Polymerization of Amphiphilic Dienes in Langmuir–Blodgett Multilayers

A. Laschewsky and H. Ringsdorf*

Institute of Organic Chemistry, Universität Mainz, D-6500 Mainz, FRG.

Received September 3, 1987

ABSTRACT: Amphiphilic derivatives of octadiene and docosadiene were investigated in monolayers and Langmuir–Blodgett multilayers, with respect to their self-organization and their polymerization behavior. All amphiphiles investigated form monolayers. However, only acid and alcohol derivatives were able to build up multilayers. Those multilayers are rapidly photopolymerized in the layers via a two-step process: Irradiation with long-wavelength UV light yields soluble polymers, whereas additional irradiation with short-wavelength UV light produces insoluble and presumably cross-linked polymers. The reaction mechanism is discussed according to the polymer characterization by UV spectroscopy, small-angle X-ray scattering, NMR spectroscopy, and gel permeation chromatography. All multilayers undergo structural changes during the polymerization; substantial changes result in defects in the polymerized layers as observed by scanning electron microscopy. In contrast to the acids and alcohols, the deposition of monolayers of the aldehyde derivatives did not yield well-ordered multilayers, but rather amorphous films. In this different film structure, the photopolymerization process differs from the one observed in multilayers.

The transfer of lipid monolayers from the air–water interface to solid supports by the Langmuir–Blodgett (LB) technique[1,2] yields ultrathin, homogeneous, and well-ordered multilayer films. Such multilayers are of considerable interest for both scientific and technical uses.[3] The polymerization of reactive amphiphiles within LB multilayers[4] provides increased stability of the rather sensitive multilayers.[5] Additionally, the well-defined multilayer structure enables studies of the interdependence between molecular organization and reactivity.[6,7] Up to now, the most extensive studies of polymerization in LB multilayers have been performed with fatty acids containing the diyne moiety[7] which are known to exclusively polymerize under topochemical control.

For our investigations, amphiphiles bearing a reactive diene moiety were chosen. The polymerization of dienes is not restricted by a strict topochemical control, as shown by studies of amphiphilic dienes in lipid monolayers and vesicles.[8-12] Such studies in LB multilayers are scarce yet; diene amphiphiles investigated so far include esters and amides of fatty alcohols or amines with pentadienoic acid,[11] sorbic acid,[7] and muconic acid,[6,7] respectively. In addition, the octadecadiene derivatives **4–6** and docosadienoic acid **3** (see Table I) have been studied to some extent in LB multilayers.[6,9,10] However, in some cases the existence of well-ordered multilayers is questionable,[9,10] and detailed results are missing.

The amphiphilic dienes used in the present study are shown in Table I. They are comprised of fatty alcohols, fatty aldehydes, and fatty acids of docosadiene **1–3** and octadecadiene **4–6**. The effect of the variation of the hydrophilic headgroup on self-organization and on photopolymerization was studied as well as the effect of the length of the hydrophobic chain.

Experimental Section

Materials. The synthesis of dienes **4–6** has been described elsewhere.[12] Docosadienal **2** was synthesized according to the preparation procedure for octadecadienal **5**, starting with octadecanal. The latter was prepared by oxidation of octadecanol by pyridinium chlorochromate following a general procedure.[13] Docosadienol **1** was synthesized by reduction of **2** by $LiAlH_4$, docosadienoic acid **3** by oxidation of **2** with Ag_2O; procedures and yields are the same as in the synthesis of **4–6**.[12] Compound **1** was purified by repeated recrystallization from diethyl ether and ethanol. Compounds **2** and **3** were purified by liquid chromatography on silica gel (eluents: petroleum ether/ethyl acetate, 10/1 v/v; and petroleum ether/ethyl acetate/acetic acid, 90/10/1 v/v/v).

Table I
Polymerizable Amphiphiles Investigated

1	$CH_3-(CH_2)_{16}-CH=CH-CH=CH-CH_2OH$
2	$CH_3-(CH_2)_{16}-CH=CH-CH=CH-CHO$
3	$CH_3-(CH_2)_{16}-CH=CH-CH=CH-COOH$
4	$CH_3-(CH_2)_{12}-CH=CH-CH=CH-CH_2OH$
5	$CH_3-(CH_2)_{12}-CH=CH-CH=CH-CHO$
6	$CH_3-(CH_2)_{12}-CH=CH-CH=CH-COOH$

Characterization. **1**: waxy, colorless platelets; mp 70 °C. Anal. Calcd for $C_{22}H_{42}O$ (mw 322.6): C, 81.92; H, 13.12. Found: C, 81.58; H, 13.10. FD-mass spectrum, mass at 322. ^1H NMR δ 0.9 (t, 3 H, CH_3), 1.1–1.5 (m, 30 H, $CH_3(C\mathit{H}_2)_{15}$), 2.05 (m, 2 H, $C\mathit{H}_2CH{=}CHCH{=}CH$), 4.1 (m, 2 H, CH_2O), 5.7 (m, 2 H, $C\mathit{H}{=}CHCH{=}C\mathit{H}$), 6.1 (m, 2 H, $CH{=}C\mathit{H}C\mathit{H}{=}CH$).

