Langmuir and Langmuir–Blodgett Films of Poly(vinylpyridine)s Quaternized with Long-Chain Alkyl Halides

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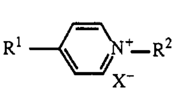
ABSTRACT: A series of poly(*N*-alkyl-4-vinylpyridinium halide)s was prepared by reacting two poly(4-vinylpyridine)s [$\bar{M}_v$ 25 000 and 42 700] with a range of straight-chain alkyl halides. The smallest alkyl halide used was 1-bromooctane; the largest was 1-bromodocosane. The percentage of pyridine moieties quaternized was usually ≥91%, though several polymers were prepared where the percentage was deliberately ca. 50%. Monolayers of the various products on water displayed good isotherms which included significant "solid" regions and collapse pressures ≥26 mN/m. The monolayers could be transferred onto silicon wafers that had been treated to make them hydrophobic. The monolayers of polymers with side chains containing $\leq C_{11}$ transferred well on the upstroke and not at all or only partially on the downstroke, though low-angle X-ray diffraction experiments indicated that the multilayers produced had Y-type structures. Monolayers of polymers with side chains containing $\geq C_{12}$ deposited well on both the upstrokes and downstrokes to give Y-type multilayers in which the side chains were interdigitated. Evidence for the latter was obtained by low-angle X-ray diffraction experiments and FTIR measurements. As judged by X-ray diffraction experiments, the best interdigitated structures were obtained when the side chains contained 18-, 20-, or 22-carbon atoms. Two of these displayed four Bragg peaks and one five. UV irradiation of Langmuir–Blodgett multilayers prepared from the polymer with 10-undecenyl side chains were rendered insoluble as a consequence of cross-linking.

Introduction

Monolayers of amphiphiles ordered at an air–water interface (Langmuir films) are one of the simplest types of organized molecular systems.[1] In favorable cases, the ordered monolayers can be transferred onto solid supports to give Langmuir–Blodgett (LB) films, and it is often possible to assemble thick multilayers in this manner.[1,2] LB films have numerous potential applications,[2,3] but films prepared from nonpolymeric amphiphiles are generally physically fragile, and they have a tendency to molecularly reorganize.[4,5] LB films prepared from polymeric amphiphiles, although less well-organized initially, are generally physically more stable, and they can be expected to be less prone to reorganization. This has prompted numerous studies of Langmuir and LB films of polymers in recent years.[2,6–9]

We now report our studies of Langmuir and LB films of poly(vinylpyridine)s quaternized with long-chain alkyl halides. These studies were initiated because such polymers can be synthesized easily and because two nonpolymeric long-chain alkylpyridinium salts, the *N*-octadecyl- and *N*-docosylpyridinium tetracyanoquinodimethane radical anion salts (1 and 2), have been shown to give LB films in which the lipophilic side chains interdigitate.[10–12] Polymers that form interdigitated LB films are potentially very attractive for several applications on account of their compactness and potentially greater stability, both mechanically and thermally, than most other types of polymeric LB film.



1: $R^1 = H^-$; $R^2 = nC_{18}H_{37}-$; $X^- =$ tetracyanoquinodimethane radical anion
2: $R^1 = H^-$; $R^2 = nC_{22}H_{45}-$; $X^- =$ tetracyanoquinodimethane radical anion
17: $R^1 = C_2H_5-$; $R^2 = nC_{16}H_{33}-$; $X^- = Br^-$
18: $R^1 = C_2H_5-$; $R^2 = nC_{22}H_{45}-$; $X^- = Br^-$

Experimental Section

4-Ethylpyridine, undec-10-en-1-ol, and all the alkyl halides used except 11-bromoundec-1-ene were purchased either from Aldrich Chemical Co. Ltd. or from Fluka Chemie AG. 11-Bromoundec-1-ene was prepared from undec-10-en-1-ol by the method of Chen and Joullie.[13] All solvents were used as purchased. Melting points were determined using a Kofler hot stage apparatus and are uncorrected. Infrared spectra were measured using a Nicolet MX-1 FTIR. ^1H NMR spectra were measured on a Varian Gemini 200-MHz instrument.

Polymer Syntheses. Poly(vinylpyridine)s. Two samples of poly(vinylpyridine) were used. Sample H, with the higher molecular weight, was purchased from Polysciences Ltd. It was sold as having a molecular weight of 50 000. By viscometry using solutions in ethanol at 25 °C, it had $\bar{M}_v$ 42 700. Sample L, with the lower molecular weight, was prepared in-house by polymerization of 4-vinylpyridine in toluene at reflux temperature with AIBN (1.5 mol %) as the initiator. This sample had $\bar{M}_v$ 25 000. There was no evidence to suggest other than that both polymers were essentially atactic.

Poly(vinylpyridinium salt)s. The reaction conditions used to react the above poly(vinylpyridine)s with alkyl halides and the results obtained are summarized in Table 1. The following reaction procedure is typical.

