Polymerization of eicosenoic acid and octadecyl fumarate in Langmuir–Blodgett multilayers

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Langmuir–Blodgett multilayers of 2-eicosenoic acid and octadecyl fumarate were irradiated by ultra-violet (u.v.) light. The reaction was monitored by u.v. spectroscopy, and the photoproducts were isolated and identified to be polymers. The multilayers of both amphiphiles undergo substantial structural changes during polymerization, as observed by u.v. spectroscopy, small-angle X-ray scattering and scanning electron microscopy. The kinetics of the changes were investigated. The long-term stability and the thermal behaviour of monomeric and polymeric multilayers were studied as well. Partially polymerized samples underwent phase separation on storage. The melting of the multilayer structure was found to be partially reversible. Models for the different processes observed and their correlation are discussed.

(Keywords: multilayer; amphiphile; photopolymerization; structural change; thermal stability)

INTRODUCTION

In recent years, the widely recognized importance of supermolecular structures has created a strong interest in organized polymers. One aspect of this interest is the polymerization of monomers within organized structures such as crystals, inclusion compounds or liquid-crystalline matrices. A second aspect is the preparation of polymers capable of self-organization, such as polymeric liquid crystals, polysoaps or polymeric lipids. In particular, both aspects are combined in polymerizations of reactive amphiphiles within self-organized assemblies[1,2] like vesicles, monolayers at gas–water interfaces, or Langmuir–Blodgett (LB) multilayers: polymerization in an organized matrix and formation of a supermolecular polymer structure.

LB multilayers are characterized by a well defined, homogeneously ultrathin structure[3,4], which may offer some unique applications[4–8]. The polymerization of LB multilayers[10–20] has gained special interest because their well ordered structure enables valuable mechanistic studies of polymerizations[13], and because polymerization may provide the required stability for potential applications[5]. Up until now, applications of conventional LB multilayers have been restricted by their lack of stability, e.g. against ageing and solvents[9,10].

However, for all amphiphiles studied so far, polymerization not only provides enhanced stability but causes structural changes of the multilayers[10–19] which can result in defects[15–19]. In spite of the impact of such structural changes on any application considered for LB multilayers, little is known about the mechanisms involved.

We have studied the polymerization of 2-eicosenoic acid (**1**) and octadecyl fumarate (**2**) in LB multilayers (*Figure 1*). Multilayers of both amphiphiles undergo major structural changes on polymerization[15,21]. Because the structural changes observed are exceptionally large, they can be easily followed in the course of polymerization, and detailed studies of some processes involved are possible.

EXPERIMENTAL AND RESULTS

Materials

Eicosenoic acid (**1**) was synthesized starting from octadecanol (Fluka). Octadecanol is oxidized to octadecanal by pyridinium chlorochromate according to the general procedure reported in ref. 22. To a solution of 0.37 g malonic acid in 2.3 ml pyridine are added 0.66 g octadecanal. The mixture is reacted under nitrogen for 2 weeks at 40°C, and for an additional 12 h at 50°C. The mixture is poured onto half-concentrated HCl, and the precipitate is collected and washed with cold, dilute HCl and cold methanol. The colourless product is recrystallized twice each from methanol and petroleum ether. (Notes: Presence of oxygen produces notable amounts of stearic acid. Higher reaction temperatures yield a 50:50 mixture of 2-eicosenoic acid (**1**) and 3-eicosenoic acid.)

Yield: 0.45 g, waxy, colourless platelets, m.p. 65°C.

Elemental analysis: found, C 77.35%, H 12.21%; calcd for $C_{20}H_{38}O_2$ (*MW* 310.5), C 77.36%, H 12.34%. FD mass spec: mass at 310, 311.

^{1}H n.m.r.: δ (ppm) 0.9 (3H, t, CH_3–), 1.2–1.5 (30H, m, CH_3–$(C\underline{H}_2)_{15}$–), 2.2 (2H, m, –$C\underline{H}_2$–CH=CH–COO–), 5.8 (1H, d, –CH=C$\underline{H}$–COO–), 7.05 (1H, m, –C$\underline{H}$=CH–COO–).

