux for 1–2 days. The polymer was then recovered by using the procedure given above.

Derivatives of α-Olefin–Maleic Anhydride Copolymers. The following procedures are typical. Long reaction times were used simply to ensure virtually quantitative reaction. Polymer **2g** and **13** were a gift from Dr. E. Khoshdel.

Half methyl ester 2e: Polymer **1e** (1.00 g) was treated with methanol (50 mL) at reflux temperature for 14 days. Excess methanol was then evaporated off and the residue dissolved in a minimum of THF (10 mL). The solution was added slowly to ice-cold petroleum ether (100 mL) to precipitate the polymer. The polymer was collected and dried. The product (0.77 g, 70%) had ν_{max} 1730 and 1710 cm^{-1}; no carbonyl bands attributable to anhydride residues were detected. By elemental analysis it had C = 71.0%, H = 10.5%; expected C = 71.1%, H = 10.7%.

The half methyl esters **2a–2d**, **2f**, and **2h–2m**, the half ethyl ester **4**, and the 2,2,2-trifluoroethyl ester **5** were prepared similarly.

Diacid 3: Polymer **1e** (1.60 g) was treated with sodium hydroxide (2.0 g) in water (50 mL) for 1 week at reflux temperature. The cooled solution was then added to aqueous hydrochloric acid (2 M, 500 mL). The precipitate was collected, dissolved in THF, and reprecipitated into water (500 mL). The polymer was collected, washed with water, and dried. The product (1.58 g, 95%) had ν_{max} 3800–2200 (broad) and 1705 cm^{-1}; no carbonyl bands attributable to anhydride residues were detected. By elemental analysis it had C = 70.2%, H = 10.3%; expected C = 70.5%, H = 10.6%.

Acid-amide 6: Polymer **1e** (0.50 g) in THF (10 mL) was added dropwise to a stirred aqueous ammonia solution (SG 0.88, 50 mL). A solid precipitated immediately but slowly redissolved. The mixture was stirred at 20 °C for 10 days. It was then acidified (2 M hydrochloric acid). This precipitated the polymer. It was collected, dissolved in THF (10 mL), and reprecipitated into dilute hydrochloric acid (100 mL). It was then dried and reprecipitated from THF into petroleum ether (100 mL). The dried product (0.30 g, 57%) had ν_{max} 3400 (broad), 1710, and 1660 cm^{-1}; no bands attributable to anhydride residues were detected. By elemental analysis it had C = 70.4%, H = 11.1%, N = 4.2%; calculated C = 70.7%, H = 10.9%, N = 4.1%.

Half hexadecyl ester 9: Hexadecanol (1.79 g, 7.4 mmol) in THF (30 mL, freshly distilled from calcium hydride) was treated under nitrogen with sodium hydride (2.2 g as a 40% dispersion in oil). After 30 min polymer **1h** (1.48 g) was added and the mixture heated under reflux for 14 days. The cooled mixture was treated with hydrochloric acid (100 mL, 2 M) and stirred for 30 min. The upper layer was collected and retreated with fresh hydrochloric acid (100 mL, 2 M). The polymer was filtered off and dissolved in THF and the solution dried ($MgSO_4$). Precipitation into cold methanol gave the product, which was collected and dried (1.72 g). It had ν_{max} 1730 and 1711 cm^{-1};

Table II
Properties of Langmuir and Langmuir–Blodgett Films of Polymers

polymer	Langmuir films area per repeat unit, Å²		X-ray data			molar vol of repeat unit in LB films, Å³		
	at 0 mN/m[a]	at 30 mN/m	no. of layers in LB films[b]	no. of Bragg peaks	d-spacing per bilayer, Å	exptl[c] (V_{exp})	calcd (V_{calc})	V_{calc}/V_{exp}
2a	50	21.5	*d*	0				
2b	50	37.0	288	1	21.7	401	430	1.1
2c	48	39.5	332	2	26.4	521	511	1.0
2d	40	34.6	400	3	35.0	606	618	1.0
2e	41	33.9	500	3	33.6	570	646	1.1
2f	41	34.0	500	3	35.3	600	646	1.1
2g	41	35.1						
2h	45	35.6	400	3	35.0	623	704	1.1
2i	39	33.1	500	3	38.2	632	704	1.1
2j	50	41.0						
2k	39	30.0	400	2	37.0	555	733	1.3
2l	40	31.6	400	2	44.8	708	755	1.1
2m	34	24.2	400	1	45.0	545	836	1.5
3	39	32.7	334	3	36.1	590	611	1.0
4	37	34.0	500	2	34.1	580	698	1.2
5	39	34.9	262	2	37.1	647	732	1.1
6	40	32.2	500	2	38.6	621	648	1.0
7	39	32.0	500	2	33.8	541	721	1.3
8	50	39.8	348	1	37.6	748	756	1.0
9	52	46.0	500	3	47.3	1087	1155	1.1
10	59	47.7	312	2	45.0	1073	1299	1.2
11	51	39.0	322	2	37.0	722	901	1.3
12	60	44.0	372	1	*e*			
13	61	53.0	434	3	40.0	1060	1143	1.1

[a] By extrapolation of the solid section of the isotherm to zero pressure. [b] Transferred onto silicon at a surface pressure of 30 mN/m from over water containing $CdCl_2$. Unless indicated otherwise, deposition occurred on both up and down strokes with a deposition ratio of 0.95–1.05. [c] Experimental volume using surface area at a pressure of 30 mN/m. [d] Transferred at a surface pressure of 20 mN/m. [e] Bragg peak not sufficiently well resolved to give a significant value.

there were no bands due to anhydride residues. Found: C = 76.1%, H = 11.9%; expected C = 76.5%, H = 12.0%.