Polymer 6. A solution of poly(vinylpyridine) H (1.00 g, 9.51 mmol) and 1-bromododecane (4.10 g, 16.45 mmol) in methanol (30 mL) was heated under reflux for 74 h. The solution was then cooled and added dropwise to cold ether (200 mL). The precipitate that formed was collected and reprecipitated twice from methanol into cold ether. The final product (6) was dried to constant weight in a vacuum oven at 25 °C and 0.2 mmHg. Yield 2.30 g (74%). Elemental Anal.: N, 3.7%; Br, 22.2%. Calcd for 100% quaternized polymer: N, 4.0%; Br, 22.6%. The infrared spectrum (KBr disk) and the ^1H NMR spectrum of a solution of the product in $CDCl_3$ were both satisfactory.

***N*-Hexadecyl-4-ethylpyridinium Bromide (17).** A solution of 1-bromohexadecane (3.00 g) and 4-ethylpyridine (1.00 g) in tetrahydrofuran (30 mL) was heated under reflux for 8 h. The solution was then cooled to 20 °C. Addition of ether precipitated the desired product as a white solid. It was collected, recrystallization from ethanol, and dried. Yield 1.56 g (40%), mp 44–45 °C. Elemental Anal.: N, 3.1%; Br, 19.6%. Calcd for $C_{23}H_{42}NBr$: N, 3.4%; Br, 19.4%.

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Table 1. Preparation of Poly(vinylpyridinium salt)s

polymer	poly(vinylpyridine) used[a]	alkyl halide used	reaction conditions[b] solvent[c]	reaction conditions[b] time, h	halide anion content,[d] %	DQ[e]
3	H	*n*-$C_8H_{17}Br$	M	77	28.0	1.01
4	H	*n*-$C_{10}H_{21}I$	M	72	33.6	0.95
5	H	$CH_2CH(CH_2)_9Br$	M	84	22.9	0.90
6	H	*n*-$C_{12}H_{25}Br$	M	74	22.2	0.91
7	H	*n*-$C_{14}H_{29}Br$	M	74	20.4	0.91
8	H	*n*-$C_{16}H_{33}Br$	TM1;	92	14.2	0.41
9	H	*n*-$C_{18}H_{37}Br$	TM1	72	18.4	1.03
10	L	*n*-$C_{18}H_{37}Br$	TM2	72	18.5	1.05
11	H	*n*-$C_{20}H_{41}Br$	TD	72	17.2	1.01
12	H	*n*-$C_{20}H_{41}Br$	TM2	72	13.9	0.49
13	H	*n*-$C_{22}H_{45}Br$	TM2	72	16.2	1.00
14	L	*n*-$C_{22}H_{45}Br$	TM2	72	14.8	0.66
15	H	$CF_3(CF_2)_7(CH_2)_2I$	TM1	168	18.5	0.93
16	H	$CF_3(CF_2)_0(CH_2)_2I$	TM1	168	9.7	0.16

[a] Two poly(vinylpyridine)s were used: "H" had $\bar{M}_v$ = 42 700, "L" had $\bar{M}_v$ = 25 000. [b] Reactions were carried out using the general procedure indicated in the Experimental Section. Reactions used the solvent indicated, and the mixture was heated under reflux for the period shown. [c] M = methanol; TM1 = a mixture of THF and methanol (equal volumes); TM2 = a mixture of THF and methanol (ratio of volumes 1:2); TD = a mixture of THF and *N,N*-dimethylformamide (2 volumes to 1 volume). [d] By precision titration of halide anion. [e] DQ = degree of quaternization calculated from halide analysis. Given possible errors in analysis, the DQ quoted is accurate to ±0.07.

***N*-Docosyl-4-ethylpyridinium Bromide (18).** This was prepared in an analogous manner to compound 17. Product 18 (90% yield) had mp 83–84 °C. Elemental Anal.: N, 2.7; Br, 15.7%. Calcd for $C_{29}H_{54}NBr$: N, 2.8%; Br, 16.1%.

Langmuir Isotherms and Film Deposition. Langmuir isotherms were measured for monolayers on water, water containing potassium bromide (2.5 × 10^{-4} M), and/or water containing potassium iodide (2.5 × 10^{-4} M) using the apparatus and general procedures described previously.[9] For polymers 3 and 4, the spreading solvent was chloroform:methanol (9:1). For the other materials, it was pure chloroform. The results are summarized in Table 2. Typical isotherms are shown in Figures 1 and 2.

LB films were deposited onto hydrophobic silicon wafers as described before.[9] Deposition was generally carried out at 30 mN/m and a dipping speed of 8 mm/min. These results are also summarized in Table 2.

X-ray Studies. X-ray studies were carried out as described previously[9] except that with the present materials KBr or KI (and no $CdCl_2$) were sometimes (see Table 2) added to the aqueous subphase. The results are summarized in Table 2 and, in the case of polymer 14, Figure 4.

Infrared Studies of LB Films. Transmission (T-FTIR) and grazing incidence (GI-FTIR) spectra were measured for polymers 11 and 13 using the procedures described previously.[9] In each case, the LB film consisted of 30 layers. For T-FTIR, films were deposited onto chalcogenide glass plates. For G-FTIR, films were deposited onto clean glass microscope slides coated with 20 nm of evaporated gold: a standard Harrick reflection accessory was used.