1 $CH_3—(CH_2)_{16}—CH{=}CH—COOH$

2 $CH_3—(CH_2)_{17}—OOC—CH{=}CH—COOH$ *trans*

Figure 1 Investigated amphiphiles

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Octadecyl fumarate (**2**) was purchased from Merck and recrystallized several times from methanol.

^{1}H n.m.r.: δ (ppm) 0.9 (3H, t, CH_3–), 1.2–1.4 (30H, m, CH_3–$(C\underline{H}_2)_{15}$–), 1.65 (2H, m, –$C\underline{H}_2$–CH_2–O–), 4.2 (2H, t, –CH_2–$\overline{O}$–), 6.8 (1H, d, –CH_2–$O\overline{O}C$–CH=CH–COO–), 6.9 (1H, d, –CH_2–OOC–$C\underline{H}$=CH–COO–).

Spreading experiments and monolayer deposition

Eicosenoic acid (**1**) was spread from hexane solution, octadecyl fumarate (**2**) from hexane/ethanol (9:1 by vol.) mixture. The concentrations were ~0.1 mg ml^{-1}. All solvents were Uvasol grade (Merck). Spreading experiments were performed on a computer-controlled film balance[23], on pure aqueous subphase (equilibrated in air, pH = 5.8). The water was purified by distillation and subsequently by a millipore water purification system.

Multilayers were built up on a commercial film balance (Lauda), from pure water at 20°C. For the deposition of **1**, the surface pressure was 22 mN m^{-1}, the dipping speed downwards 5 cm min^{-1} and upwards 2 cm min^{-1}. For the deposition of **2**, the surface pressure was 30 mN m^{-1}, the dipping speed 3 cm min^{-1} downwards and 2 cm min^{-1} upwards. A drying period of 2 min between two subsequent dipping cycles was allowed for both **1** and **2**, to prevent retransferring of the last deposited monolayer to the water surface.

As support materials the following were chosen: quartz slides (Suprasil, Heraeus-Schott), foils of polypropylene (Trespaphan PED6, Kalle), foils of polyester (Hostaphan RE 3.0, Kalle), foils of polyvinylidenefluoride (30 μm, DKI Darmstadt) and a porous polypropylene membrane (Celgard 2400, Celanese). The quartz supports were freshly hydrophobized[24] prior to use. The polyester foil, the polyvinylidene foil and the polypropylene membrane were washed immediately before use with diethyl ether and water. The polypropylene foil was washed with acetone and water.

Polymerization

The multilayer samples were polymerized in air, by exposure to an unfiltered low-pressure mercury lamp (Hamamatsu model 937-002, maximum intensity at 254 nm), at a distance of 10 cm.

Analysis

^{1}H n.m.r. spectra were recorded with a 400 MHz n.m.r. spectrometer (Aspect, Bruker). U.v. spectra were recorded with a Beckman DU-6 spectrophotometer. The samples were built on hydrophobized quartz. Small-angle X-ray studies were performed with a powder diffractometer (Siemens type D-500), using Ni-filtered Cu Kα radiation (λ = 0.1541 nm). Layer spacings were calculated from the Bragg equation. The samples were built on polyester foil. In the experiments in which the influence of the support material was tested, the polypropylene foil and the polyvinylidene foil were used additionally. Scanning electron micrographs were taken with a Cambridge mark IIA model SEM. The samples were built on the porous polypropylene membrane and sputtered with gold.

Spreading behaviour

The surface pressure–area diagram of eicosenoic acid (**1**) at 20°C is displayed in *Figure 2*. Below 40°C, **1** forms solid-analogous phases exclusively with a high collapse pressure of ~50 mN m^{-1} and a collapse area of 0.19 nm/molecule, illustrating the tight packing of the hydrocarbon chains. The solid–solid phase transition at 15 mN m^{-1} is clearly visible, in analogy to isotherms of saturated fatty acids[25].

The spreading behaviour of octadecyl fumarate (**2**) has been described in detail previously[14]. At 20°C, solid-analogous phases with 50 mN m^{-1} collapse pressure and 0.19 nm/molecule collapse area are formed.

Both amphiphiles thus match the basic requirement for the preparation of ordered LB multilayers, the formation of solid–analogous phases.

