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Langmuir–Blodgett films of poly(*N*-vinyl-*N*′-alkylimidazolium bromide)s

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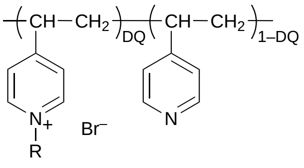
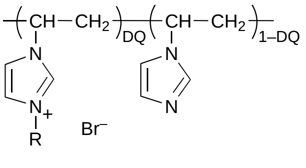
Langmuir–Blodgett (LB) multilayers were prepared from poly(*N*-vinyl-*N*′-alkylimidazolium bromide)s synthesised using long-chain alkyl bromides. In X-ray reflection experiments the best multilayers displayed five orders of Bragg peaks. The derived bilayer spacings and an FTIR study of selected films indicate that these LB multilayers have Y-type structures in which the long alkyl side chains interdigitate.

Introduction

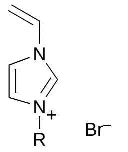
Langmuir–Blodgett (LB) films, being ordered at the molecular level, have numerous potential applications in sensors and in micro- and opto-electronics.[1–4] However, films prepared from non-polymeric amphiphiles are in general physically fragile and prone to molecular reorganisation.[5–7] LB films prepared from amphiphilic polymers, although less well organised initially, are generally physically more stable and can be expected to be less prone to reorganisation. This has prompted numerous studies in recent years of monolayers of polymers at the air–water interface and of the derived LB multilayers.[8–14] On the basis of X-ray reflection experiments some of the best organised LB multilayers prepared from preformed polymers are those prepared from poly(vinylpyridine)s quaternised to a high degree with long chain alkyl bromides, for example, polymer **1**.[12] These show up to five orders of Bragg reflections. LB multilayers of these polymers have a Y-type structure in which the long alkyl side chains interdigitate.[12] This is shown schematically in Fig. 1. We have now studied LB films of poly(*N*-vinyl-*N*′-alkylimidazolium bromide)s prepared using long-chain alkyl bromides and report the results here. We find that the films of certain of these polymers also have a structure of the type indicated in Fig. 1. Thus, they are a further family of readily available polymers which form relatively well-ordered LB films. Polymeric LB films of this general type can, therefore, be expected to be some of the best for use in LB film devices.



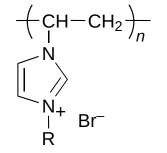
1 R = n-$C_{22}H_{45}$, DQ = 0.66
10 R = n-$C_{18}H_{37}$, DQ = 1.00



2 R = n-$C_{16}H_{33}$, DQ = 0.28
3 R = n-$C_{22}H_{45}$, DQ = 0.18



4 R = n-$C_{16}H_{33}$
5 R = n-$C_{18}H_{37}$
6 R = n-$C_{22}H_{45}$



7 R = n-$C_{16}H_{33}$
8 R = n-$C_{18}H_{37}$
9 R = n-$C_{22}H_{45}$

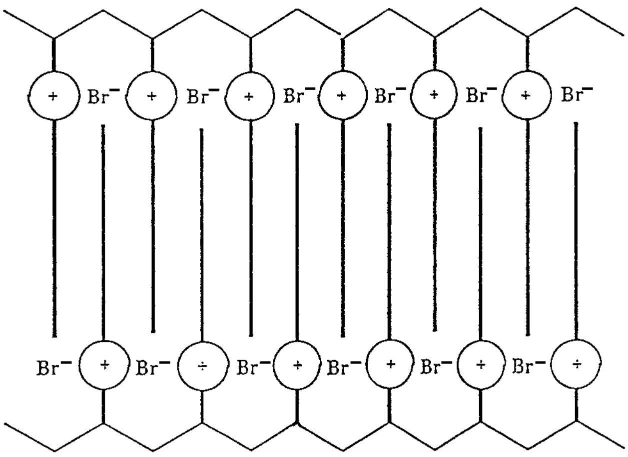


Fig. 1 General packing arrangement of certain long-chain poly(vinylpyridinium salt)s and poly(*N*-vinyl-*N*′-imidazolium bromide)s

Experimental

Melting points were determined using an electrothermal melting point apparatus. Samples were dried to constant mass in a vacuum oven (1 mmHg) at 25 °C. Elemental analyses were obtained using a Carlo-Erba CHNS-O EA instrument. Viscometry was carried out using a Schott-Gerate CT150 semi-automated viscometer.