Cross-Linking Studies. A mask with a regular pattern of circular holes (2 mm in diameter) was prepared from a piece of thin brass. The substrates used were pieces of silicon wafer, with an ca. 100-nm oxide layer, made hydrophobic by treatment with hexamethyldisilazane.[10]

Table 2. Properties of Langmuir Films and Langmuir–Blodgett Films of Various Polymers

		Langmuir film area of repeating unit, Å²			LB film deposition ratio[c]		X-ray data		
polymer	subphase[a]	at 0 mN/m,[b] A_0	at 30 mN/m, A_{30}	collapse pressure π_c, mN/m	downstroke	upstroke	no. of layers in LB film[d]	no. of Bragg peaks	*d* spacing, Å
3	A	40	30.3	26	ca. 0	1.00	62[e]	1	38.4
4	A	42	33.1	45					
	B	41	31.8	40					
	C	42	30.8	36	0.40–1.00	1.00	150	1	39.4
5	A	37	30.6	26	ca. 0	1.00	75[e]	1	41.5
6	A	36	28.6	30	1.00	1.00	68	1	34.3
	B	34	24.6	32					
7	A	41	30.9	33	1.00	1.00	64	1	36.8
	B	35	26.8	38					
8	A	50[f]	41.6[f]	40	1.00	1.00	66	1	39.1
	B	50[f]	40.8[f]	40	1.00	1.00	60	1	40.7
9	A	48	36.4	38	1.00	1.00	150	4	37.1
	B	43	35.2	42	1.00	1.00	150	4	37.1
10	A	40	30.9	42	1.00	1.00	150	3	37.4
	B	42	32.9	42	1.00	1.00	150	3	37.4
11	A	43	35.2	50	1.00	1.00	150	3	40.1
	B	42	35.0	43	1.00	1.00	70	1	42.7
12	A	40[g]	33.3[g]	42	1.00	1.00	50	1	39.8
	B	38[g]	32.4[g]	41	1.00	1.00	150	4	42.8
13	A	46	36.4	42	1.00	1.00			
	B	43	35.2	44	1.00	1.00	150	3	43.3
14	A	44[h]	36.8[h]	47	1.00	1.00	150	5	45.4
	B	43[h]	35.8[h]	47	1.00	1.00	150	4	45.6
	C	43[h]	35.8[h]	40	1.00	1.00	150	4	45.2
18	A	39	23.0[i]	22	0	0			

[a] A = subphase water with no added electrolytes. B = subphase water containing potassium bromide (2.5 × 10^{-4} M). C = subphase water containing potassium iodide (2.5 × 10^{-4} M). [b] By extrapolation of the "solid" section of the isotherm to zero pressure. [c] Values within ±5%. [d] Unless indicated otherwise, the monolayer was transferred onto hydrophobic silicon at a surface pressure of 30 mN/m. See text for discussion of deposition ratios which, in some cases, were very low. [e] At 25 mN/m. [f] Value quoted is the area per *quaternized* unit. With subphase A, the value of A_0 was 21 Å² per repeating unit, and the value of A_{30} was 17.1 Å² per repeating unit. With subphase B, the corresponding values were 21 and 16.9 Å². [g] Value quoted is the area per *quaternized* unit. With subphase A, the value of A_0 was 21 Å² per repeating unit, and the value of A_{30} was 17.0 Å² per repeating unit. With subphase B, the corresponding values were 19 and 16.0 Å². [h] Value quoted is the area per *quaternized* unit. With subphase A, the value of A_0 was 32 Å² per repeating unit, and the value of A_{30} was 24.4 Å² per repeating unit. With subphase B, the corresponding values were 31 and 23.1 Å². With subphase C, the corresponding values were 31 and 23.1 Å². [i] At 20 mN/m.

