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Preparation and characteristics of perfluorodiacetylene Langmuir–Blodgett films

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The surface pressure–area curve for the novel perfluorodiacetylene, $C_{24}F_{42}$, showed that a monolayer was formed on the surface of the water. The monolayer was deposited on KRS-5, Al and quartz plates by the Langmuir–Blodgett (LB) technique. The LB film on the KRS-5 plate showed excellent water repellency with a contact angle of 162°. Comparison of the reflection–absorption and transmission i.r. spectra showed that the difluoromethylene chains in the $C_{24}F_{42}$ LB film were oriented perpendicular to the substrate surface. The $C_{24}F_{42}$ LB film on the quartz plate was polymerized by u.v. irradiation giving a highly electroconductive film without doping or further treatment. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: diacetylene LB film; water repellency; electroconductivity)

INTRODUCTION

Only amphiphilic molecules with a polar head and hydrophobic tail have been considered to form monolayers at the air-water interface[1–3]. Li *et al.*, however, showed that perfluoroeicosane formed a stable, ordered Langmuir monolayer on water, in which the molecules were aligned vertically and packed in a hexagonal array, but the compound was not amphiphilic[4]. We also reported that linear perfluoroalkanes of appropriate chain length form monolayers on water as well as conventional amphiphiles do, and that the monolayers can be deposited on various substrates by the Langmuir–Blodgett (LB) technique, the perfluoroalkane molecules being oriented perpendicularly to the substrate surface and the coated surfaces having excellent water repellency[5].

Coating the substrates with polymeric fluorinated materials is expected to afford fluorinated surfaces with durable high water and oil repellencies[6,7]. The deposition of perfluorodiacetylene monolayers by the LB technique, followed by solid-state polymerization, gives such a coating. Furthermore, because ultrathin LB films in which the perfluorodiacetylene molecules are aligned orderly and have a highly extended π-conjugated system, they are expected to have high electroconductivity. Electroconductive LB films have attracted much interest as ultrathin film conductors at the molecular level[8–10].

We synthesized the novel perfluorodiacetylenes $C_{20}F_{34}$ and $C_{24}F_{42}$ and evaluated their surface pressure (π)–area (A) curves on water. A $C_{24}F_{42}$ monolayer was deposited on various substrates by the LB technique, after which the contact angles of water to the coated surfaces were measured. The orientation of the perfluorodiacetylene molecules in the LB films was evaluated by comparing the reflection–absorption (RA) and transmission i.r. spectra. An LB film on a quartz plate was polymerized by u.v. irradiation, and its electroconductivity measured.

EXPERIMENTAL

Materials

1,2-Dibromo-1,1,2-trihydroperfluorododecane (**1**). A mixture of 1,1,2-trihydroperfluorododecene (10.3 g, 18.9 mmol), Br_2 (4.52 g, 28.3 mmol) and CCl_4 (5 ml) was heated in a sealed tube at 120°C for 5 h. The solvent and excess Br_2 were removed *in vacuo* giving **1** (12.5 g, 94% yield).

Analysis: m.p. 87°C. M.s. (20 eV, *m/z*): 708 (relative intensity: 1.5), 706 (3.3), 704 (1.5) $[M]^+$, 627 (98.5), 625 (100) $[M - Br]^+$ 189 (12.7), 187 (23.8), 185 (12.1) $[C_2H_3Br_2]^+$, 169 (24.6) $[C_3F_7]^+$, 157 (30.8), 155 (31.3) $[C_3F_2H_2Br]^+$, 131 (25.7) $[C_3F_5]^+$, 119 (28.2) $[C_2F_5]^+$, 94 (57.8), 92 (60.7) $[CHBr]^+$, 77(78.8) $[C_3F_2H_3]^+$, 69(58.0) $[CF_3]^+$. ^{19}F n.m.r.: −81.3 (A, t, $J = 9.9$ Hz), −111.8 (B, d, $J = 72.0$), −119.3 (C, s), −122.1 (D, s), −123.1 (E, s), −126.6 (F, s). ^{1}H n.m.r.: 3.61 (H, dd, $J = 9.0$ and 11.8 Hz), 4.03 (I, dd, $J = 3.7$ and 11.8), 4.28–4.71 (G, m).

$$CF_3^ACF_2^FCF_2^ECF_2^DCF_2^DCF_2^DCF_2^DCF_2^DCF_2^CCF_2^BCH^GBrCH_2^{H,I}Br \quad (1)$$

*2-Bromo-1,1-dihydro-1-perfluorododecene (***2***).* A 10% solution of alcoholic KOH (1.31 g, 23.2 mmol) was added dropwise with stirring to **1** (12.5 g, 17.7 mmol) in ether (40 ml) at 0°C. This mixture was stirred for an additional 2 h at room temperature then poured into water (150 ml). The ether layer was separated, and evaporation gave **2** (10.4 g, 94% yield).