Esters **10–12** were prepared similarly. It is interesting to note, however, that the infrared spectrum of polymer **12**, but not that of polymer **11**, showed only one carbonyl band, which was at 1734 cm^{-1}. The carbonyl band due to the carboxyl group in polymer **12** almost certainly occurs at a higher frequency than usual due to an interaction with the PEG chain.

Acid–dimethylamide 7: Polymer **1e** (0.50 g) was dissolved in a solution of dimethylamine in ethanol (33%, 50 mL), and the mixture was heated under reflux for 4 days. The cooled mixture was acidified (2 M hydrochlloric acid). This precipitated the polymer, which was collected and reprecipitated into water and then petroleum ether as described for derivative **6**. The dried product (0.25 g, 44%) had ν_{max} 1738 (very weak, ethyl ester), 1705 (strong, carboxyl), and 1655 cm^{-1} (strong, amide); no bands attributable to anhydride residues were detected. By elemental analysis it had C = 72.1%, H = 11.6%, N = 3.6%; calculated C = 71.9%, H = 11.2%, N = 3.8%.

Langmuir Isotherms and Film Deposition. The LB trough was designed and built in-house. A general description of the trough and dipping procedure is given below for future reference followed by specific details of the experimental conditions used in the present work.

The whole apparatus was supported on an antivibration mounting and was used in a dust-free environment. The subphase was contained in a borosilicate glass trough seated in a heatable copper jacket. The surface film was confined by a constant-perimeter polytetrafluoroethylene tape, and the area was measured from the barrier positions by a 10-turn potentiometer attached to the drive gearing, giving the barrier position to an accuracy of 0.5%. The surface pressure was monitored with a Wilhelmy plate and a CI Microforce balance. For film deposition the surface pressure was maintained constant by using the Wilhelmy plate reading to control the dc motors driving the barriers. The sample was moved vertically through the air–water interface by a dc motor-driven micrometer screw. The deposition ratio was recorded continuously throughout the dipping process. For the preparation of thick LB films (>50 layers) an automated trough was used. This had a device for automatically spreading the polymer solution and all the operations were computer controlled.

In the present work the subphase was deionized, double-distilled, 0.2-μm-filtered water at room temperature (20 °C). The pH of the water was 5.3–5.6 (due to exposure to carbon dioxide). For X-ray experiments $CdCl_2$ was added to the subphase (to a concentration of 2.5×10^{-4} M). Surface films were prepared by dissolving the polymer in ethyl acetate to a concentration of 0.1–0.3 mg/mL. An appropriate amount of this solution was carefully placed on the water surface and the solvent allowed to evaporate. The film was compressed almost to the collapse pressure and then expanded, and this procedure was repeated several times until reproducible isotherms were obtained. Unless indicated otherwise LB films were deposited on silicon wafer slices (treated to make them hydrophobic as previously described[25]) operating at a surface pressure of 30 mN/m [except for polymer **2a**; 20 mN/m] and a dipping speed of 5 mm/min.

X-ray Studies. For X-ray studies thick (250–500) layers were deposited on silicon wafers using the automated trough. The Bragg peaks were detected and measured with a Raymax RX3D X-ray diffractometer using nickel-filtered Cu Kα radiation. The results are summarized in Table II.

Infrared Studies of LB Films. Infrared spectroscopic studies were carried out on polymer **2e** as described by Mumby et al.[12] and Duda et al.[15] Both transmission (T-IR) and grazing incidence (GI-IR) studies were performed. For the T-IR 20 layers of polymer were deposited from an aqueous solution of pH 3.0 on to chalcogenide glass plates; for the GI-IR 20 layers of polymer were deposited on to clean glass microscope slides with 20 nm of gold evaporated onto one side. GI-IR was carried out by using a standard Harrick reflection accessory. All the spectra were recorded on a Nicolet MX-1 spectrometer. For the T-IR a scan time of 20 min was used; for the GI-IR a scan time of 200 min was used. The results, and those obtained for films cast from THF, are summarized in Table III.

Hydrolysis of a Monolayer of Polymer 1e. A monolayer of polymer **1e** was prepared on pure water at 20 °C by using the usual procedure. It was compressed to a surface pressure of 30 mN/m, and the area per repeat unit, i.e., a pair of the alternating monomers, was noted (22.2 Å). The layer was then reexpanded.

Table III
Intensities of Principal Bands in the Infrared Spectra of Polymer 2e[a]

band, cm^{-1}	cast film	LB film		GI-IR/ T-IR
		GI-IR	T-IR	
2950	63	73	52	1.40
2927	142	162	147	1.10
2875	72	40		
2850	100	100	100	1.00
1740	139	208	73	2.74
1705	114	113	49	2.31
1460	31	38	26	1.46
1430	38	46	23	2.00
1200	47	52	22	2.36
1170	54	52	31	1.68

[a] Peak heights relative to the 2850-cm^{-1} band arbitarily set at 100. Assignments of bands can be found in refs 12 and 26 or standard IR texts.