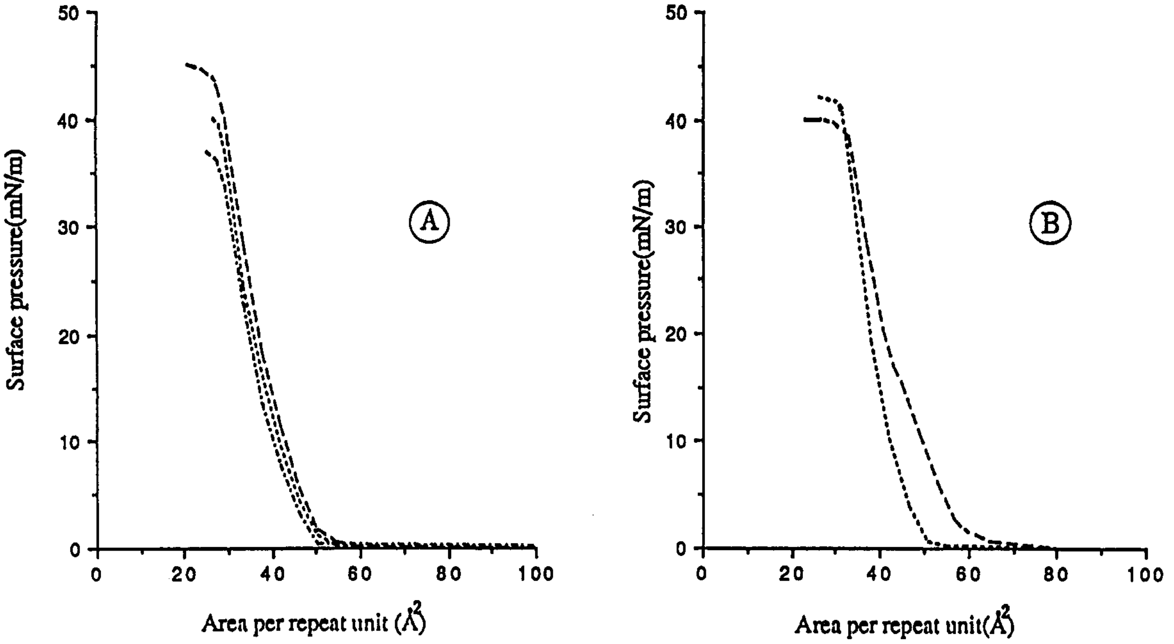


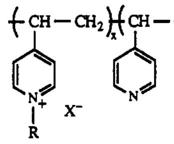
Figure 1. Typical isotherms. All isotherms were measured at 20 °C and pH 5.3–5.6. (A) For polymer **4**: on an aqueous subphase with no added salts (– –), with added potassium bromide (---), and with added potassium iodide (- • • -). (B) For polymer **9**: on an aqueous subphase with no added salts (– –) and with added potassium bromide (---). For further details, see the Experimental Section.

An LB film (20 layers) of the polymer under investigation was deposited oto the substrate. The dried film was covered with the mask and exposed for 5 min to the UV irradiation from a Spectroline Model R-51/F lamp held 30 cm from the film. The mask was then removed and the film carefully washed with chloroform for 1–2 min. With polymer **6**, all the film was washed away. With polymer **5**, the unexposed parts of the film were washed away, but the exposed parts were insoluble. The presence of the oxide layer on the substrate aided contrast between the LB film and the substrate.

Results and Discussion

Polymer Syntheses. Two poly(vinylpyridine)s were used. The one used more extensively, sample H, was a commercial sample which, by viscometry using solutions in ethanol, had $\bar{M}_v$ 42 700. The second sample, sample L, was prepared by a free-radical-initiated polymerization of 4-vinylpyridine. It had $\bar{M}_v$ 25 000.

These two polymers were quaternized by reaction with various alkyl bromides or iodides to give polymers **3–16**. Most quaternizations were carried out by treating the poly(vinylpyridine) with an excess of the alkyl halide in methanol or mixtures of THF and methanol at reflux temperatures for several days. The polymers and alkyl halides used and the results obtained are summarized in Table 1. The degrees of quaternization (DQs) obtained were determined by halide analyses. The DQs were usually >0.91. The difficulties of achieving quantitative quaternizations have been discussed numerous times before, most recently by Gramain's group.[15] Polymers **8**, **12**, and **14** were deliberately prepared with lower DQs by using a deficiency of the alkyl halide. Polymer **16** had a very poor solubility and the DQ obtained, even after carrying out the quaternization reaction for a week, was only 0.16. All the polymeric products had satisfactory infrared and ^{1}H NMR spectra.



3	R = nC$_8$H$_{17}$;	X$^-$ = Br$^-$
4	R = nC$_{10}$H$_{21}$;	X$^-$ = I$^-$
5	R = CH$_2$=CH(CH$_2$)$_9$;	X$^-$ = Br$^-$
6	R = nC$_{12}$H$_{25}$;	X$^-$ = Br$^-$
7	R = nC$_{14}$H$_{29}$;	X$^-$ = Br$^-$
8	R = nC$_{16}$H$_{33}$;	X$^-$ = Br$^-$
9 and 10	R = nC$_{18}$H$_{37}$;	X$^-$ = Br$^-$
11 and 12	R = nC$_{20}$H$_{41}$;	X$^-$ = Br$^-$
13 and 14	R = nC$_{22}$H$_{45}$;	X$^-$ = Br$^-$
15	R = CF$_3$(CF$_2$)$_7$(CH$_2$)$_2$;	X$^-$ = I$^-$
16	R = CF$_3$(CF$_2$)$_9$(CH$_2$)$_2$;	X$^-$ = I$^-$

Details of the molecular weights of the polyvinylpyridines used to prepare these polymers and the DQs obtained are summarised in Table I.

Langmuir Films of Polymers 3–14. Initially monolayers of polymers **3–14** were prepared (by using solutions of the polymers either in chloroform–methanol or in chloroform alone) on a subphase of water at pH 5.3–5.6 and 20 °C, and their isotherms were measured. In each case, the monolayer was successively compressed (without ever exceeding the collapse pressure of the monolayer) and then relaxed through several cycles until reproducible isotherms were obtained. Usually two or three cycles were sufficient.