Multilayer preparation and characterization

Although LB multilayers are built most easily by monolayers of their cadmium salts[12,15,26,27], multilayers of the free acids of **1** and **2** can be built up without difficulty on hydrophobic supports. Deposition takes place during both the downwards and the upwards dip (Y-type deposition[25]). Small-angle X-ray scattering (SAXS) of the obtained coatings shows sharp reflections of several orders, thus confirming the ordered multilayer structure (*Table 1* and *Figure 3*). For both **1** and **2** the corresponding layer spacings are larger than the calculated lengths of the molecules, i.e. the multilayers consist of sandwich bilayers (Y-type structure[25]). However, as the spacings found are smaller than twice the calculated length of the fatty acids, the amphiphiles must be tilted against the layer normal, a well known effect[11–17]. Because the thickness dependence of multilayer properties has been discussed recently[15,28,29], we investigated the thickness dependence of the layer spacing for **1** in detail. In the range studied from 6 to 30 layers, the layer spacing was independent of the number of layers deposited, and was independent of the hydrophobic support material chosen (polypropylene, poly(ethylene terephthalate), poly(vinylidene fluoride)).

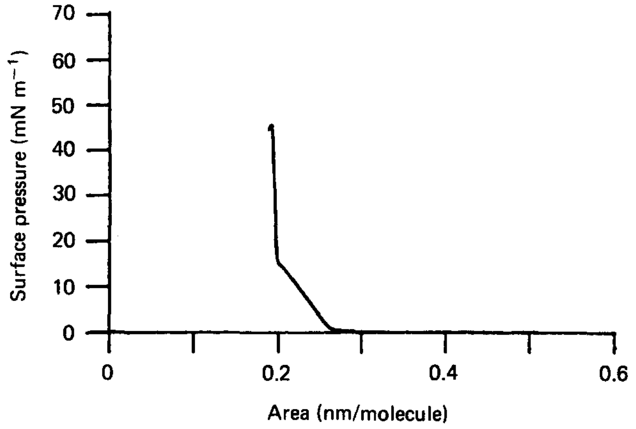

Figure 2 Surface pressure–area diagram of 2-eicosenoic acid (**1**) at 20°C on water

Table 1 Layer spacings of monomeric and polymeric LB multilayers of 2-eicosenoic acid (**1**) and octadecyl fumarate (**2**)

Amphiphile	Layer spacing (nm) Monomeric	Layer spacing (nm) Polymeric	Calculated length (nm)
1	3.98	5.10	2.9
2	4.41	5.68	3.3

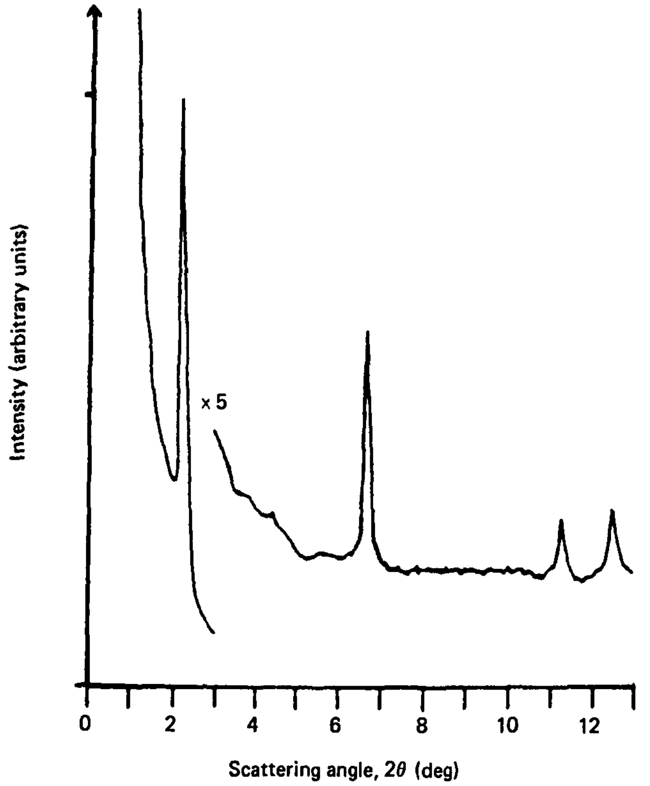

Figure 3 SAXS diffraction pattern of LB multilayers of 2-eicosenoic acid (**1**): 30 layers deposited on polyester foil. The reflection at $2\theta = 12.35°$ is due to the support

Scanning electron microscopy showed nearly defect-free multilayer coatings of **1** and **2** on the porous polypropylene membrane (magnification 20000×), the pores of which were already bridged by bilayers[14,30,46].