After various intervals this process was repeated. The area was found to increase with time. This was taken to indicate hydrolysis. The monolayer was finally left overnight, after which time it was assumed that hydrolysis was essentially complete. The area per repeat unit was found to be 32.3 $Å^2$, the same as that measured separately for the diacid **3**. The progress of the reaction is shown in Figure 8.

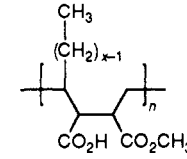
Results and Discussion

Synthesis and Structures of Polymers. Most of the α-olefins required for this project were commercial samples. The remainder were synthesized by reacting the appropriate alkyl bromide with allylmagnesium chloride in the presence of dilithium tetrachlorocuprate.[21] The α-olefins were copolymerized with maleic anhydride in dioxane by using 0.5–2.0% of AIBN as the initiator. The copolymers **1a–1m**, isolated in yields of 17–60%, had, except in one case, $\bar{M}_n$'s in the range 8000–15 000 as determined by GPC using polystyrene standards: see Table I. Low molecular weight polymers were prepared deliberately in the belief that the higher the molecular weight of a polymer, the more difficult it is likely to be to organize it well on the water surface. It is well-known that maleic anhydride copolymerizes with unactivated α-olefins to give highly alternating 1:1 copolymers,[27] and the elemental analyses of the present copolymers and their derivatives were consistent with this.

The ^{13}C NMR spectrum of polymer **1d**, a typical product, was very similar to those reported by Rätzsch et al. for the alternating copolymers of maleic anhydride with ethene and with propene.[24] Using their type of analysis, on the basis of the signals of the backbone carbons bearing the pendant carbonyl groups, it was found that in the present product 85% of the maleic anhydride residues was incorporated by trans addition and 15% by cis addition. This compares with the proportion of 88%:12% for the copolymer with ethene and 80%:20% for the copolymer with propene.

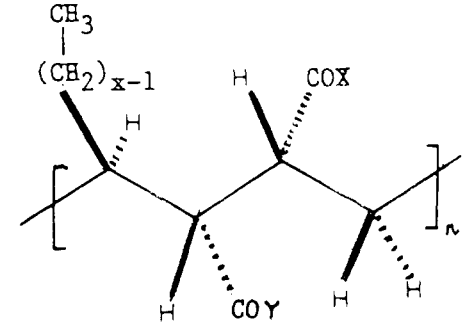
All the α-olefin–maleic anhydride copolymers listed in Table I were reacted with methanol over a prolonged period to give the methyl half esters (**2a–2m**): see Chart I. That the reactions had proceeded in high conversions was indicated by the disappearance of the anhydride carbonyl bands near 1850 and 1780 cm^{-1} in the infrared spectrum and the appearance of strong bands near 1730 and 1710 cm^{-1} due to the ester carbonyl group and acid carbonyl group, respectively. The ^{13}C NMR spectra of representative products were very similar to that reported[20] for the methyl half esters derivative of the propene–maleic anhydride copolymer referred to above, and they indicate that reaction occurred at the two possible positions in the

Chart I[a]
Half Methyl Ester Derivatives of α-Olefin–Maleic Anhydride Copolymers



2a, $x = 4$ **2b**, $x = 6$ **2c**, $x = 9$ **2d**, $x = 13$ **2e**, $x = 14$ **2f**, $x = 14$ **2g**, $x = 14$ **2h**, $x = 16$ **2i**, $x = 16$ **2j**, $x = 16$ **2k**, $x = 17$ **2l**, $x = 18$ **2m**, $x = 21$

[a] These polymers were prepared from the corresponding polymers **1a–1m**, where more than one polymer has the same value of x, the samples differ in molecular weight: see Table I. For simplicity the formulas are written as though alternation is 100% and the anhydride residues reacted at just one of the two carbonyl groups.



X and Y = -OH and -OCH_3 in either order

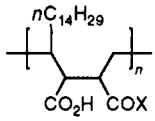
Figure 1. Most probable stereochemical arrangements of the repeat unit in polymers **2**.

anhydride moiety in the ratio of approximately 60:40. It is not clear which carbonyl group was the more reactive, but the major moiety produced is probably that shown in formula **2**.

The data presented above suggest that the *predominant* configuration in the various polymer derivatives is that shown (for convenience as the chain extended conformation) in Figure 1. The lipophilic side chain is placed in the position shown because it is assumed that, as it cannot have any favorable interaction with the maleic anhydride moiety, it will react during polymerization mainly in the arrangement that minimizes steric interactions. The net result is that the *major* chain extended conformation is probably that which has the two hydrophilic groups on the same side of the polymer backbone and the lipophilic chain on the opposite side. As a consequence, if the polymer lies at the water surface with its backbone parallel to the surface, the two hydrophilic groups can easily interact with the water while the lipophilic chain can easily minimize its contact with the water.