Analysis: m.p. 58°C. M.s. (70 eV, *m/z*): 626 (relative intensity: 0.9), 624 (12.2) $[M]^+$, 157 (99.4), 155 (100) $[C_3F_2H_2Br]^+$, 131 (27.9) $[C_3F_5]^+$, 119 (15.3) $[C_2F_5]^+$, 107 (10.8) $[C_4F_3H_2]^+$, 100 (10.8) $[C_2F_4]^+$, 76 (10.6) $[C_3F_2H_2]^+$,

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75 (21.0) $[C_3F_2H]^+$, 69 (100) $[CF_3]^+$. ^{19}F n.m.r.: −81.3 (A, t, $J = 9.9$ Hz), −109.0 (B, s), −120.9 (C, s), −122.1 (D, s), − 123.1 (E, s), −126.6 (F, s). ^{1}H n.m.r.: 6.18–6.24 (H, *trans* H, m), 6.48 (1, *cis* H, d, $J = 3.3$ Hz) I.r. (KBr): 1623 cm^{-1} (C=C).

$$\mathrm{CF_3^ACF_2^FCF_2^ECF_2^DCF_2^DCF_2^DCF_2^DCF_2^DCF_2^CCF_2^BCBr{=}CH_2^{H,I}} \quad (\mathbf{2})$$

*1,2,2-Tribromo-1,1-dihydroperfluorododecane (**3**).* A mixture of **2** (13.2 g, 21.1 mmol) Br_2 (5.06 g. 31.7 mmol) and CCl_4 (7 ml) was heated in a sealed tube at 120°C for 5 h. The solvent and excess Br_2 were removed *in vacuo* giving **3** (16.3 g, 98% yield).

Analysis: m.p. 81°C. M.s. (20 eV, *m/z*): 707 (relative intensity: 43.7), 705 (84.7), 703 (44.9) $[M - Br]^+$, 267 (11.7), 265 (10.5) $[C_3F_6Br]^+$, 237 (10.9), 235 (23.6), 233 (8.7) $[C_3F_2HBr_2]^+$, 219 (10.7) $[C_4F_9]^+$ 181 (12.0) $[C_4F_7]^+$, 169 (40.1) $[C_3F_7]^+$ 157 (93.8), 155 (92.6) $[C_3F_2H_2Br]^+$, 131 (38.6) $[C_3F_5]^+$, 119 (40.4) $[C_2F_5]^+$, 94 (19.2), 92 (21.6) $[CH_2Br]^+$, 75 (11.8) $[C_3F_2H]^+$ 69(100) $[CF_3]^+$. ^{19}F n.m.r.: −81.3 (A, t, $J = 9.9$ Hz), −102.8 (B, s), −115.0 (C, s), −122.1 (D, s), −123.1 (E, s), −126.6 (F, s). ^{1}H n.m.r.: 4.26 (s).

$$\mathrm{CF_3^ACF_2^FCF_2^ECF_2^DCF_2^DCF_2^DCF_2^DCF_2^DCF_2^CCF_2^BCBr_2CH_2Br} \quad (\mathbf{3})$$

*1-Hydro-1-perfluorododecyne (**5**).* A 10% solution of alcoholic KOH (1.28 g, 22.8 mmol) was added dropwise with stirring to **3** (16.3 g, 20.7 mmol) in ether (100 ml) at 0°C. This mixture was stirred for an additional 2 h at room temperature then poured into water (300 ml). The ether layer was separated, and evaporation gave a mixture (13.2 g) of 1,2-dibromo-1-hydro-1-perfluorododecene (**4**), 1-bromo-1-perfluorododecyne and **2**.

A mixture (10.3 g) containing 62 mol% of **4** (9.48 mmol, as determined by ^{19}F n.m.r.), was added dropwise to a stirred suspension of Zn dust (2.1 g) and $ZnCl_2$ (0.071 g) in ethanol (50 ml), then heated at refluxing temperature for 4 h. Ethanol was removed *in vacuo*. Product **5** (5.0 g, 96% yield based on **4**) was separated from the mixture under reduced pressure (75 Torr, 95°C).