U.v. spectroscopic studies of the polymerization in LB multilayers

The progress of the u.v.-radiation-induced polymerization of **1** and **2** in LB multilayers can be monitored by the decrease of their u.v. absorbance. Both amphiphiles exhibit a single absorption peak, at 202 nm for **1** and at 214 nm for **2**, the intensities of which decrease on irradiation of the multilayers with u.v. light. While the u.v. peak of **1** slowly vanishes with irradiation, in the case of **2** some residual absorbance is left, even on prolonged exposure to u.v. light, indicating incomplete conversion.

Additionally, in the course of the photopolymerization of **1** and **2**, shifts of the absorbance maxima are observed. In the case of **1**, the absorbance maximum is shifted to longer wavelengths, from 202 nm to 215 nm (*Figure 4*). In the case of **2**, the absorbance maximum is shifted to shorter wavelengths, from 214 nm to 206 nm. The shifts of the absorbance maxima as functions of the irradiation time are exhibited in *Figure 5*. The graphs show that the major shifts take place in the initial stage of the polymerization. After 120 min irradiation, the final absorbance maxima have been reached.

As the shift of the absorbance maxima might imply changes of the extinction coefficient in the course of the polymerization too, the u.v. spectra are of limited use only to determine the degree of conversion. Additionally, the final baselines are difficult to determine exactly, as at the end of the polymerization, the initially transparent multilayer samples of both **1** and **2** look cloudy. Nevertheless, the decrease in dependence of the absorbance on the irradiation time still provides an approximate estimation of the time–conversion curve (*Figure 6*). Under the conditions applied, the polymerization rates of **1** and **2** are comparable, but only in the case of eicosenoic acid (**1**) is complete conversion achieved. The incomplete conversion of octadecyl fumarate (**2**), implied by its residual absorbance, was attributed to its topochemically controlled photopolymerization in LB multilayers[12,14].

Characterization of the polymers

The decrease of the monomer absorbances indicates the conversion of the monomers. However, it cannot be taken for granted that polymers are formed, i.e. octadecyl fumarate (**2**) might undergo dimerization reactions[31]. To verify the polymeric nature of the photoproducts, irradiated samples were extracted from hydrophobized

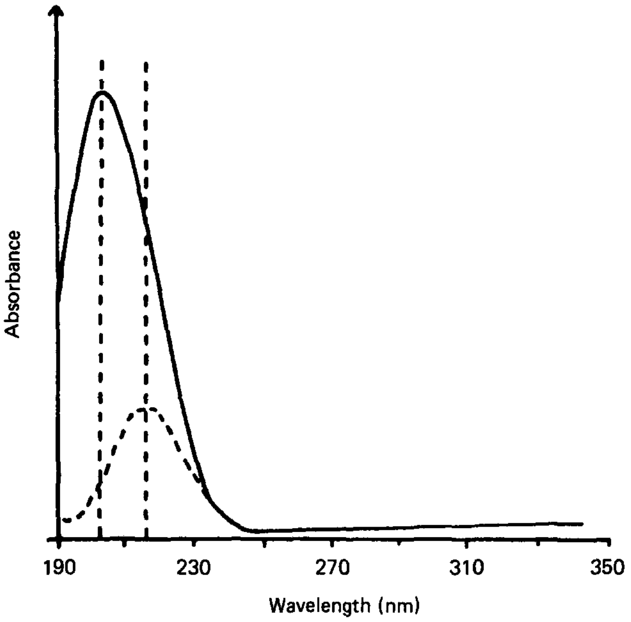

Figure 4 U.v. spectra of LB multilayers of 2-eicosenoic acid (**1**). Change of the absorbance maxima with irradiation time: (———) monomer; (– – – –) 150 min irradiation with u.v. light. For monomer, $\lambda_{max} = 202$ nm; for irradiated sample, $\lambda_{max} = 214$ nm