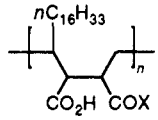
For selected α-olefin–maleic anhydride copolymers other derivatives (see Chart II) were prepared by hydrolysis of the anhydride residues and by reaction of the anhydride residues with ethanol, 2,2,2-trifluoroethanol, ammonia, dimethylamine, morpholine, docosanol, triethylene glycol monomethyl ether, and poly(ethylene glycol) monomethyl ether [$HO(CH_2CH_2O)_nCH_3$ where $n = 7.2$]. All these reactions were carried out for long periods to ensure high conversions. The latter were confirmed by elemental analyses and infrared spectroscopy. An interesting point with polymer **12** is that, unlike the other half methyl esters, including polymer **11**, it showed only one carbonyl peak

Chart II[a]
Various Derivatives of α-Olefin–Maleic Anhydride Copolymers



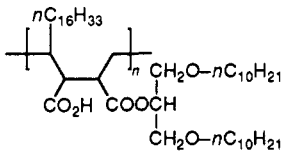
all prepared from polymer **1e**

3, X = –OH
4, X = –OCH_2CH_3
5, X = –OCH_2CF_3
6, X = –NH_2
7, X = –$N(CH_3)_2$
8, X = –N⟨O⟩



all prepared from polymer **1h**

9, X = –O–$nC_{16}H_{33}$
10, X = –O–$nC_{22}H_{45}$
11, X = –O–$[CH_2CH_2O]_3CH_3$
12, X = –O–$[CH_2CH_2O]_{7.2}CH_3$



13 ($\bar{M}_n$ = 50 000)

[a] For simplicity the formulas are written as though alternation is 100% and the anhydride residues reacted at just one of the two carbonyl groups.

(1734 cm^{-1}) in the infrared spectrum. It is probable that in this polymer the carboxylic acid group hydrogen bonds strongly to the poly(ethylene oxide) side chain.

Langmuir Films of the Methyl Half Esters (2a–2m). Langmuir films of all the methyl half esters (**2a–2m**) were prepared (by using solutions in ethyl acetate) on a subphase of water at pH 5.3–5.6 at 20 °C, and their isotherms were measured. Most of these are shown in Figure 2. Several points merit comment.

First, there is an interesting trend in the quality of the isotherms, and presumably the order in the monolayers, as the length of the lipophilic side chain increases. When it consists of only a 4-carbon chain, the isotherm is not very steep and the collapse pressure is only ca. 25 mN/m. However, as it becomes longer, both features improve, and when it contains 13–16 carbon atoms, the isotherms are steep and the collapse pressures exceed 50 mN/m. With slightly longer chains of 17 and 19 carbon atoms, the isotherms are still excellent though they are not quite as steep as with the slightly shorter chains. With 21 carbon atoms, the isotherm is less steep again and the collapse pressure has now fallen to 45 nM/m. Thus, with this series of polymers, there appears to be an optimum length for the side chain of 13–16 carbons. This is not surprising because with an increasing proportion of lipophilic groups in the polymer a point must eventually be reached where the interaction of the hydrophilic groups with the water no longer justifies organizing the polymer at the air–water interface.

Second, with a lipophilic side chain of 13–16 carbon atoms the surface area per repeat unit, i.e., per each alternating pair, is close to 35 $Å^2$ at 30 mN/m; see Table II for the actual values. Since these values are much larger than the cross-sectional area of a simple methylene chain (approximately 20 $Å^2$), this suggests that the hydrophilic head groups are relatively large and that they therefore include both the carboxylic acid and the ester groups; i.e., both these groups are in contact with the water surface.

Third, it is of interest to note that polymers **2e–g**, which differ only in molecular weight, vis., $\bar{M}_n$ = 37 000, 15 000, and 8000, gave essentially the same isotherms, indicating that in this molecular weight range the actual value of $\bar{M}_n$ does not significantly affect monolayer formation.

Fourth, in our earlier work the half methyl ester derivative **2j** of a commercial octadec-1-ene–maleic anhydride copolymer gave an isotherm of shape similar to the present polymer **2i**, but the cross-sectional area per repeat unit was somewhat greater.[19,20] We have remeasured the isotherm of polymer **2j** and find that it is essentially the same as that reported before: see Figure 2b. The reason for the difference is not known but, in view of the results discussed in the preceding paragraph, is unlikely to be due to differences in $\bar{M}_n$. Preparative details for the commercial polymer, in particular, whether or not the octadec-1-ene used contained any other olefins such as octadec-2-ene, are unfortunately not known.

Finally, it will be noted that none of the present half methyl ester polymers exerted any detectable surface pressure at an average area per repeat unit of more than ca. 65 $Å^2$. It is probable that on the water surface the polymers are in the form of "islands", each consisting of one or more polymer chains, and that the islands only come into contact below an average surface area per repeat unit of ca. 65 $Å^2$.

Langmuir Films of Other Derivatives. Isotherms for the polymer derivatives **3–13** were measured similarly. They are shown in Figure 3. Again several points merit comment.

First, the isotherms obtained for polymers **3–7**, all of which are simple acid, ester, or amide derivatives of polymer **1e**, are very similar to that of the half methyl ester **2e**, and, as before, at a surface pressure of 30 mN/m the cross-sectional area per repeat unit is close to 35 $Å^2$: see Table II for actual values. This strongly suggests that polymers **3–7** organize at the air–water interface in a manner similar to that of half methyl ester **2e**. It should be noted that polymers **3** and **6** each have two very strongly hydrophilic groups which can confidently be expected to be at the water surface. The fact that these polymers have a similar cross-sectional area per repeat unit to the various half esters strongly supports the suggestion made above that in the latter series also both the acid and ester moieties are in contact with the water surface. The isotherm for polymer **8**, prepared using morpholine, is of a shape similar to that of the other polymers, but the area per repeat unit is somewhat larger. Presumably this is simply because the head group is larger.