Polymers **3–14** are cationic polyelectrolytes, and it was considered that bicarbonate anions, present in the subphase due to dissolved aerial carbon dioxide, might exchange with the halide anions in the monolayer. Accordingly, isotherms were also measured for most polymers over aqueous subphases containing potassium bromide or potassium iodide (2.5 × 10^{-4} M). Under these conditions, the concentration of halide anions in the subphase would be overwhelmingly greater than the concentration of bicarbonate anions. The halide anions would be able to ion exchange with those in the monolayer. The isotherms determined under these conditions were also found to be reproducible after just two or three compression–relaxation cycles.

Polymers **3–14** all gave good isotherms under the various conditions used; i.e., all the isotherms showed substantial "solid" regions and collapse pressures, π_c, greater than 26

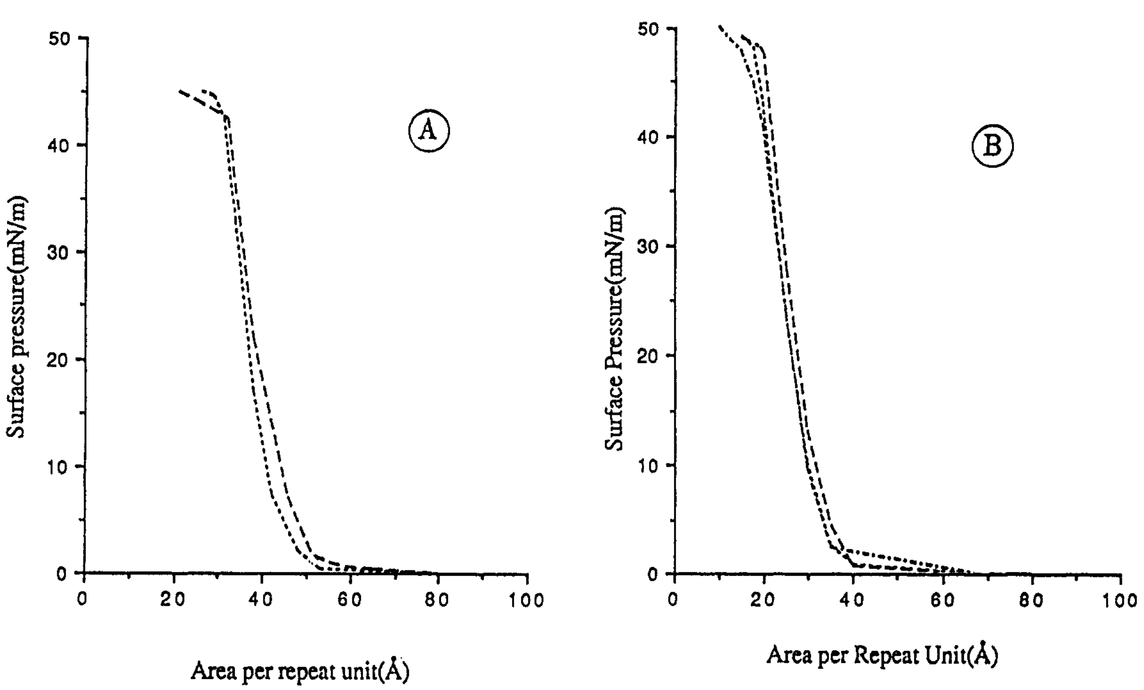


Figure 2. Typical isotherms. All isotherms were measured at 20 °C and pH 5.3–5.6. (A) For polymer **13**: on an apparent subphase with no added salts (– –) and with added potassium bromide (---). (B) For polymer **14**: on an aqueous subphase with no added salts (– –), and with added potassium bromide (---), and with added potassium iodide (– • • –). For further details, see the Experimental Section.

mN/m. Some typical isotherms are shown in Figures 1 and 2. The main features are summarized in Table 2. The following points are apparent from a comparison of the various isotherms.

(i) For a given polymer, the nature of the aqueous subphase used generally makes little or no difference to the shape and position of the isotherm. However, at any given pressure, the areas observed when potassium bromide or iodide had been able to the subphase were, if anything, very slightly smaller (typically ca. 2 Å^2) than when no addition had been made. The reasons for these small differences are not clear. We are currently carrying out X-ray and neutron-scattering studies of some of the monolayers over subphases containing different halides or other anions.

(ii) For polymers **3–7**, **9–11**, and **13**, i.e., those with DQs greater than 0.90, the length of the hydrocarbon chain in the polymer generally made only a modest difference to the areas per repeating unit measured at surface pressures of 30 mN/m, A_{30}, or those obtained by extrapolating the "solid" section of the isotherms to zero pressure, A_0. These areas were usually in the range 30–37 and 40–50 Å^2, respectively. Given that the cross-sectional area of the pyridinium moiety is ca. 28 Å^2 and that halide anions, which may well be hydrated, and the polymer backbone are present, these values are not surprising.