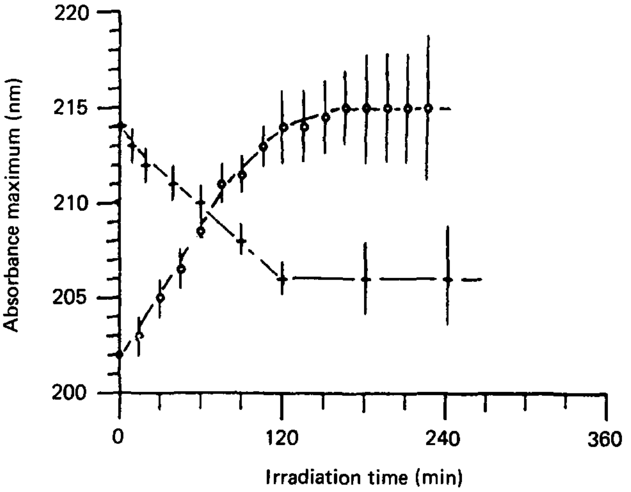

Figure 5 Shift of the absorbance maxima of LB multilayers with u.v. irradiation time: (○) 2-eicosenoic acid (**1**); (+) octadecyl fumarate (**2**)

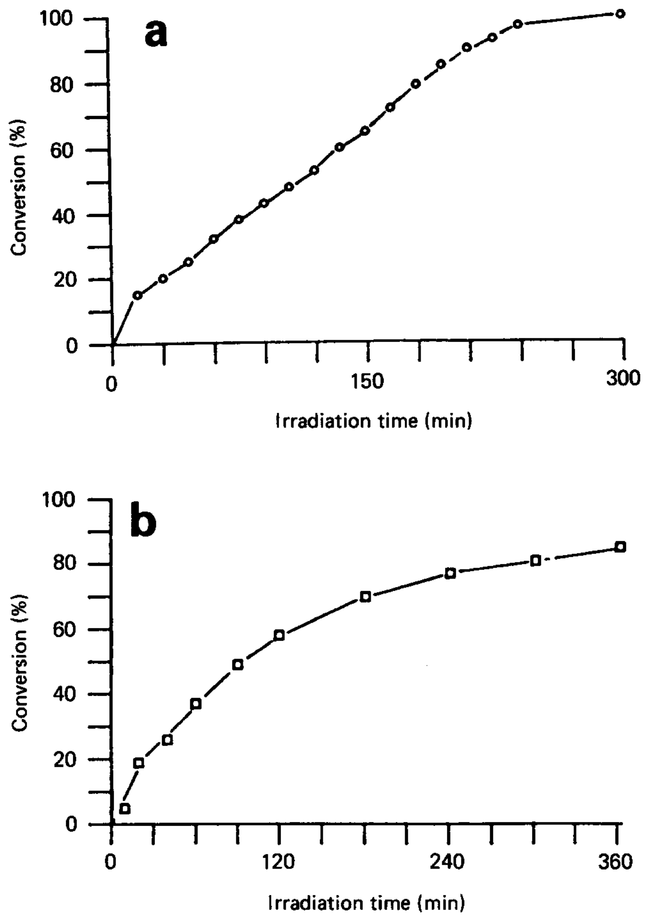

Figure 6 Estimated conversion–time curves for the polymerization in LB multilayers. Conversion estimated by $[E(0)-E(t)]/E(0)$ with $E(0)$ = maximal monomer absorbance, $E(t)$ = maximal actual absorbance: (a) = 2-eicosenoic acid (**1**); (b) = octadecyl fumarate (**2**)

quartz plates with chloroform, as described previously[32]. The photoproducts of **1** and **2** were completely soluble, leaving the plates cleanly hydrophobic after the extraction. The products were characterized by ^{1}H n.m.r. spectroscopy.

The n.m.r. spectrum of irradiated **1** showed that the signals of the vinyl and allyl protons at 2.2, 5.8 and 7.05 ppm have disappeared. All residual signals are broadened strongly. Two broad new signals are observed at 2.3 and 2.5 ppm. Any signals pointing to the presence of cyclobutanes or oxidized photoproducts are missing.