Polymerisation of *N*-vinylimidazole

A mixture of *N*-vinylimidazole (31.1 g, 330 mmol, freshly distilled) and azoisobutyronitrile (AIBN) (542 mg, 3.3 mmol) in absolute ethanol (70 ml) was degassed and then heated at 70 °C for 5 h.[15] The solution was cooled and slowly added to ice-cold diethyl ether (500 ml). The precipitate that formed was collected and reprecipitated twice from ethanol into diethyl ether. The product was dried to constant mass (16.2 g, 52%).

The molecular masses were estimated by viscometry, using solutions in 5 M aqueous sodium chloride, to be $\bar{M}_n$ 27 900 and $\bar{M}_w$ 38 300. The relevant Mark–Houwink equations are given by Bamford and Schofield.[15]

Quaternisations of poly(*N*-vinylimidazole)

Using 1-bromohexadecane. A solution of poly(*N*-vinylimidazole) (1.00 g, 10.62 mmol) and 1-bromohexadecane (5.52 ml, 18.05 mmol) in methanol (30 ml) was heated under reflux for 96 h. The mixture was then cooled and added dropwise into hexane (200 ml). The precipitate was collected, washed twice with hexane and dried. This gave polymer **2** (1.78 g) (Found:

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N, 8.9; Br, 20.55%). The gain in mass corresponds to a degree of quaternisation (DQ) of at least 0.24. The elemental analysis corresponds to a DQ of 0.28.

Using 1-bromodocosane. Poly(*N*-vinylimidazole) (1.00 g) was treated with 1-bromodocosane and the product isolated using the procedure described in the previous paragraph. This gave polymer **3** (1.65 g) (Found: N, 10.2; Br, 10.25%). The gain in mass corresponds to a DQ of at least 0.16. The elemental analysis corresponds to a DQ of 0.18.

Quaternisations of *N*-vinylimidazole

Using 1-bromohexadecane. A solution of *N*-vinylimidazole (5.50 g, 58 mmol) and 1-bromohexadecane (15.0 g, 49 mmol) in chloroform (150 ml) was heated under reflux for 3 d. The product was then isolated by precipitation into ethyl acetate (1 l). This gave, after drying, the imidazolium salt **4** (16.4 g, 84%). It had mp *ca.* 180 °C (decom.) (Found: C, 63.3; H, 9.9; Br, 19.6; N, 7.0%. $C_{21}H_{39}BrN_2$ requires C, 63.3; H, 9.9; Br, 19.8; and N 7.0%).

Using 1-bromo-octadecane. Reaction of *N*-vinylimidazole with 1-bromo-octadecane using the above procedure gave imidazolium salt **5** (77%), mp *ca.* 180 °C (decomp.) (Found: C, 64.8; H, 10.5; Br, 18.8; N, 6.3%. $C_{23}H_{43}Br\ N_2$ requires C, 64.75; H, 10.2; Br, 18.5; N, 6.6%).

Using 1-bromodocosane. Reaction of *N*-vinylimidazole with 1-bromodocosane using the above procedure gave imidazolium salt **6** (88%). It had mp *ca.* 180 °C (decomp.) (Found: C, 67.1; H, 10.3; Br, 16.5; N, 5.5%. $C_{27}H_{51}BrN_2$ requires C, 67.2; H, 10.7; Br, 16.4; N, 5.8%).

Polymerisation of imidazolium salts

The following procedure is typical.

A solution of imidazolium salt **4** (5.00 g) and AIBN (50 mg) in chlorobenzene (20 ml) was degassed and then heated at 80 °C for 24 h. The cooled solution was slowly added to methanol (250 ml). The precipitate which formed was collected and reprecipitated from chloroform into methanol. After drying polymer **7** (3.70 g, 74%) was obtained as a white powder. By viscometry, using 0.1% solutions in 1,1,2,2-tetrachloroethane at 25 °C, the inherent viscosity, $[\eta]$, was 1.48 dl g^{-1}.

Similar polymerisations of imidazolium salts **5** and **6** gave polymers **8** and **9** respectively. These had, respectively, $[\eta]$ 0.84 and 0.55 dl g^{-1}.