2: waxy, colorless platelets; mp 48 °C. Anal. Calcd for $C_{22}H_{40}O$ (mw 320.6): C, 82.43; H, 12.58. Found: C, 80.35; H, 12.05. FD-mass spectrum, mass at 320. ^1H NMR δ 0.9 (t, 3 H, CH_3), 1.1–1.5 (m, 30 H, $CH_3\ (C\mathit{H}_2)_{15}$), 2.2 (m, 2 H, $C\mathit{H}_2CH{=}CHCH{=}CH$), 5.4–6.0 (m, 4 H, $CH{=}CH{-}CH{=}CH$), 9.4 (d, 1 H, CHO).

3: waxy, colorless platelets; mp ca. 85 °C dec. Anal. Calcd for $C_{22}H_4O_2$ (mw 336.6): C, 78.51; H, 11.98. Found: C, 78.93; H, 11.66. FD-mass spectrum, mass at 336. ^1H NMR δ 0.9 (t, 3 H, CH_3), 1.1–1.5 (m, 30 H, $CH_3(C\mathit{H}_2)_{15}$), 2.2 (m, 2 H, $C\mathit{H}_2CH{=}CHCH{=}CH$), 5.65 (m, 2 H, $C\mathit{H}{=}CHCH{=}C\mathit{H}COO$), 5.8 (m, 1 H, $CH{=}C\mathit{H}CH{=}CHCOO$), 6.1 (m, 1 H, $CH{=}CHC\mathit{H}{=}CHCOO$).

Methods. Monolayer Experiments and Monolayer Transfer. The amphiphiles **1–6** were spread from hexane (Merck, Uvasol grade) solutions of concentration ca. 0.1 mg/mL. The monolayer experiments were performed on a computer-controlled film balance, equipped with a Wilhelmi pressure pick-up system.[14] All monolayers were spread on pure aqueous subphase. The water was purified by distillation and subsequently by a Millipore water purification system and equilibrated in air (pH 5.8). For deposition experiments, a commercial film balance (Lauda) equipped with a Langmuir pressure pick-up system was used. Monolayers were deposited on hydrophobized[15] quartz slides (75 mm × 25 mm, Suprasil, Heraeus-Schott), polypropylene foil (Celgard 2400, Celanese), and polyester foil (Hostaphan RE 3.0, Kalle). The flexible polymer foils were backed by Teflon slides. The quartz supports were used for UV/vis spectroscopic studies, the polypropylene ones for scanning electron microscopy, and the polyester ones for small-angle X-ray scattering experiments.

0024-9297/88/2221-1936$01.50/0

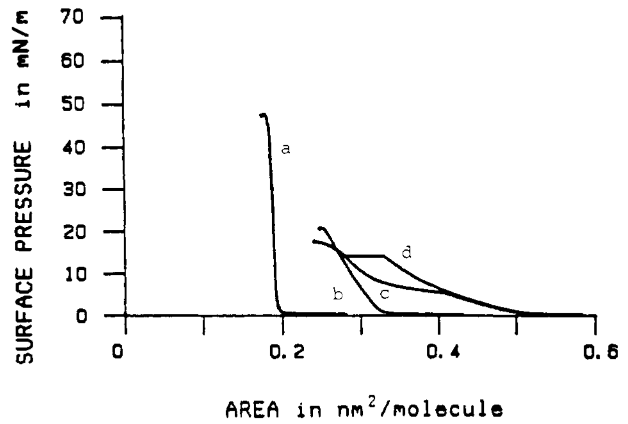

Figure 1. Isotherms of docosadienol 1: (a) $T = 20$ °C. Isotherms of docosadienal 2: (b) $T = 20$ °C; (c) $T = 30$ °C; (d) $T = 45$ °C. Pure aqueous subphase.

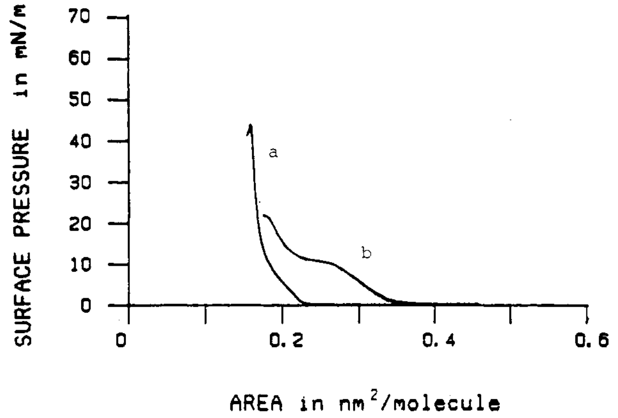

Figure 2. Isotherms at 20 °C on pure aqueous subphase: (a) docosadienoic acid 3; (b) octadecadienoic acid 6.

Polymerization. The LB multilayers and LB films were polymerized by exposure to UV light in air. Two different UV lamps were used. Lamp A (mercury low-pressure lamp, Heraeus Typ 5340, 6 W) provides filtered UV light with 230 nm $< \lambda <$ 410 nm. Lamp B (mercury low-pressure pen-ray, Hamamatsu Corp. Model 937-002) provides unfiltered UV light with the main intensity at 254 nm. The samples were kept at a distance of 10 cm from the UV lamps. Fresh air was constantly flown over the samples to minimize the concentration of ozone and nitroxides present as well as to prevent heating.

The polymers formed in the multilayers were taken off the solid support by refluxing them in $CHCl_3$ for 1 week. Then the solutions were freeze-dried.