The n.m.r. spectrum of irradiated **2** shows nearly complete loss of the signals of the vinyl protons at 6.8 and 6.9 ppm and of the α-methylene protons at 4.2 ppm. Only traces of these signals can be seen, indicating small amounts of residual monomer in agreement with the u.v. spectra. However, according to the n.m.r. spectrum, the amount of residual monomer is well below 10%, which is less than estimated from the residual u.v. absorbance. All other proton signals are strongly broadened, with new broad signals observed at 3.2 and 4.0 ppm. Any signals pointing to the presence of cyclobutanes or oxidized photoproducts are missing, as observed for irradiated **1**.

Thus, the characterization of the photoproducts verifies that the irradiation of **1** and **2** in LB multilayers yields polymers or oligomers. There is evidence neither for the formation of dimers by 2+2 photocycloaddition[31] nor for photo-oxidation[57] of the amphiphiles.

Small-angle X-ray scattering (SAXS) experiments of the polymerization in LB multilayers

As reported for all studied polymerizable amphiphiles[10–19], polymerization of **1** and **2** in LB multilayers is coupled with changes of the layer spacings. For both **1** and **2**, polymerization leads to increases of the layer spacings by nearly 30% (*Table 1*), which are among the largest observed so far. As reported, substantial increases of the layer spacing can cause defects in polymerized multilayers[14–19,41]. Large defects can be visualized by the use of porous support materials[14,46]. For example, SEM micrographs of polymerized multilayers of **1** and **2** deposited on the porous polypropylene membrane show clearly the pores of the support, although the pores have been completely covered by the monomeric layers.

The exceptionally big changes of the layer spacings enable irradiation-time-dependent studies. The layer spacings as functions of irradiation time are shown in *Figures 7* and *8*. The increases of the layer spacings can be described by an S-shaped curve. In the initial stage of the

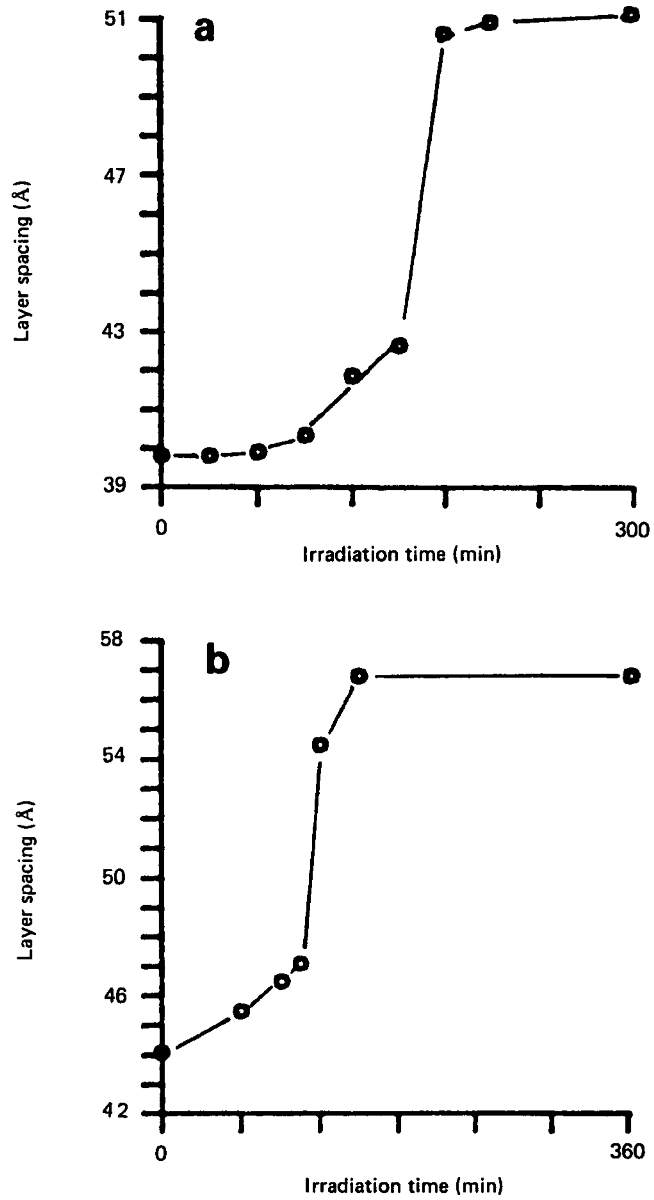

Figure 7 Change of layer spacing of LB multilayers during the polymerization: (a) = 2-eicosenoic acid (**1**); (b) = octadecyl fumarate (**2**)