(iii) For polymer **8**, **12**, and **14**, which had DQs of 0.41, 0.49, and 0.66, respectively, the areas per repeating unit were found to be substantially less than for the polymers discussed in ii above. Figure 2B shows a typical isotherm. However, in each case, the areas per *quaternized moiety* are essentially the same as the areas per repeating unit found for the polymers discussed in ii. This indicates that with each of the present polymers the unquaternized pyridine moieties contribute little or nothing to the surface area of the monolayer and suggests that these moieties are above or below other parts of the polymer at the water surface.

(iv) As the length of the side chains increases, the collapse pressures, π_c, tend to increase, and for side chains containing 16 or more carbon atoms, π_c is always greater than 38 mN/m.

(v) Although only two pairs of polymers were studied, polymers **9** and **10** and polymers **13** and **14**, which allow the effect of polymer molecular weight to be assessed, the results suggest that in the range of molecular weights studied the magnitude of the molecular weight makes very little difference to the isotherm.

Studies of Amphiphiles 15–18. Polymers **15** and **16** were of interest because they contain fluorocarbon side chains. Such chains are neither hydrophilic nor *simply* lipophilic. Unfortunately, neither polymer could be dissolved in a reasonably volatile water-immiscible solvent suitable for use as a spreading solvent.

Compound **17** did not give a stable monolayer and appeared to dissolve on compression. Compound **18** gave a stable monolayer, but the isotherm was less steep and the collapse pressure lower than that of the corresponding polymer **9**: see Figure 3. It is not unusual to find that nonpolymeric models of polymers have inferior monolayer properties to the polymers themselves.[16] All attempts to deposit monolayers of compound **18** onto silicon wafers that had been treated to make them hydrophobic[14] were unsuccessful.

Langmuir–Blodgett Films of Polymers 3–14. All the polymers that formed stable monolayers on water and/or on aqueous potassium bromide or iodide could be transferred at surface pressures of 25 mN/m (polymers **3** and **5**) or 30 mN/m (polymers **4** and **6–14**) onto silicon wafers that had been treated to make them hydrophobic.[14]

Although polymers **3–5** deposited well on the "upstroke" (deposition ratios 1.00 ± 0.05), deposition was variable on the "downstroke". Indeed, polymers **3** and **5** deposited essentially Z-type. Sufficiently thick multilayers were deposited (62–150 layers) to allow low-angle X-ray diffraction experiments to be carried out. All the multilayers displayed just one Bragg peak and thus were not highly ordered. Space-filling molecular models of polymers **3–5** indicate that the *maximum* distances from the backbone to the ends of the side chains range from 18 Å for polymer

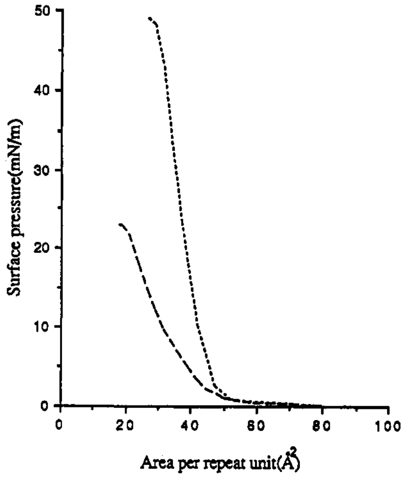


Figure 3. Comparison of isotherms of polymer 13 (---) and compound 18 (– –) on an aqueous subphase at 20 °C and pH 5.3–5.6 with added potassium bromide.

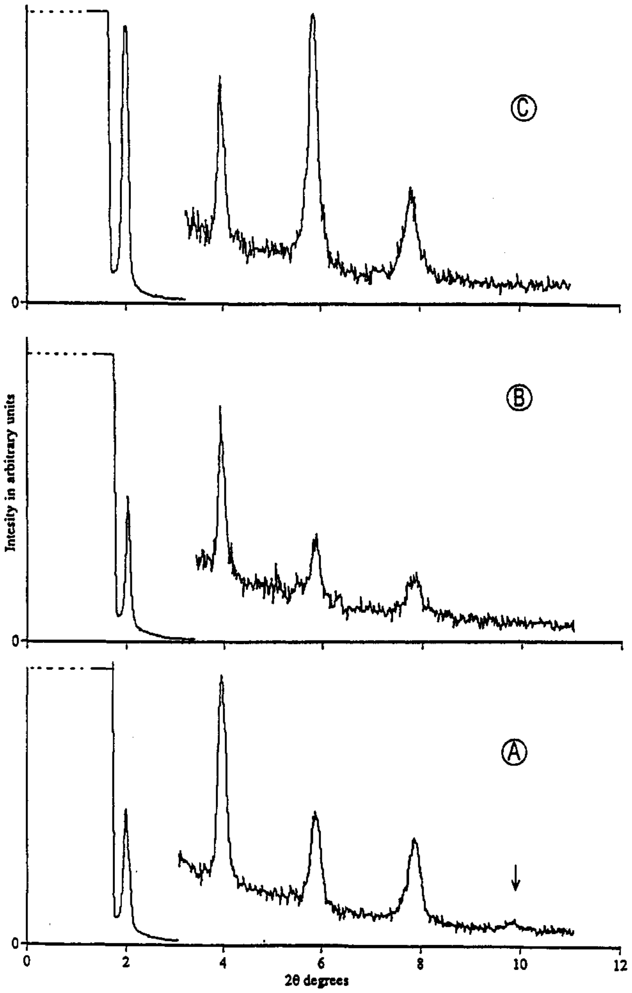


Figure 4. Low-angle X-ray diffraction results for polymer 14: (A) deposited from an aqueous subphase with no added salts, (B) with added potassium bromide, and (C) with added potassium iodide. Sensitivity was changed in each case by a factor of 25 near $2\theta = 3°$.