Analysis. ^1H NMR spectra were recorded with a Bruker WH90 instrument (90 MHz) and a Bruker aspect 3000 instrument (400 MHz). UV/vis spectra were recorded with a Beckman DU-6 spectrophotometer. X-ray scattering was performed with a powder diffractometer Siemens D500 using Ni-filtered Cu Kα radiation ($\lambda = 0.1541$ nm). Scanning electron micrographs were taken with a Cambridge Mark II electron microscope; the samples were sputtered with gold. Gel permeation chromatography was performed with the column combination Hilda 1,[16] using THF as solvent. The column was calibrated with poly(methyl methacrylate). The exclusion volume of $V_e = 32$ counts corresponds to ca. 20 000 Dalton molecular weight.

Results and Discussion

Spreading Behavior. The spreading behavior of the amphiphiles 1–3 is illustrated in Figures 1 and 2a. The surface pressure–area isotherms of docosadienol 1 show exclusively a condensed phase in the temperature range investigated, i.e., up to 40 °C (Figure 1a). According to its low collapse area of 0.19 nm²/molecule and its high collapse pressure of 50 mN/m, the monolayer is tightly packed. In contrast, the surface pressure–area isotherms of docosadienal 2 show the formation of an expanded phase at elevated temperatures (Figure 1b–d). At 45 °C only the expanded phase is observed (Figure 1d), whereas at 30 °C the condensed and expanded phases coexist (Figure 1c). At 20 °C only a condensed phase is observed (Figure 1b). The collapse pressure of the condensed phase is low with a value of ca. 20 mN/m, and the collapse area has a high value of 0.25 nm²/molecule. Both values point out a loose packing of the hydrophobic chains in the condensed phase of 2. Docosadienoic acid 3 shows exclusively the formation of a condensed phase (Figure 2a). The collapse area of 0.19 nm²/molecule and the high collapse pressure of 45 mN/m demonstrate the tight packing of the hydrophobic chains.

Table II

Conditions for the Deposition of Monolayers of 1–6 at 20 °C

amphiphile	surface pressure, mN/m	dipping speed, cm/min down	dipping speed, cm/min up	drying period, min	deposition type[a]
1	30	5	1	1	Y
2	10	2	0.5	1	Z
3	20	5	2	2	Y
4	30	2	1	1	Y
5	*b*				
6	20				*c*

[a] Y = deposition on downward and upward dip; Z = deposition on upward dip only. [b] Monolayer does not exhibit a condensed phase. [c] Monolayer unstable in the condensed phase.

Surface pressure–area isotherms of the homologous octadiene derivatives 4–6 have been published previously.[10,12] The isotherms of octadecadienol 4 show exclusively a condensed phase up to 40 °C and are in good agreement with the ones of docosadienol 1. Octadecadienal 5 exhibits only an expanded phase at 20 °C.[12] In the case of the octadecadienoic acid 6 at 20 °C, both condensed and expanded phases coexist (Figure 2b), in agreement with ref 10. The originally published isotherm of 6 displayed a second expanded phase at surface areas of ca. 0.4 nm²/molecule.[12] However, this additional phase is not real and was probably caused by impurities.

A remarkable feature of these surface pressure–area isotherms is the rather high collapse area of 0.25 nm²/molecule in the condensed phase of the dienoic aldehydes 2 and 5 (Figure 1b). In contrast, both dienols and dienoic acids exhibit the maximal packing density of 0.19 nm²/molecule in their condensed phase (figures 1a and 2a). The different packing densities observed suggest a different arrangement of the polymerizable diene/dienoyl group in the monolayers.

Buildup of Multilayers. The deposition conditions of the monolayers onto solid supports are listed in Table II. The dienols 1 and 4 were easily deposited as well as docosadienoic acid 3. However, at 20 °C the monolayer of the homologous octadecadienoic acid 6 is not stable in the condensed state on pure aqueous subphase and thus cannot be used to prepare high-quality LB multilayers. Hence, no further experiments were performed with 6. The deposition of monolayers of 6 in the expanded phase has been recently reported.[10] However, conclusions drawn from studies on such films are questionable since coatings obtained by deposition of expanded monolayers have been shown to be fairly disordered.[5,23] For the same reasons, no attempts were made to transfer monolayers of octadecadienal 5, which are in the expanded state at 20 °C.[12]

Although condensed monolayers of docosadienal 2 could be transferred onto supports, the coatings obtained proved not to be well-ordered multilayers. Indeed, small-angle X-ray scattering (SAXS) of these coatings did not show layer reflections which are characteristic of real LB mul-

Table III
Layer Spacings of Monomeric and Polymeric LB Multilayers of 1-4 Measured by SAXS[a]

amphiphile	layer spacing, nm: monomer	layer spacing, nm: polymer I[b]	layer spacing, nm: polymer II[c]	calcd length of molecule, nm
1	5.89	5.78	5.64	3.1
2	*d*	*d*	*d*	
3	5.05	5.32	5.21	3.1
4	4.88	4.59	3.96	2.6

[a] 30 layers deposited on the polyester support. [b] Soluble. [c] Insoluble. [d] No layer reflection observed.