Analysis: m.p. 21°C. M.s. (70 eV, *m/z*): 525 (relative intensity: 0.4) $[M - F]^+$, 169 (10.8) $[C_3F_7]^+$, 131 (22.0) $[C_3F_5]^+$, 119 (20.5) $[C_2F_5]^+$, 100 (13.1) $[C_2F_4]^+$, 75 (100) $[C_3F_2H]^+$, 69 (73.0) $[CF_3]^+$. ^{19}F n.m.r.: −81.3 (A, t, $J = 9.9$ Hz), −99.7 (B, s), −121.7 (C, s), −122.3 (D, s), −123.1 (E, s), −126.6 (F, s). ^{1}H n.m.r.: 3.09 (t, $J = 5.7$ Hz). I.r. (neat liquid): 3315 cm^{-1} (≡C–H), 2146 cm^{-1} (C≡C).

$$\mathrm{CF_3^ACF_2^FCF_2^ECF_2^DCF_2^DCF_2^DCF_2^DCF_2^DCF_2^CCF_2^BC{\equiv}CH} \quad (\mathbf{5})$$

*Perfluoro(11,13-tetracosadiyne) (**6**).* The acetylene **5** (1.0 g, 1.8 mmol) was added to a stirred suspension of $Cu(CH_3COO)_2$ (0.83 g, 4.6 mmol) in DMF (10 ml) at room temperature. The mixture then was stirred for 2 h at room temperature and poured into water (200 ml). The precipitated **6** was filtered and dried *in vacuo* (0.90 g, 91% yield).

Analysis: m.p. 197°C. M.s. (20 eV, *m/z*): 617 (relative intensity: 27.4) $[M - C_9F_{19}]^+$, 179 (16.1) $[C_7F_5]^+$, 169 (12.6) $[C_3F_7]^+$, 148 (21.9) $[C_6F_4]^+$, 131 (18.9) $[C_3F_5]^+$, 119 (19.9) $[C_2F_5]^+$, 100 (10.1) $[C_2F_4]^+$, 69 (100) $[CF_3]^+$. I.r. (KBr) 2185 cm^{-1} (C≡C–C≡C).

*Perfluoro(9,11-icosadiyne) (**7**).* 1-Hydro-1-perfluorodecyne[11] (0.62 g, 1.4 mmol) was added to a stirred suspension of $Cu(CH_3COO)_2$ (0.65 g) in DMF (5 ml) at room temperature. The mixture then was stirred for 2 h at room temperature and poured into water (200 ml). The precipitated **7** was filtered and dried *in vacuo* (0.54 g, 91% yield).

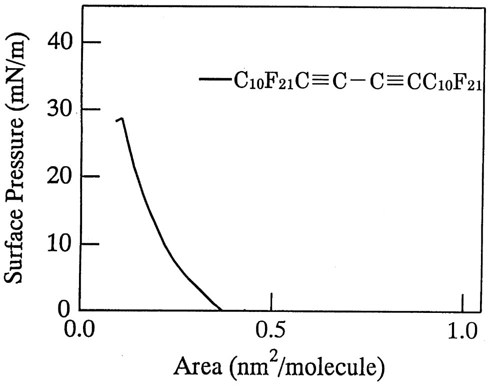

Figure 1 Surface pressure–area isotherms of perfluorodiacetylene at 5°C

Analysis: m.p. 143°C. M.s. (20 eV, *m/z*): 886 (relative intensity: 0.1) $[M]^+$, 867 (4.5) $[M - F]^+$, 517 (60.7) $[M - C_7F_{15}]^+$, 298 (11.2) $[C_9F_{10}]^+$, 179 (20.5) $[C_7F_5]^+$, 148 (26.6) $[C_6F_4]^+$, 131 (15.4) $[C_3F_5]^+$, 119 (18.5) $[C_2F_5]^+$, 69 (100) $[CF_3]^+$. I.r. (KBr): 2187 cm^{-1} (C≡C–C≡C).

Measurements

I.r. spectra were obtained with a Shimadzu FTIR-8000PC. ^{19}F n.m.r. (84.67 MHz) and ^{1}H n.m.r. (90 MHz) measurements were recorded on a Hitachi R-90F, the chemical shifts being defined as the δ values respective to $CFCl_3$ and TMS. Mass spectra were obtained with a Shimadzu QP-5000 apparatus at 70 eV or a Hitachi M-80 at 20 eV.