Preparation and measurement of film properties

The Langmuir trough used was a NIMA Alternate Layer Type 622. The general procedures for the measurement of isotherms and for the preparation of LB multilayers have been described before.[10] In the present work the amphiphiles were spread from solutions in chloroform. The subphase was doubly-distilled deionised water with no added salts, pH 5.2–5.6, at 20 °C. The LB films were deposited at a surface pressure of 30 mN m^{-1} and a speed of 12 mm min^{-1} onto either silanized silicon wafers, Pyrex microscope slides or Pyrex microscope slides coated with 22 nm of evaporated gold. Deposition ratios were as indicated in Table 1. The alternating LB films were prepared by depositing polymer **8** on the upstroke and polymer **10**[12] on the downstroke. X-Ray reflectivity experiments[10] and FTIR experiments[10,12] were carried out as described before.

Results and Discussion

Polymer synthesis

Polymers were synthesised using two methods. In the first method, *N*-vinylimidazole in ethanol was polymerised using AIBN as a free radical initiator,[15] then the product was quaternised by treatment separately with 1-bromohexadecane and with 1-bromodocosane in methanol at 56 °C for 96 h. This procedure worked well[12] for the preparation of quaternised poly(4-vinylpyridine)s but, as judged by the elemental analyses, the present products, polymers **2** and **3** respectively, had degrees of quaternisation (DQ) of only 0.28 and 0.18. This prompted the use of the second synthetic method which produced fully quaternised polymers. In this method *N*-vinylimidazole was first quaternised separately with 1-bromohexadecane, 1-bromooctadecane and 1-bromodocosane to give respectively monomers **4–6**. These monomers in chlorobenzene solutions were then separately polymerised using AIBN as the initiator. The products, polymers **7–9**, had inherent viscosities, $[\eta]$, of 1.48, 0.84 and 0.55 respectively, consistent with them having substantial molecular masses.

Properties of monomers 4–6 and polymers 2, 3 and 7–9 at the air–water interface

Monolayers of the various amphiphiles at the air–water interface were prepared using solutions in chloroform. The subphase was water at 20 °C, pH 5.3–5.6, with no added salts. The monolayers prepared using polymers **2** and **3** were unable to sustain any significant surface pressure, even for a few minutes. This was attributed to the relatively low DQs. Thus, at pH 5.3–5.6 most of the unalkylated imidazole residues will be protonated (the pK_a of protonated *N*-methylimidazole is 7.4[16]). Electrostatic interactions between neighbouring residues will, however, probably prevent all such residues being protonated. The net effect is that monolayers of these lightly alkylated polymers will likely be too hydrophilic to remain at the air–water interface. Accordingly no further experiments were carried out with these polymers. However, monolayers of all the other amphiphiles sustained significant surface pressures and 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. Two or three cycles was generally sufficient.

The final isotherms of monomers **4–6** are shown in Fig. 2 and of polymers **5–7** in Fig. 3. It is evident that, as observed in other series,[12,17,18] the polymers give much better isotherms than the monomers. This is probably mainly because a water-insoluble amphiphilic polymer molecule is held at the air–water interface by numerous favourable head group–water interactions, many of which would be lost simultaneously if a major segment of the molecule left the interface. With a simple non-polymeric amphiphile there is only one such interaction. The isotherms of the monolayers of the monomers are either less steep and/or have areas per repeat unit much smaller than expected for well-ordered monolayers of these amphiphiles (*ca.* 30–40 Å^2). The isotherms of the polymers were good, *i.e.* they were steep, had collapse pressures in excess of 55 mN m^{-1}, and had areas per repeat unit at 30 mN m^{-1}, A_{30}, and, by extrapolation of the steepest part of the isotherm, at zero pressure, A_0, in the expected region: see Table 1 for the actual values.

Langmuir–Blodgett films

Attempts were made to deposit the monolayers of monomers **4–6** and polymers **7–9**, at surface pressures of 30 mN m^{-1}, onto silicon wafers that had been treated[19] to render them hydrophobic. No success was achieved, even at dipping rates as low as 2 mm min^{-1} with any of the monomers nor with polymer **9**. The latter gave a relatively rigid monolayer, possibly due to strong interactions between the *n*-docosyl side chains, and this would be expected to make transfer difficult. Polymers **7** and **8** transferred well (deposition ratios 1.00 ± 0.05), however,