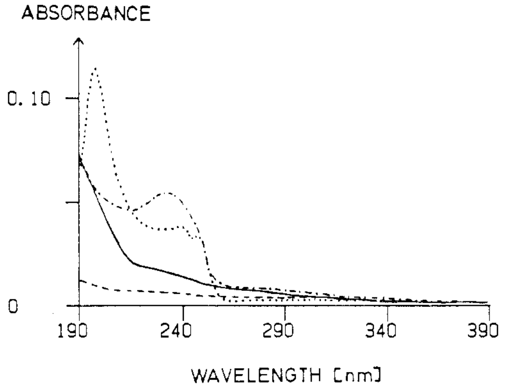

Figure 3. UV spectra of LB multilayers of docosadienol 1 (16 layers deposited on quartz): (···) = 0-min, (-·-) 15-min, and (—) 120-min irradiation with the filtered lamp A; (---) 120-min irradiation with lamp A and then 90-min irradiation with the unfiltered lamp B.

tilayers as those obtained for **1**, **3**, and **4** (Table III). To avoid confusion and to distinguish from the well-ordered LB multilayers we will refer to the coatings obtained with **2** as "LB films". It is noteworthy that the absorbance of the LB films increases linearly with the number of dipping cycles, although no ordered layer structure is obtained. Thus, the linear relationship between absorbance and the number of layers deposited is no proof of the successful preparation of well-ordered LB multilayers, as is often assumed.

UV Spectroscopic Studies of the Photopolymerization. The UV-induced photoreaction of the LB multilayers and LB films can be followed by UV spectroscopy. The irradiation time dependent UV spectra of multilayers of docosadienol **1** and docosadienoic acid **3** are presented in Figures 3 and 4, respectively. The photoreaction was carried out in two steps, by irradiation with the filtered UV lamp A (230 nm $< \lambda <$ 410 nm) and then by subsequent irradiation with the unfiltered UV lamp B.

The UV spectra of LB multilayers of dienol **1** are characterized by a major absorption maximum at 198 nm and a structured minor one between 230 and 250 nm (Figure 3). At the beginning of the photoreaction, when irradiated with the filtered lamp A for 15 min, the intensity of the 198-nm maximum decreases quickly, whereas the one at 230 nm increases. If the irradiation time exceeds 15 min, the 198-nm maximum as well as the 230-nm one lose intensity and finally disappear after 120-min irradiation. Simultaneously, a new and intense shoulder appears at 190 nm. At this stage of the reaction, the photoproduct is completely soluble (polymer I). Thereafter, an additional 90-min irradiation with the unfiltered lamp B causes the newly formed shoulder to nearly disappear (Figure 3). Then, the photoproducts become insoluble (polymer II). LB multilayers of octadecadienol **4** behave virtually the same as the ones of docosadienol **1** under irradiation.

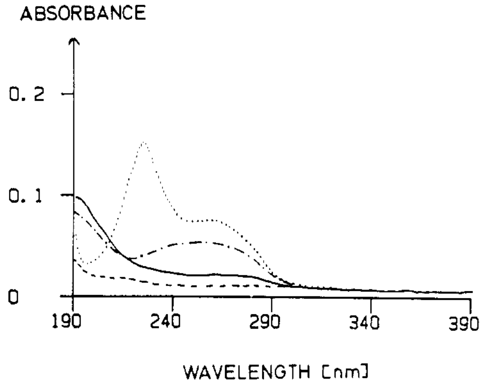

Figure 4. UV spectra of LB multilayers of docosadienoic acid **3** (20 layers deposited on quartz): (···) 0-min, (-·-) 10-min, and (—) 30-min irradiation with the filtered lamp A; (---) 30-min irradiation with lamp A and then 90-min irradiation with the unfiltered lamp B.

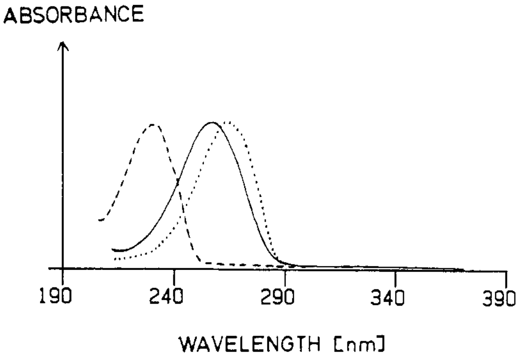

Figure 5. UV spectra of the dienes **1**–**3** in hexane: (---) docosadienol **1**; (···) docosadienal **2**; (—) docosadienoic acid **3**.

The monomeric LB multilayers of docosadienoic acid **3** are characterized by a major absorption maximum at 224 nm and a minor one at 260 nm (Figure 4). Initial irradiation with the filtered UV lamp A causes a drastic decrease of the intensity of the 224-nm maximum, whereas the minor one stays nearly constant in intensity. After 30 min of irradiation, both monomer maxima have disappeared and a new and intense shoulder at 190 nm appears. These photoproducts are soluble (polymer I). Additional irradiation with the unfiltered lamp B causes the newly formed shoulder to nearly disappear after 90 min. The photoproducts obtained are insoluble (polymer II). It is obvious that the UV spectra of **1**, **3**, and **4** and their changes upon irradiation show striking similarities, thus suggesting analogous photoreactions.