Monolayers were formed in a Kyowa Interface Science Co., Ltd. HBM-AP polytetrafluoroethylene (PTFE)-coated trough, the surface pressures being measured by the Wilhelmy plate method. A perfluorohexane solution of perfluorodiacetylene (*ca.* 0.25 mg ml^{-1}) was spread on purified water (Milli-Q system, Millipore Ltd.) at 5°C, and the resulting monolayer compressed at the rate of 56 cm^2 mm^{-1} after standing for 3 min.

Perfluorodiacetylene $C_{24}F_{42}$ LB films (Y-type) were prepared on the substrate at the transfer rate of 5 mm min^{-1} in the vertical mode at 15 mN m^{-1} and 5°C. The KRS-5, Al and quartz plates were obtained commercially and used after washing them with alcohol. The contact angles of the water to the LB films (30 layers) were measured with an Erma goniometer G-1. RA-i.r. spectra were obtained with an RAS-8000 reflection attachment at the incident angle of 75°. Polymerization was done by exposing the LB films to u.v. light from a 23 W u.v. lamp at a distance of 3 cm. U.v.-visible spectra of the LB films were recorded on a Shimadzu UV-2400PC. The electroconductivity of the polymerized LB film was measured by the d.c. four-probe method with evaporated Au as the electrode.

RESULTS AND DISCUSSION

The π-A isotherm of perfluorodiacetylene $C_{24}F_{42}$ at 5°C is shown in *Figure 1*. $C_{24}F_{42}$ forms a monolayer with a collapse pressure of 27.1 mN m^{-1}. Conventional linear extrapolation of the high-pressure limb of the isotherm to zero pressure gives a limiting area of 0.24 nm^2 per

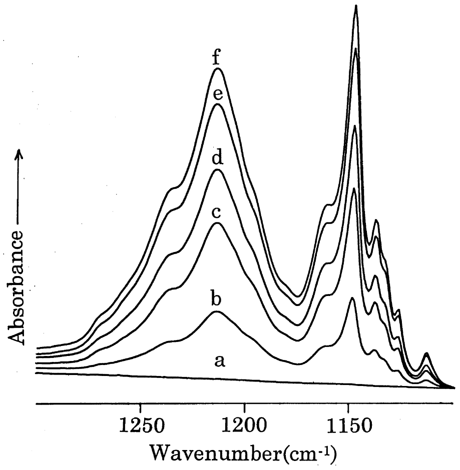

Figure 2 Transmission i.r. spectra for a $C_{24}F_{42}$ LB film on a KRS-5 plate: curve a, bare; curve b, 10 layers; curve c, 20 layers; curve d, 30 layers; curve e, 40 layers; curve f, 50 layers

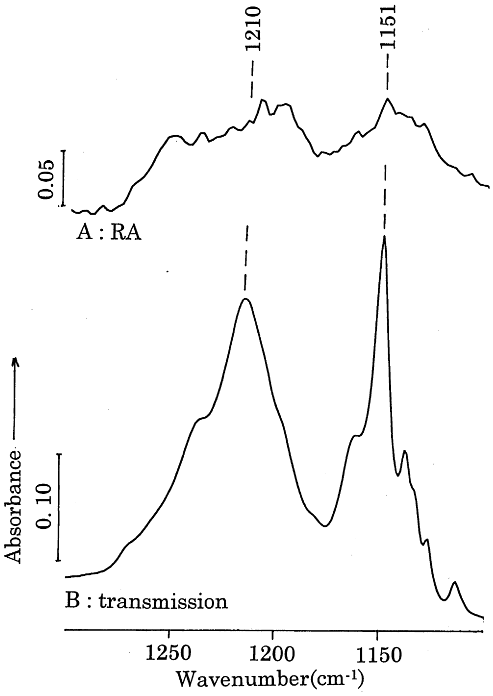

Figure 3 *FT*i.r. spectra for a $C_{24}F_{42}$ LB film (50 layers): (A) reflection-absorption spectrum for deposition on an Al plate; (B) transmission spectrum for deposition on a KRS-5 plate

molecule, the value of which is somewhat smaller than that (0.30 nm^2 per molecule) for perfluoroalkane $C_{24}F_{50}$[5]. This indicates that the molecules sublimate after the solution is spread over the water, although they do not sublimate under compression at 15 mN m^{-1}. In the case of perfluorodiacetylene $C_{20}F_{34}$, the π-A isotherm could not be obtained because of its rapid sublimation on spreading over water.