Table 1 Properties of monolayers and Langmuir–Blodgett films of various polymers

polymer	monolayer properties area per repeat unit/Å^2 at 0 mN m^{-1}, A_0[a]	at 30 mN m^{-1}, A_{30}	monolayer collapse pressure π_c, mN m^{-1}	LB film deposition ratio[b] upstroke	downstroke	X-ray data[c] no. of layers in LB film	no. of Bragg peaks	d-spacing /Å
7	39	35.1	57	1.00	1.00	60	5	34.5±0.5
8	37	34.1	57	1.00	1.00	60	5	36.5±0.5
9	34	30.0	54	—	—	—	—	—
10[d]	50	43.2	42	1.00	1.00	150	3	37.4±0.5
8[e] and **10**[f]	—	—	—	1.00	1.00	50	2	39.4±0.7

[a]By extrapolation of the 'solid' section of the isotherm to zero pressure. [b]Monolayer transferred onto hydrophobic silicon wafer at a surface pressure of 30 mN m^{-1}. [c]For multilayers deposited on Pyrex glass microscope slides. [d]This polymer was first described in ref. 12. Data presented are from the present work. [e]Deposited on upstroke. [f]Deposited on downstroke.

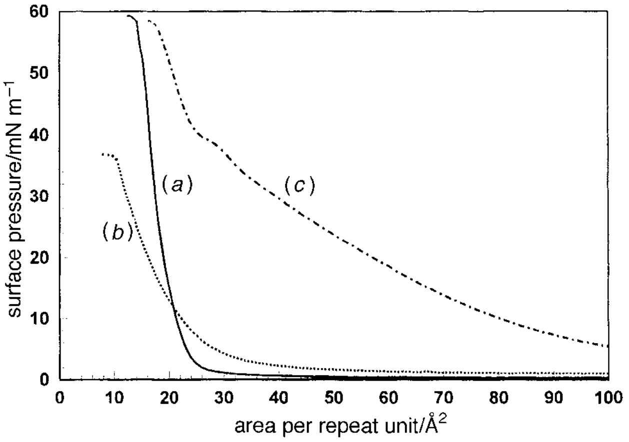

Fig. 2 Isotherms of monomers (*a*) **4**, (*b*) **5** and (*c*) **6** measured at 20 °C and pH 5.2–5.6. See Experimental section for further details.

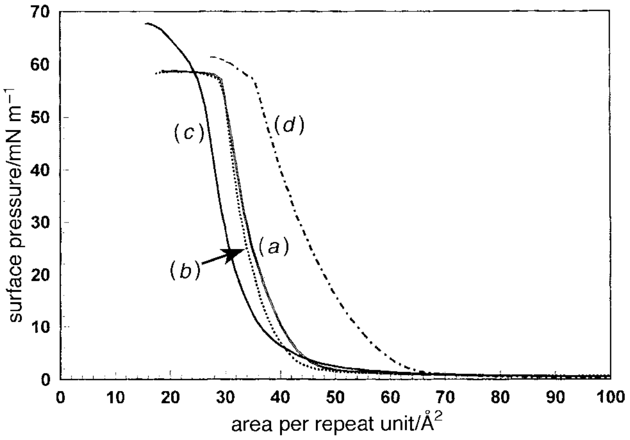

Fig. 3 Isotherms of polymers (*a*) **7**, (*b*) **8**, (*c*) **9** and (*d*) **10** measured at 20 °C and pH 5.2–5.6. See Experimental section for further details.

on both the upstrokes and downstrokes to give Y-type structures.

Sufficiently thick layers (60 layers) of polymers **7** and **8** were deposited onto Pyrex microscope slides for X-ray reflection experiments. The multilayer prepared from polymer **7** displayed five orders of Bragg peaks corresponding to a d-spacing of 34.5±0.5 Å, whilst that prepared from polymer **8** displayed five peaks corresponding to a d-spacing of 36.5±0.5 Å. The X-ray reflection results obtained with polymer **7** are shown in Fig. 4. Inspection of space-filling molecular models of Y-type films of the polymers with the side chains vertical (and ignoring the counter ions) predict bilayer thicknesses of 57 Å for polymer **7** and 63 Å for polymer **8**. Since the actual values are very much less than these values, the result indicated that either (*i*) the side chains tilt *ca.* 60° from the vertical, or (*ii*) the side chains interdigitate and tilt only slightly if at all. An