3 to 22 Å for polymer 5. In all cases, these values are approximately half the found *d* spacings. This suggests that on and/or after deposition the polymers rearrange to Y-type structures. It is well-known that nonpolymerc X- and Z-type systems can rearrange for Y-type systems, and we have observed the same phenomenon with several polymers.[17]

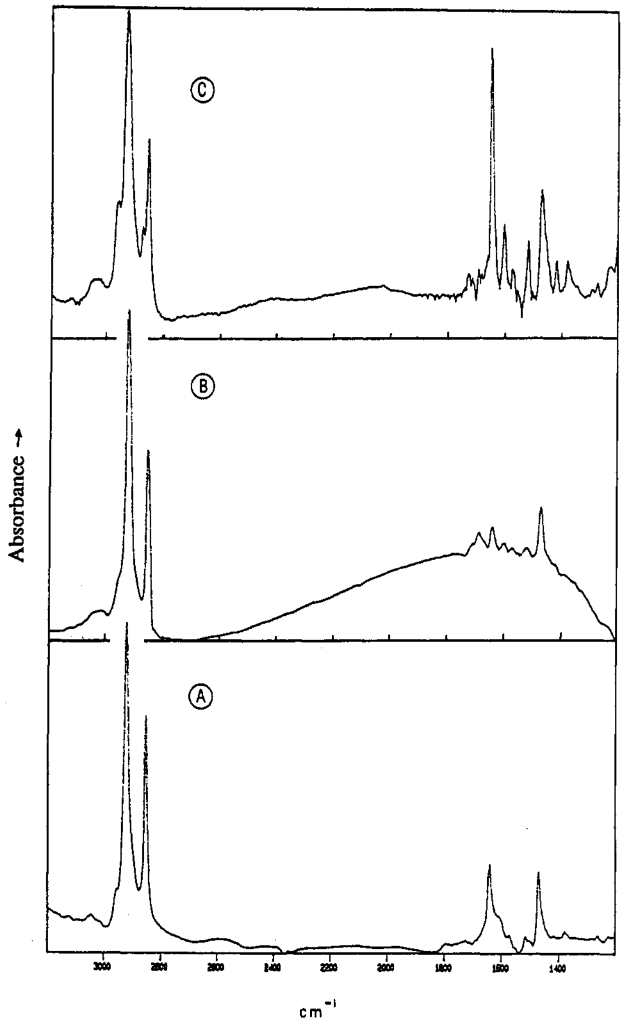


Figure 5. FTIR spectra for polymer 13. (A) Transmission spectrum for a film cast from a solution in chloroform. (B) Transmission spectrum for a 30-layer LB film. (C) Grazing incidence spectrum for a 30-layer LB film.

Polymers 6–14 deposited well to give Y-type films (deposition ratios 1.00 ± 0.05). Sufficiently thick films were deposited (60–150 layers) for low-angle X-ray diffraction studies. All the films displayed Bragg peaks, but the best films were those prepared from polymers 9–14, i.e., those with the C_{18}, C_{20}, and C_{22} side chains. The best of these displayed five Bragg peaks: see Figure 4. As far as we are aware, this is the highest number ever reported for an LB film of a preformed polymer. It should be noted that where *d* spacings were measured for multilayers prepared from monolayers over different aqueous subphases, the *d*-spacings were essentially the same. This implies that the organization of the multilayers is essentially the same whether the counterions are bicarbonate, bromide, or iodide.

A particularly interesting feature of these Y-type films is that they have surprisingly small *d* spacings. Space-filling molecular models of Y-type films with the side chains vertical (and ignoring the counterions) predict bilayer thicknesses ranging from 47 Å for polymer 6 (C_{12} side chains) to 75 Å for polymers 13 and 14 (C_{22} side chains). In practice, they ranged from 34.3 Å for polymer 6 to 43.3 and 45.4 Å for polymers 13 and 14, respectively. The substantial differences can be rationalized by (i) the side chains having a large tilt from the verticle or (ii) the side chains interdigitating and tilting only slightly if at all. An FTIR study of LB films of polymers 11 and 13 involving a comparison of transmission (T-FTIR) and of grazing incidence (GI-FTIR) spectra (see Figure 5 for the spectra of polymer 13) indicated that the side chains were in fact close to being vertical.[9,18] Thus, in the T-FTIR spectra,