The $C_{24}F_{42}$ monolayers were deposited on KRS-5, Al and quartz plates by the LB technique. The i.r. spectra for the $C_{24}F_{42}$ LB film on the KRS-5 plate are shown in *Figure 2*. Deposition was confirmed by the i.r. spectra, in which absorption owing to the CF_2 symmetric and anti-symmetric stretching bands (1151 and 1210 cm^{-1})[12] increased with the deposition cycle. The orientation of the perfluorodiacetylene molecules on the substrate was evaluated by RA and transmission i.r. spectrometry. In the RA-i.r. measurements, only transition moments perpendicular to the film surface are observed, while those parallel are not observed. As seen in *Figure 3*, the absorption caused by the CF_2 symmetric and anti-symmetric stretching bands (1151 and 1210 cm^{-1}) apparently is weaker in the RA than in the transmission spectrum. This shows that the difluoromethylene chains are oriented perpendicularly to the substrate surface[13,14].

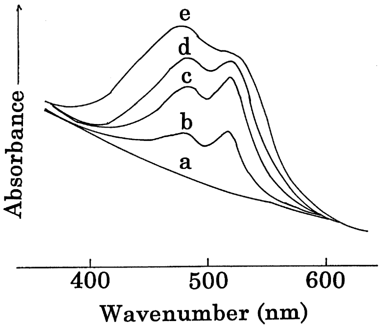

Figure 4 Change in the absorption of $C_{24}F_{42}$ LB film (50 layers) on photopolymerization: curve a, 0 min; curve b, 15 min; curve c, 30 min; curve d, 60 min; curve e, 120 min

The contact angle of the water to the $C_{24}F_{42}$ LB films on the KRS-5 and quartz plate increased with increasing the number of layers and became almost constant over 30 layers. The LB film (30 layers) on the KRS-5 plate had excellent water repellency with a contact angle of water of 162°, much larger than the values for PTFE (108°), fluorinated graphite (143°) and [2-(perfluorooctyl)ethyl] trichlorosilane monolayer (130°)[15]. This is owing to the large CF_3 content at the LB film surface due to the molecular arrangement because the surface energy of the CF_3 group is lower than that of the CF_2 group[5]. The contact angle of the water to the $C_{24}F_{42}$ LB film (30 layers) on the quartz plate (135°) is somewhat smaller than that on the KRS-5 plate. This is attributable to the surface properties of the substrates, such as the hydrophilicity and unevenness, which cause imperfections in the LB films resulting in a decrease in the CF_3 content at the film surfaces.

The LB film on the quartz plate (15 mN m^{-1}, 50 layers) was polymerized by u.v. irradiation. The u.v.-Visible spectra of the film are shown in *Figure 4*. The peaks at $\lambda = 480$ and 520 nm increased with the photoirradiation time, saturation occurring at an irradiation of more than 2 h. Change in the spectra is attributed to the alternating double bond produced by photopolymerization. As shown by the spectra the LB films were coloured red. These films were not polymerized by heating them at 80°C.

In the absence of doping or further treatment, polymerized LB film had the property of a semi-conductor with an electroconductivity of 3.0×10^{-5} S cm^{-1}. The conductivity is much larger than that for the polybutadiyne crystal (2×10^{-10} S cm^{-1})[16] which is classified as an insulator. This finding suggests that the energy gap between the conduction and valence bands in the polymerized LB film is smaller than that in the polybutadiyne crystal owing to the effect of the large electron-withdrawing of the perfluoroalkyl group[17]. The electroconductivity of the polymerized LB film prepared under a different condition (20 mN m^{-1}, 50 layers) was 2.7×10^{-5} S cm^{-1}, comparable to that of the film described above (15 mN m^{-1}, 50 layers).

CONCLUSIONS

A novel perfluorodiacetylene, $C_{24}F_{42}$, forms a monolayer on water as well as conventional amphiphiles do. The perfluorodiacetylene monolayer was deposited on various substrates by the LB technique. Its molecules were oriented perpendicular to the substrate surface, and the coated surface had excellent water repellency. The perfluorodiacetylene LB films were polymerized by u.v. irradiation and gave a highly electroconductive film without doping or further treatment.

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