For both the dienols and the dienoic acid, the minor maxima in the UV spectra of the monomeric LB multilayers (Figures 3 and 4) correspond to the absorption maxima of these amphiphiles in isotropic solution (Figure 5). Thus, the observed maxima, which are shifted to shorter wavelengths, may be attributed to aggregates of these amphiphiles in the densely packed LB multilayers. Such aggregates have been previously observed in vesicles of other lipids containing the diene moiety.[17] This explanation agrees well with the observed initial increase of the free monomer absorbance: In the initial stage of the photoreaction, the cleavage of the aggregates presumably produces more free amphiphiles than consumed by the photoreaction. Whether or not this cleavage occurs independently of the photopolymerization cannot be decided on the basis of the present data.

The diene moiety may undergo a variety of photoreactions. The reaction could take place in position 1,2 in position 3,4 or in position 1,4 ($C_nH_{2n+1}C^4H{=}C^3HC^2H{=}$

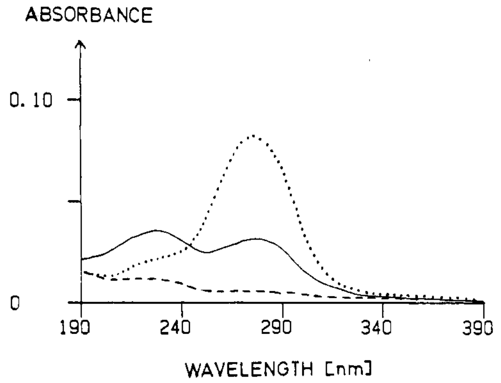

Figure 6. UV spectra of LB films of docosadienal 2 (10 layers deposited on quartz): (···) 0-min, (—) 5-min, and (- - -) 60-min irradiation with the filtered lamp A.

C^{1}HX). In addition, either dimers or oligomers and polymers can be produced.[10,12] For amphiphilic sorbates, a 1,4-polymerization mechanism is most likely.[7] However, for amphiphilic pentadienoates and muconates, a 3,4-dimerization mechanism is probable.[6,11] In our studies, in the case of the dienoic acid 3, the possible reaction in position 3,4 must be excluded. Such a reaction would result in a new absorption maximum of ca. 200–210 nm of an acrylic moiety. This is in contradiction with the absorbance band observed at much lower wavelengths (shoulder at 190 nm, Figure 5), which can be attributed to an isolated double bond. The 1,2-mechanism is also unlikely because the residual double bond and the carboxylic group would be left isolated. Therefore, the UV spectra (Figure 5) support the originally proposed 1,4-mechanism.[7,12]

In the case of the dienols 1 and 4, the UV spectra cannot give direct information about the mechanism of the photoreaction because an isolated double bond will be always formed. However, the analogy between the UV spectra of the dienols and the dienoic acid suggests also a 1,4-mechanism for the dienols. In the second reaction step, the additional irradiation of LB multilayers of 1, 3, and 4 yields mostly insoluble photoproducts, obviously due to cross-linking of the double bond newly formed in step I.

The UV spectra of the poorly ordered LB films of 2 are presented in Figure 6. These spectra show pronounced differences compared with those of the well ordered LB multilayers of 1 and 3 (Figures 3 and 4 versus Figure 6). The 285-nm absorption maximum of LB films corresponds to the one of an isotropic solution of 2 (Figure 5). Moreover, there is no band that can be attributed to aggregates. Upon irradiation with the filtered lamp A, the 285-nm band decreases and a new band at 230 nm appears. This new band reaches its maximal intensity after 5-min irradiation. Upon prolonged irradiation, both bands disappear after 60 min. However, in the case of 2, no 190-nm shoulder is observed (Figure 7) which would be indicative of an isolated double bond. In contrast, the 230-nm intermediate band suggests that an acrolein moiety is formed, i.e., a reaction in position 3,4 takes place. Obviously, the dienoyl moiety of 2 in the LB films is differently arranged compared to the dienoyl/diene moieties in LB multilayers of 1, 3, and 4 and therefore undergoes a different photoreaction. Such a different arrangement of the reactive groups is supported by the observed differences in the packing of condensed monolayers of the dienoic aldehydes 2 and 5 compared to the dienols and dienoic acids, as discussed in Figures 1 and 2.

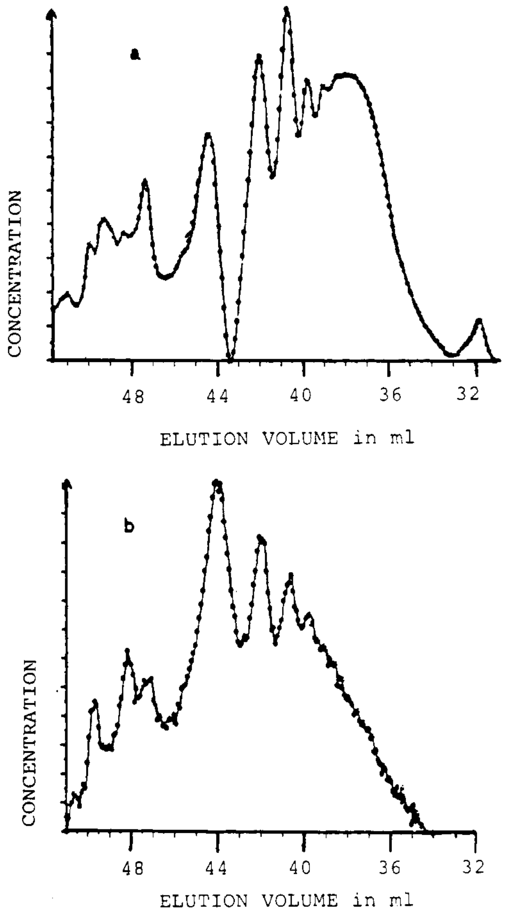

Figure 7. GPC plots of docosadienol 1 polymerized in LB multilayers: (a) polymer I; (b) soluble fraction of polymer II.