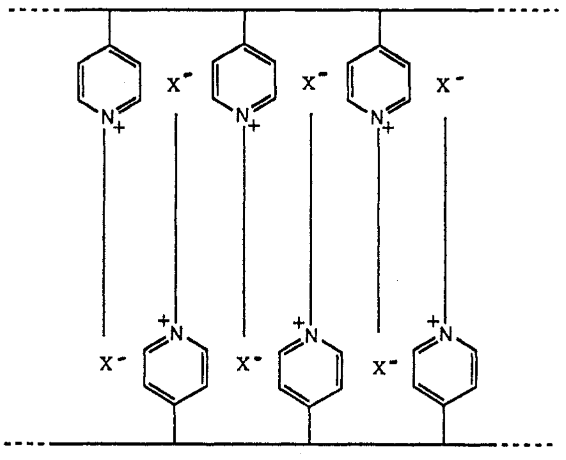
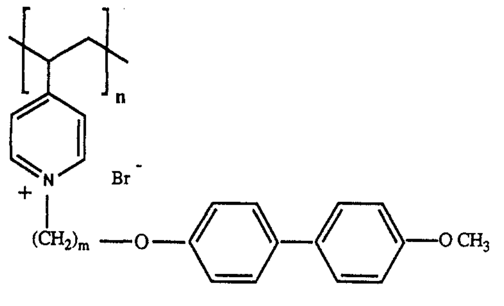


Figure 6. Scheme showing general packing arrangement of various long-chain poly(vinylpyridinium salt)s.

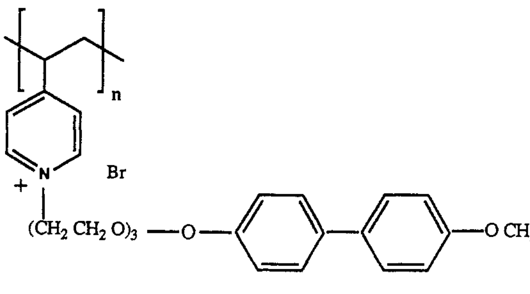
the stretching vibration bands due to the C–H of the methylene groups were relatively strong, whereas in the GI-FTIR spectra they were extremely weak. Although it is difficult to quantify these results because the spectra contain so few sharp bands other than those due to the hydrocarbon chains, it is nevertheless clear that the films must have interdigitated side chains. Assuming the side chains were straight and vertical space-filling molecular models of interdigitated structures of polymers **9** and **13**, for example, predict bilayer thicknesses of 39 and 45 Å, respectively, the values were very close to the observed values (see Table 2). Finally, on this topic, it should be noted that the interdigitated structures require monolayers in which the area per repeating unit is at least equal to twice the cross-sectional area of a hydrocarbon side chain, i.e., $>(2 \times 20)$ Å^2 = >40 Å^2. As indicated earlier, the monolayers of all these polymers have an area per repeating unit, A_0, in the range 40–50 Å^2.

While the present work was in hand, Gramain's group reported that polymers **19–21** form liquid-crystal phases.[19] Analogy with closely related nonpolymeric liquid-crystalline salts, which were studied carefully using X-ray methods by Skoulios's group,[20] suggests that the mesophases have the general type of structure shown in an idealized form in Figure 6. The polymer side chains are interdigitated and the counterions lie between neighboring pyridinium moieties. It is evident that the LB films of the polymers **6–14** discussed in the present paper have similar structures to Gramain's liquid-crystal polymers.



(19) m = 8

(20) m = 12



(21)

Cross-Linking of Langmuir–Blodgett Films

Polymer **5** was studied because it contains a olefinic group. It is known that such groups in ω-tricosenoic acid undero *polymerization* when irradiated by an electron beam,[21] and we have shown in several cases that polymers containing such groups can be *cross-linked* by electron beam irradiation[14] or by UV irradiation.[22] It should be noted that successful polymerization requires a very efficient reaction (usually >99%), whereas cross-linking can be carried out successfully with relatively inefficient reactions, cross-linking of the order of a few percent often being adequate to render a polymer insoluble. Since polymer **5** gives a Y-type LB film, all the vinyl groups will be in proximity at the lipophilic–lipophilic interface. UV irradiation of an LB film of polymer **5** caused it to become insoluble rapidly, and simple patterns could be prepared using a metallic mask. We believe the insolubility to be due to cross-linking, and in support of this, it was shown that polymer **6** did not become insoluble on UV irradiation.

Conclusions

It is evident that of the polymers described in this paper, polymers **6–14**, give the best LB films. Indeed, some of these polymers give some of the best LB films prepared to date from preformed polymers. The LB films have a similar interdigitated structure to the LB films prepared from the related nonpolymeric pyridinium salts **1** and **2**,[10–12] to the liquid-crystal polymers **19–21**,[19] and to their liquid-crystalline nonpolymeric analogues.[20] It is probable that the anions in the LB films of polymers **6–14** sit between the pyridinium moieties.

Polymeric LB films of the general type prepared from polymers **6–14** can be expected to find application in LB film devices on account of their excellent order, compactness, expected stability to reorganization, and ease of synthesis. We are currently carrying out work which exploits some of these features and also X-ray and neutron-scattering studies of the polymers at the water surface.

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