Second, excellent isotherms were also obtained for polymers **9** and **10**, which have long chain ester groups, and similarly for the glycerol derivative **13**. The area per repeat unit in these cases was substantially larger (11–18 $Å^2$) than the area obtained for the half methyl esters, and it is not clear how they are organized at the air–water interface. It may be that each polymer organizes essentially as before but with the additional lipophilic chain(s) passing from the ester linkage below the water surface to join the other lipophilic chains above the water. However, the drive to keep as much as possible of the lipophilic chains above the water may result in quite a different arrangement. We are currently trying to clarify this point by neutron reflectivity experiments.

Third, the polyether derivatives **11** and **12** also gave good isotherms. The areas per repeat unit (39 and 44 $Å^2$, respectively, at 30 mN/m) were somewhat higher than that with the simple methyl half ester **2h**. However, since the poly(ethylene oxide) chain is hydrophilic, polymers **11** and **12** probably organize at the interface essentially as the half methyl ester **2h** but with most of the polyether chains beneath the head group in the aqueous layer.

Langmuir–Blodgett Films. Isotherms of the various polymer derivatives were, within experimental error, unchanged when they were measured over water containing cadmium chloride. Monolayers of most of the derivatives (see Table II) could be transferred successfully at 30

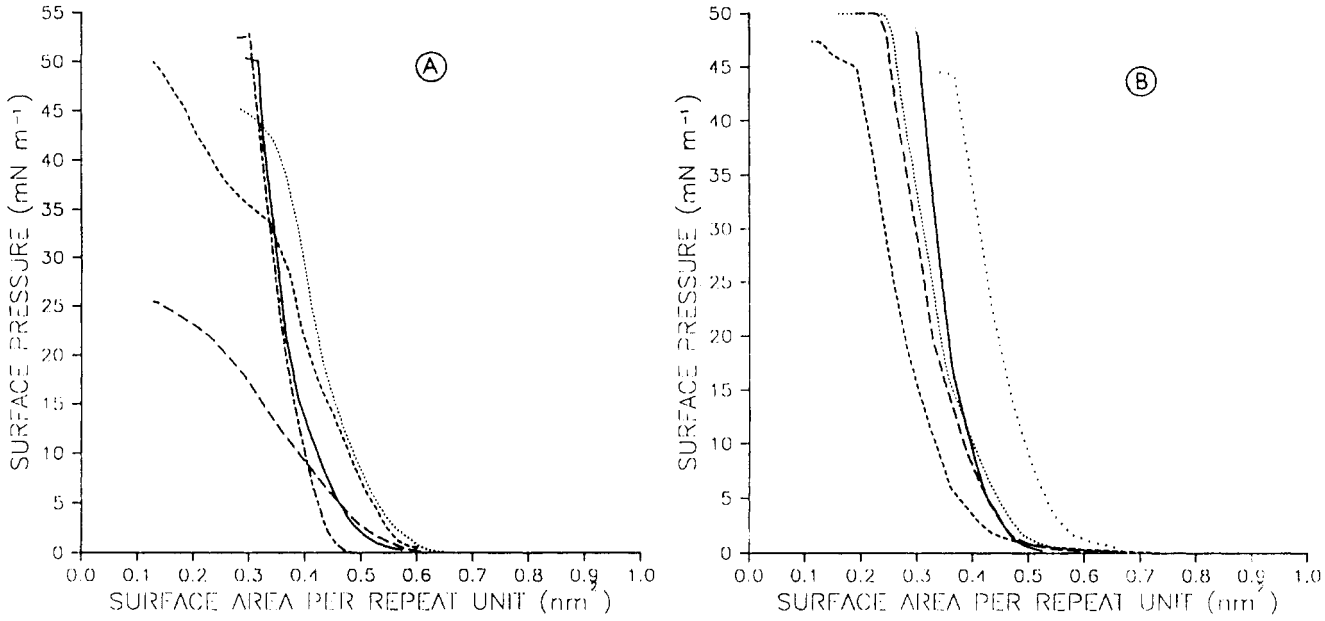


Figure 2. Isotherms of half methyl ester polymers. All isotherms measured at 20 °C and pH 5.3–5.6. (A) Polymer **2a** (– –); polymer **2b** (- - -); polymer **2c** (···); polymer **2d** (– · –); polymer **2e** (—). (B) Polymer **2i** (—); polymer **2j** (· · ·); polymer **2k** (– –); polymer **2l** (···); polymer **2m** (- - -).