Characterization of the Polymers. For the photoreaction of dienols and dienoic acids, dimerization as well as polymerization has been considered,[10] although dimerization via a 4 + 4 cycloaddition in the solid state seems very unlikely.[18] To verify the formation of polymers, LB multilayers of 1 were built up and polymerized and the photoproducts taken off from the supports for analysis by ^{1}H NMR spectroscopy and gel permeation chromatography (GPC). For these studies, docosadienol 1 was chosen because its absorbance at 254 nm is much lower than the one of docosadienoic acid 3 (Figures 3 and 4). Indeed, a high absorbance of the LB multilayers would result in different reaction rates and states in the upper and lower layers of thick samples because the intensity of the UV light is strongly decreased during the sample penetration. Furthermore, 1 shows excellent deposition characteristics. Its transfer ratio is constant over several hundred dipping cycles (within the accuracy of the measurement, i.e., 5%). The deposition of 200 layers on hydrophobic quartz slides produces a shiny, clear coating of metal luster. The samples were irradiated for 120 min with the filtered lamp A, thus yielding the polymer I. The spectral changes during the reaction are in good agreement with those in Figure 3. After the initial 20 min of irradiation, the samples become faintly turbid. One of them was irradiated for an additional 90 min with the unfiltered lamp B, thus yielding polymer II. Polymer I was completely soluble, leaving the quartz slides with a clean hydrophobic surface. The multilayers of polymer II were mainly insoluble. Only little material could be dissolved and the quartz slides showed an irregular hydrophilic surface after the extraction attempts.

^{1}H NMR spectroscopy of polymer I showed the loss of the signals at 2.05, 4.1, 5.7, and 6.1 ppm, thus indicating the conversion of the diene moiety. All other signals are strongly broadened. Broad and new signals are observed at 2.3 and 3.5 ppm. No signal was observed which could

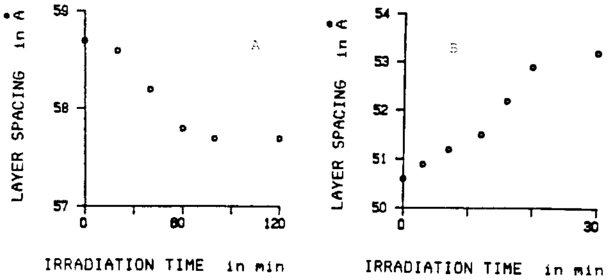

Figure 8. Change in layer spacings of LB multilayers upon irradiation with the filtered UV lamp A, 30 layers deposited on polyester: (a) docosadienol 1; (b) docosadienoic acid 3.

be attributed to a residual double bond, in spite of the UV absorption of polymer I. This might be explained by extreme broadening of such signals due to the location of the double bond in the polymer backbone. Also, no signals indicative of low molecular weight oxidation products could be detected. This is remarkable since the photoreaction is performed under air atmosphere. Presumably, oxygen diffusion into the layers is too slow to interfere with the polymerization process.

The ^{1}H NMR spectra of polymer I and polymer II are the same, except for the presence of an additional broad and intense multiplet signal at 3.7 ppm in that of the latter. This signal might point out the incorporation of oxygen in polymer II. It is well-known that oxygen is involved in the curing of unsaturated oils.[19] However, this uptake of oxygen may be merely a competitive side reaction, too.

The GPC plots of polymer I and the soluble fraction of polymer II are shown in Figure 7. They indicate that indeed oligomers and polymers are formed during the photoreaction. On the basis of the calibration with poly(methyl methacrylate), molecular weights of $\bar{M}_n = 1400$ and $\bar{M}_w = 3200$ are obtained for polymer I (Figure 7a). These values are probably too low considering the tight shape of the poly(docosadienol). Nevertheless, a fraction of the polymer was found in the exclusion volume of 32 mL, thus corresponding to molecular weights higher than 20 000. The molecular weight of the small soluble fraction of polymer II (Figure 7b) is lower than that of polymer I, with $\bar{M}_n = 1200$ and $\bar{M}_w = 1800$. Most notably, the polymer fraction in the exclusion volume has disappeared. This result is not surprising since cross-linking is more probable with the high molecular weight fraction, preferentially leaving low oligomers uncross-linked.

Small-Angle X-ray Scattering Studies of the Multilayers. SAXS was used to verify the multilayer structure of the built-up films and to study structural changes of the LB multilayers induced by the polymerization. The built-up films of the dienols 1 and 4 and of docosadienoic acid 3 show sharp layer reflections, thus verifying a well-ordered multilayer structure (Table III). As the observed layer spacings exceed the calculated length of the amphiphiles, the LB multilayers must be formed by sandwich bilayers ("Y-type" structure[2]). However, as the observed layer spacings are smaller than twice the length of the molecules, the amphiphiles must be tilted with respect to the layer normal. In contrast, for built-up LB films of docosadienal 2 no layer reflection could be observed, thus implying a fairly disordered structure of the coatings.