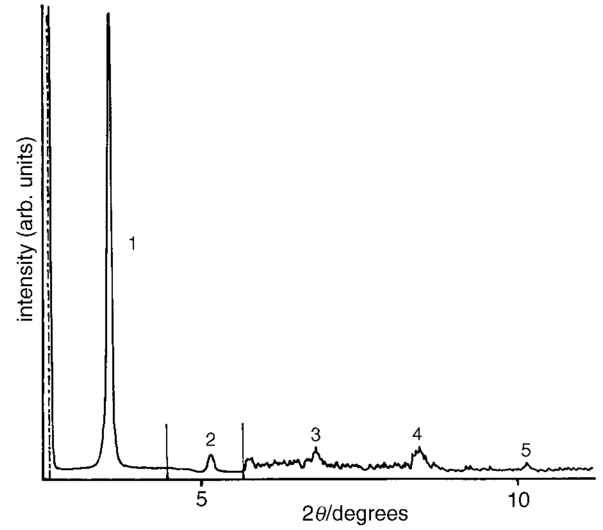

Fig. 4 Low-angle X-ray diffraction results for polymer **7**. The sensitivity was changed by a factor of 10 near $2\theta = 4.5°$ and by 50 near $2\theta = 5.6°$.

FTIR study was made of the films of polymer **7**.[10,12,20,21] This involved the comparison of a transmission spectrum of a cast film on silicon wafer, in which it is assumed the polymer chains are randomly oriented, a transmission spectrum of an LB multilayer on silicon wafer, and a grazing incidence spectrum of an LB multilayer on a Pyrex microscope slide with a thin layer of evaporated gold. The results, summarised in Table 2, indicate that the alkyl side chains were in fact close to being vertical. Thus, in the transmission spectrum of the LB film the stretching vibration bands due to the C—H of the methylene groups were much stronger relative to those in the cast film, whereas in the grazing incidence spectrum they were much weaker. Although it is difficult to quantify the average angle of tilt from these results because the spectra contain so few sharp bands, it is nevertheless clear that the side chains are close to being vertical. Assuming the side chains are straight, interdigitated and vertical space-filling molecular models of polymers **7** and **8** predict bilayer thicknesses of 34 and 36 respectively, values very close to the observed values (see Table 1). Finally, on this topic, it should be noted that the interdigitated structures require monolayers in which the area per repeat unit is at least equal to twice the cross-sectional area of the hydrocarbon side chain, *i.e.* $\geqslant(2\times18)$ Å^2 $\geqslant$36 Å^2. The monolayer of polymers **7** and **8** have experimental A_0 values of 39 and 37 Å^2 respectively. Thus, these polymers, as well as polymers such as polymer **1**, have structures of the type indicated in Fig. 1.

Finally, an alternating LB multilayer was prepared using the imidazolium polymer **8** and pyridinium polymer **10**. The latter has been discussed previously.[12] It gave four orders of Bragg reflections corresponding to a d-spacing of 37.1±0.5 Å. In the present study the alternating multilayer of the two

Table 2 Relative intensities[a] of bands in FT-IR spectra of films of polymer **7**

film type	direction of IR radiation	intensity of C—H vibration band at 2903 cm^{-1}	intensity of aromatic band at 1550 cm^{-1}	ratio of intensities ν_{2903}/ν_{1500}	ratios relative to those obtained with the cast film
cast	transmission	161	16	10.1	1.00
LB	transmission	134	8	16.8	1.66
LB	grazing incidence	111	83	1.3	0.13

[a] Arbitrary units based on the areas of the relevant bands.

polymers gave two orders of Bragg reflections corresponding to a *d*-spacing of 39.4 ± 0.7 Å. This value is just slightly larger than that of either polymer alone. This result suggests that polymers **8** and **10** can form an alternating interdigitated structure similar to that shown in Fig. 1.

Conclusions

It is evident that polymers **7** and **8** give excellent LB multilayers that have a Y-type structure in which the long alkyl side chains are interdigitated. The corresponding monomers had poor isotherms and did not give LB films, thus demonstrating the value of using preformed polymers. The less highly quaternised polymers **2** and **3** failed even to give monolayers at the air–water interface that could sustain any significant surface pressure.

Polymers of the general type of **7** and **8** are readily available and can be expected to find applications in LB film devices. They have the attractive features that, because they have interdigitated structures, they form bilayers with very small *d*-spacings and potentially they have greater stability, both mechanically and thermally, than most other types of polymeric LB films.

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