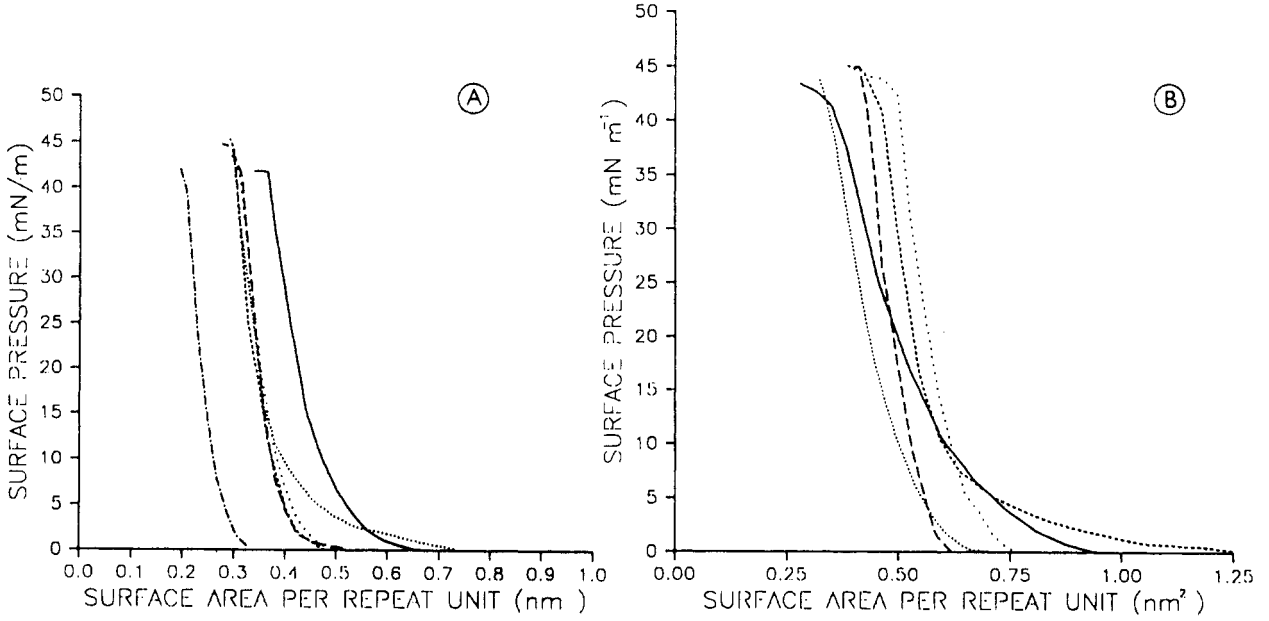


Figure 3. Isotherms of various polymer derivatives. All isotherms measured at 20 °C and pH 5.3–5.6. (A) Polymer **1e** (– · –); polymer **3** (– –); polymer **4** (- - -); polymer **6** (· · ·); polymer **7** (···); polymer **8** (—). Note that the isotherms for polymers **3** and **4** are almost identical. (B) Polymer **9** (– –); polymer **10** (- - -); polymer **11** (···); polymer **12** (—); polymer **13** (· · ·).

mN/m from the surface of such solutions on to pieces of silicon wafer with a hydrophobic surface. Apart from polymer **12** transfer ratios were 0.95–1.05 on both the up and down stroke, suggesting Y-type depositions. Polymer **2a** transferred at 20 mN/m, but it did not give reproducible deposition ratios. Polymer **12** started to deposit as a Y-type film, but the deposition ratios on the down strokes rapidly decreased until after four to five cycles; the deposition had changed to Z-type.

Following these preliminary experiments thick LB films (250–500 layers) were deposited using the automated trough and water containing cadmium chloride. X-ray diffraction experiments were then carried out to seek Bragg peaks. The observation of Bragg peaks would indicate the presence of a layer structure and would allow the layer spacings, i.e., the spacings between layers of cadmium ions associated with the hydrophilic head groups, to be estimated. The results are summarized in Table II. Apart from polymer **2a**, which had a lipophilic side chain with only four carbon atoms and as noted above did not transfer well, and polymer **12**, the multilayers clearly showed one to three Bragg peaks. In each case the *d*-spacing was too large to correspond to a single polymer layer, and these results indicate, therefore, not only that regular layer structures were obtained but also that they were Y-type. It is interesting to note that with the half methyl esters **2** those polymers with 13–16 carbon atoms in the lipophilic side chains gave three Bragg peaks, those with 17 and 19 carbon atoms gave two Bragg peaks, while the polymer with a 21-carbon side chain gave only one peak. This supports the conclusion made earlier that in this series there is an optimum length for the lipophilic side chain.

With thickness data available it is now possible to estimate the extent to which the polymers are close packed in the LB films. Thus, for each polymer the volume occupied by the repeat unit (V_{exp}) in the multilayer can

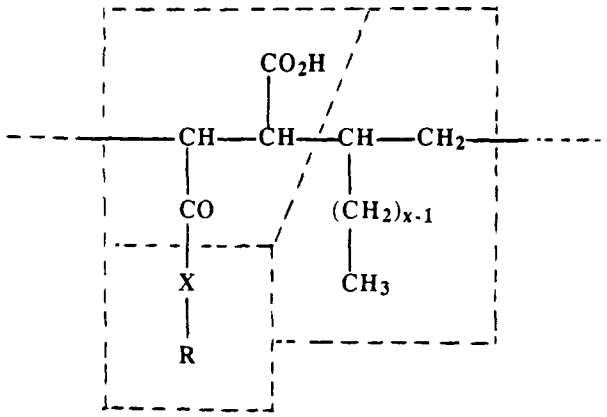


Figure 4. Formal fragmentation of polymer structure for calculation of repeat unit volumes.

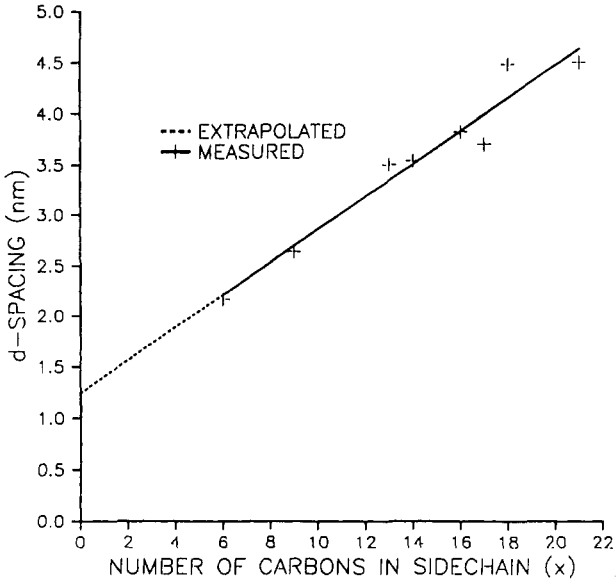


Figure 5. Plot of bilayer spacing versus the length of the lipophilic side chain for LB films of polymers of type **2**.