As reported for other amphiphiles,[6,7,20,21] the polymerization of the multilayers induces a change in layer spacing, i.e., the multilayers undergo a structural change (Table III). The layer spacings can either increase as observed for docosadienoic acid 3 or decrease as observed for the dienols 1 and 4. The two reaction steps of the polymerizations observed by UV spectroscopy (Figures 3 and 4) can be distinguished clearly by SAXS as well (Table III). LB multilayers of 3 exemplify that the initial increase in layer spacing during the first reaction step can be followed by a subsequent decrease during the second reaction step.

The changes in layer spacing in the first reaction step, i.e., the reaction of the diene moiety, are moderate, ranging from −6% for 4 to +5% for 3. Figure 8 illustrates the kinetics of the change in layer spacing. The changes take place continuously, and the curves are S-shaped. The continuous changes in layer spacing indicate a homogeneously distributed growth of polymeric chains within the layers.

The changes in layer spacing during the cross-linking reaction of the docosane derivatives 1 and 3 are also moderate with a value of ca. −2%, whereas the layer spacing of multilayers of octadecadienol 4 is decreased substantially by 16% during the cross-linking (Table III). This substantial structural change induces defects in the multilayers, which can be visualized qualitatively in the SEM when using porous support materials:[6,22] Pores of the polypropylene support (Celgard 2400) are coated by monomeric multilayers of 4 and are thus invisible. However, after the cross-linking reaction, the pores of the support become visible, indicating the creation of defects in the multilayers. This result agrees well with former studies where defects in polymeric LB multilayers become visible when the change in layer spacing exceeds a critical value.[6] In agreement, multilayers of 1 and 3, which undergo minor changes in layer spacing for both polymerization steps, cover successfully the pores of the support in the monomeric, in the polymeric, and in the cross-linked polymeric state.

Conclusions

Octadecadienol, docosadienol, and docosadienoic acid are able to build up polymerizable Langmuir–Blodgett multilayers. The photopolymerization occurs fast and can be carried out in two steps. The first one produces a soluble polymer and the second one an insoluble cross-linked polymer. NMR and GPC studies showed that indeed true polymers are produced by the photoreaction. Although not definitive, UV spectroscopic studies favor a 1,4-polymerization mechanism of the diene moiety for the first reaction step. It is noteworthy that no oxidized products were found in the soluble polymer although the samples were polymerized under air atmosphere. The characteristic change in layer spacing induced by polymerization was observed for all amphiphiles studied. In the case of octadecadienol, the cross-linking step causes such a substantial change in layer spacing that defects are created in the multilayer. In contrast, LB multilayers of docosadienol and docosadienoic acid undergo only minor changes in layer spacing. In agreement with that, no polymerization-induced defects could be observed by SEM. Therefore, and by virtue of their rapid photopolymerization, docosadienol and docosadienoic acid are well suited for the preparation of high-quality polymerizable LB multilayers.

Registry No. 1, 114583-81-2; 1 (homopolymer), 114583-83-4; 2, 114583-82-3; 3, 104118-26-5; 3 (homopolymer), 104118-27-6; 4, 77893-36-8; 4 (homopolymer), 80070-04-8; 5, 77893-37-9; 6, 629-56-1.

References and Notes

(1) Langmuir, I.; Blodgett, K. B. *Kolloid-Z.* **1935**, *73*, 257.
(2) Kuhn, H.; Moebius, D.; Buecher, H. In *Physical Methods of Chemistry*; Weissberger, A., Rossiter, B., Eds.; Wiley: New York, 1975; Vol. I, part IIIb, p 577.
(3) *Thin Solid Films* **1980**, *68*; **1983**, *99*; **1985**, *132–134*.

Macromolecules 1988, *21*, 1941–1961 1941

(4) Cemel, A.; Fort, T., Jr.; Lando, J. B. *J. Polym. Sci.* **1972**, *A-1/10*, 2061.
(5) Tieke, B.; Weiss, K. *J. Colloid Interface Sci.* **1984**, *101*, 129.
(6) Laschewsky, A.; Ringsdorf, H.; Schmidt, G. *Thin Solid Films* **1985**, *134*, 153.
(7) Tieke, B. *Adv. Polymer Sci.* **1985**, *71*, 79.
(8) Bader, H.; Dorn, K.; Hupfer, B.; Ringsdorf, H. *Adv. Polym. Sci.* **1985**, *64*, 1.
(9) Schupp, H.; Hupfer, B.; van Wagenen, R. A.; Andrade, J. D.; Ringsdorf, H. *Colloid Polym. Sci.* **1982**, *260*, 262.
(10) Fukuda, K.; Shibasaki, Y.; Nakahara, H. *Thin Solid Films* **1985**, *133*, 39.
(11) Barraud, A.; Rosilio, C.; Ruaudel-Teixier, A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1978**, *19* (2), 179.
(12) Ringsdorf, H.; Schupp, H. *J. Macromol. Sci. Chem.* **1981**, *A15*, 1015.
(13) Piancatelli, G.; Scettri, A.; d'Auria, M. *Synthesis* **1982**, 245.
(14) Albrecht, O. *Thin Solid Films* **1983**, *99*, 227.
(15) Buecher, H.; Elsner, O. V.; Moebius, D.; Tillmann, P.; Wiegand, J. *Z. Phys. Chem. NF* **1969**, *65*, 152.
(16) Gerner, J. Dissertation, Mainz, 1983.
(17) Tyminski, P. N.; Ponticello, I. S.; O'Brien, D. F. *J. Am. Chem. Soc.* **1987**, *109*, 6541.
(18) Green, B. S.; Lahav, M.; Schmidt, G. M. J. *J. Chem. Soc. B* **1971**, 1552.
(19) Kern, W.; Willersinn, H. *Angew. Chem.* **1955**, *67*, 573.
(20) Naegele, D.; Lando, J. B.; Ringsdorf, H. *Macromolecules* **1977**, *10*, 1339.
(21) Enkelmann, V.; Lando, J. B. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 1843.
(22) (a) Albrecht, O.; Laschewsky, A.; Ringsdorf, H. *Macromolecules* **1984**, *17*, 937. (b) Albrecht, O.; Laschewsky, A.; Ringsdorf, H. *J. Membrane Sci.* **1985**, *22*, 187.
(23) Fischer, A.; Sackmann, E. *Nature (London)* **1985**, *313*, 299.

Hydrogen-Bonded Highly Regular Strictly Alternating Aliphatic–Aromatic Liquid-Crystalline Poly(ester amides)

Shaul M. Aharoni

Engineered Materials Sector Laboratories, Allied-Signal Corporation, Morristown, New Jersey 07960. *Received December 18, 1987*

ABSTRACT: Forty-seven highly regular strictly alternating poly(ester amides) typified by each aromatic ring being bracketed by several methylene groups were prepared and studied. It was found that when the methylene sequences were sufficiently long, the poly(ester amides) exhibited multiple reproducible first-order transitions upon heating, which did not all reappear upon cooling. Many of the polymers with long alkylene groups grew ordered batonnet-like structures upon cooling from the isotropic melt, but not upon heating. The ordered structures grew upon cooling at temperatures far higher than the uppermost major endotherm in the heating cycle. A combination of DSC and hot-stage cross-polarized light microscopy revealed, upon heating, broad temperature intervals where spontaneous flow and intense or dull birefringence coexisted. Variable-temperature WAXD patterns coupled with X-ray scans on quick-quenched and on oriented samples revealed that in the flowing birefringent polymer upon heating, as well as the "batonnet" interval upon cooling, these poly(ester amides) are probably present in a smectic C liquid-crystalline form. The structure of these polymers, even in the mesomorphic phase, is dominated by H-bonds between amide groups in adjacent chains. Forty-one additional polymers were prepared in which the distances between amide pairs and ester pairs were randomized, the placement of ester and amide was irregular, or the ester group was replaced by either ether or amide groups. All these, as well as eight low molecular weight ester–amide model compounds, failed to show liquid crystallinity. Mesomorphicity appears to be limited to highly regular, strictly alternating aromatic–aliphatic poly(ester amides) in which the methylene sequences are neither too short nor too long and where interchain H-bonds hold the structure together.

Introduction

Polymeric liquid crystals (PLC) are categorized in two major groups: one is endowed with backbone, or main-chain, mesomorphicity and the other exhibits liquid crystallinity due to the nature of its side groups. In this paper only main-chain polymeric liquid crystals (MCPLC) will be considered. The onset of liquid-crystalline behavior of MCPLC may occur in the bulk due to changes in temperature, in which case it is termed thermotropic, or in solution as a result of changes in concentration, upon which it is called lyotropic. The MCPLC are divisible into three major subgroups according to the nature of the mesogenic groups and the interactions giving rise to mesomorphic behavior.

The first subgroup consists of rigid or semirigid wormlike macromolecules having rather large persistence length, q, and the same average rigidity all along the chain. This rigidity may arise from the backbone being aromatic with the rings connected in the para position by groups such as amides, esters, *trans*-vinylene, azo, azoxy, and azomethines, to render them rectilinear or colinear. Among such polymers one finds the lyotropic poly(*p*-benzamide),[1] poly(*p*-phenyleneterephthalamide),[1] and poly(*p*-benzanilide–terephthalamide)[2] and the thermotropic aromatic polyesters prepared from 4-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid[3] and from terephthalic acid, hydroquinone and 4,4′-biphenol.[3] Because of their rigidity these polymeric chains pack more or less in parallel bundles in space, and because of their polydispersity their liquid crystallinity is nematic in nature. Another kind of highly rigid macromolecule with very large q is the polyisocyanate family.[4] Here we have a highly rigid and extended backbone encased in substantially flexible and mobile side chains. When these are aliphatic or certain aralkyl side chains of appropriate length, the polyisocyanates exhibit both lyotropic and thermotropic liquid crystallinity.[5] In this case the main-chain extension and rigidity are mostly due to the cis–trans configuration of the adjoining amide bonds along the chain.[6,7] A third family of liquid-crystalline polymers is that of the cellulose derivatives.[8] These are mostly lyotropic even though some thermotropic cellulosics were reported in the literature. Depending on the nature and amount of substitution, the cellulose derivatives are soluble and exhibit liquid crys-

0024-9297/88/2221-1941$01.50/0