be calculated from the bilayer spacing and, since the deposition ratios were close to 1.0, from the area occupied per repeat unit on the water surface at the transfer pressure. By formally breaking the polymer down into moieties as shown in Figure 4 and using known densities (solids or liquids) at ambient temperatures for these moieties,[28] it is possible by simple calculation to predict *approximately* the volume (V_{calc}) occupied by a close-packed repeat unit. Comparison of the values allows an estimate of the fraction, F, of the experimental volume that is actually occupied by the polymer. It can be seen from Table II that in most cases the values of F are in the range 1.0–1.2. This indicates that in general the multilayers are tightly packed. Previous work from our laboratory has shown that LB films from other preformed polymers are also closely packed.[19]

For the half methyl ester series it is interesting to compare the bilayer spacings in the LB films with the length of the lipophilic side chains. Figure 5 shows such a plot. The plot is approximately a straight line. This and the fact that all the half methyl esters had a similar cross-sectional area per repeat unit suggest that all these polymers are organized in a similar manner. Extrapolation of the line to the point where x is zero gives an estimate of the thickness occupied by the moiety shown in Figure 6. The value obtained, 13.1 Å, is sufficiently large as to suggest that in the LB films the polymer backbone carbons 1 and 4 are packed above carbons 2 and 3. This type of

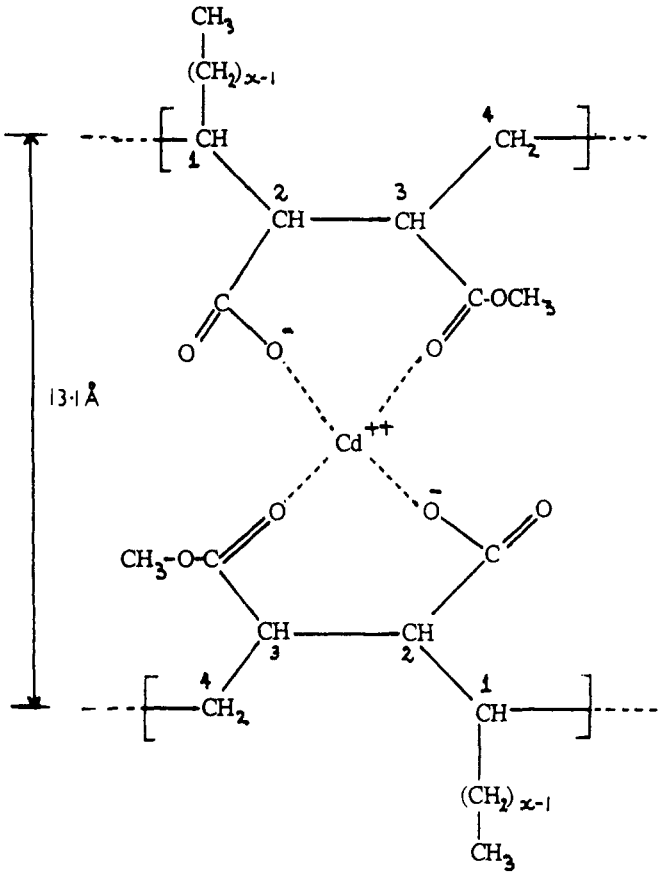


Figure 6. Possible arrangement of the head groups in LB multilayers of polymers **2**.

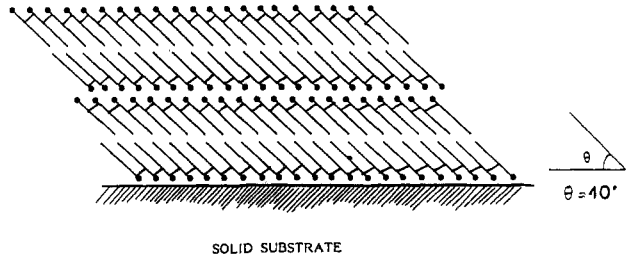


Figure 7. Probable arrangement of lipophilic side chains in LB films of polymer **2**.

arrangement is also consistent with a surface area per repeat unit of approximately 35 Å^2. The slope of the line in Figure 5 indicates that for each extra carbon added to the lipophilic side chain the thickness of the bilayer increases by 1.60 Å. If the lipophilic chains were stacked vertically, the increase would be expected to be 2.51 Å. Clearly the chains are either (a) straight but tilted at an angle of approximately 40°, (b) bent and "liquidlike", (c) interdigitating, or (d) any combination of these possibilities, though it should be noted that the extent of interdigitation cannot exceed about 50% of the chains; otherwise, the surface area per repeat unit would need to be larger than that found experimentally. We have on hand various neutron scattering experiments that should clarify some of these points.[29] The relatively high efficiency of packing favors a, and hence a *likely* arrangement is that shown in Figure 7.

The d-spacings of the derivatives **3**–**8** *suggest* that the multilayers of these polymers are organized similarly to the half methyl esters **2e** and **2h**. The situation with derivatives **9**–**13** is unclear, but they do have a regular layer structure.

Infrared Studies. Evidence on the order in LB films can be obtained from infrared spectroscopy, as demonstrated by, for example, Mumby et al.[12] and Duda et al.[15] The technique is based on the fact that grazing incidence infrared (GI-IR) spectra of films deposited on metal surfaces only show bands when the transition moment of a vibration is perpendicular to the surface, whereas transmission infrared (T-IR) spectra only show bands when the moment is parallel to the surface. The method is most powerful when an all-trans CH_2 chain is oriented perpendicular to the surface or parallel to the surface. In the former case the intensity of the C–H vibrations will be zero by G-IR but not by T-IR. If they are parallel to the surface, the situation is reversed.

The results obtained from solvent-cast films of polymer **2e** and from the GI-IR and T-IR spectra of LB films are summarized in Table III. The only major changes in the intensities of bands in both the GI-IR and T-IR spectra are those due to the carbonyl groups. The changes suggest that the transition moments for these bonds are much closer to being vertical to the plane of the film than to being horizontal. The modest changes for the various bands due to the lipophilic side chains indicate that the chains are neither vertical nor horizontal to the plane of the LB film. The data are consistent with the chains being scrambled and liquidlike or being ordered but tilted at ca. 40°. Thus, while the infrared data do not provide definitive evidence, they are consistent with the structure shown in Figure 7.

Hydrolysis of a Monolayer of Anhydride Polymer 1e. In the earliest work on LB films of preformed polymers, Tredgold and Winter studied commercial anhydride copolymer **1j**.[30] The anhydride residues were believed to be hydrolyzed while the monolayer was on the water surface prior to deposition. It was, therefore, considered of interest to investigate the hydrolysis of a typical anhydride polymer in situ on the surface of the water.

The isotherm of anhydride polymer **1e** is shown in Figure 3a. It is particularly steep, and the surface area per repeat unit (22.2 Å² at 30 mN/m; 28 Å² when the isotherm is extrapolated to zero pressure) is relatively small compared with that of polymer **2e**. This evidence suggests that the anhydride polymer forms particularly close-packed monolayers.

Since the area per repeat unit for polymer **1e** is significantly less than the corresponding diacid **3**, this provides a means for monitoring the hydrolysis of the anhydride on the water surface. The results are summarized in Figure 8, from which it can be seen that at 20 °C and pH 5.3–5.6 hydrolysis is essentially complete in ca. 24 h. At its simplest the hydrolysis would be expected (because the water is present in such large excess) to be pseudo first order in anhydride. However, a first-order plot (not shown) using the data in Figure 8 is a smooth curve. This is not very surprising because there are many reasons why the plot might not be linear, not the least being that the surface area change is not *directly* proportional to the extent of hydrolysis. Accordingly this reaction was not studied further. Nevertheless, it is clear that hydrolysis of anhydride residues occurs and that the reaction is sufficiently slow under the present conditions that it may be possible to prepare LB films with anhydride residues. This possibility and its applications to sensors will be presented in a future publication.

Conclusions

It is clear that the majority of the polymers discussed in this paper give good isotherms and form well-ordered close-packed LB films. Best results were obtained when the lipophilic side chain contained 13–16 carbon atoms and the two head groups were a carboxylic acid plus another small hydrophilic group. The X-ray and IR data for an LB film of polymer **2e** are consistent with an arrangement in which the lipophilic chains are on average tilted at an angle of ca. 40°. The anhydride polymer **1e** was hydrolyzed in situ on the water surface. The rate of the reaction was such that it may be possible to prepare LB films containing anhydride residues. Such studies are on hand.

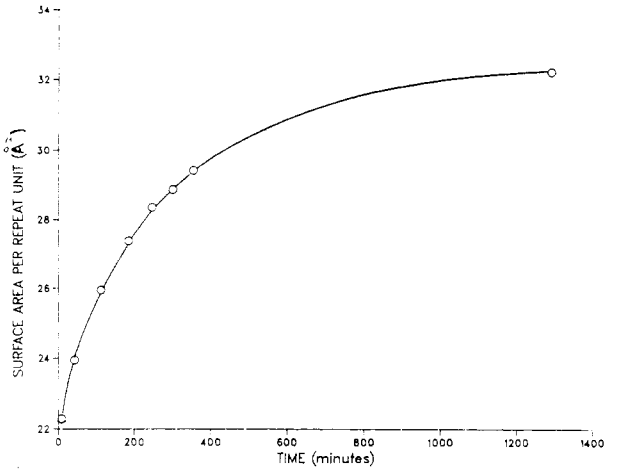


Figure 8. Hydrolysis of a hexadecene–maleic anhydride copolymer (**1e**): variation of area per molecule (at 30 dyn/cm) with time.

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Registry No. **1a** ($x = 4$), 135093-08-2; **1b** ($x = 6$), 108919-59-1; **1c** ($x = 9$), 134969-87-2; **1d** ($x = 13$), 134969-88-3; **1e** ($x = 14$), 115678-68-7; **1h** ($x = 16$), 111306-63-9; **1k** ($x = 17$), 134969-89-4; **1l** ($x = 18$), 134969-90-7; **1m** ($x = 21$), 134969-91-8; bromododecane, 30141-71-0; allylmagnesium chloride, 2622-05-1; pentadec-1-ene, 13360-61-7; nonadec-1-ene, 18435-45-5; tricos-1-ene, 18835-32-0.