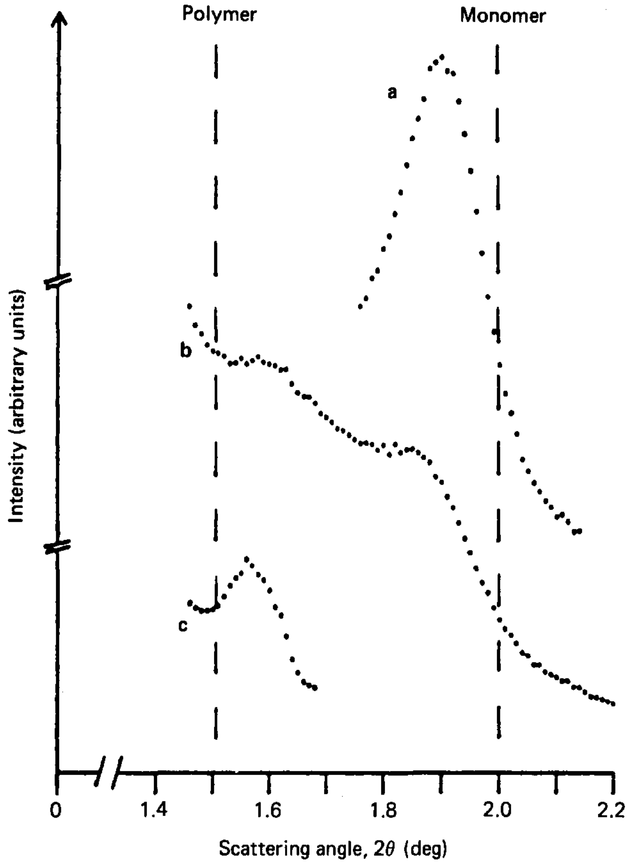

Figure 8 Change of the SAXS diffraction pattern of LB multilayers of octadecyl fumarate (**2**) during the polymerization. Irradiation time: A, 105 min; B, 120 min; C, 150 min

polymerization, the layer spacings change marginally. In the intermediate stage, after 120–180 min u.v. irradiation, the major changes takes place, and in the final stage after 180 min irradiation there are only slight increases towards the final spacing of the polymeric layers (*Figure 7*). The scattering intensities exhibit an analogous dependence on irradiation time. In the initial stage of the polymerization, the intensities of the slowly shifting layer reflection decrease, and pass through a minimum at ~150 min irradiation, when the major increases of the spacings occur. In this intermediate stage, the reflections are reduced to strongly broadened, weak signals. In the case of **2**, even two weak, broad reflections are observed, one close to the spacing reflection of the monomeric layers, one close to the spacing reflection of the final polymeric layers (*Figure 8*). After 180 min of irradiation, when the changes of the layer spacings are nearly completed, the intensities of the layer reflections increase again with irradiation time (*Figure 8*).

The observations can be explained by a transition of a monomer matrix to a polymer matrix via a distorted transition state. The polymer chains grow homogeneously distributed in the layers and distort the monomer matrix increasingly, until the increasing polymer content forces the transition into the polymer matrix. However, residual monomer distorts the newly formed polymer matrix. Further polymerization decreases the amount of monomer left, thus reducing the distortion of the polymer matrix. Accordingly, the two broad reflections of multilayers of octadecyl fumarate (**2**) in the intermediate stage show the presence of both the distorted monomer matrix and the distorted polymer matrix. Whether the phase separation occurs horizontally within the layers, or vertically, perhaps due to slightly different radiation doses in the upper and lower layers, cannot be decided. The problem is discussed in more detail below.

Comparison of the u.v. data and the SAXS data

As shifts of the absorbance maxima in the course of the polymerization have been reported only for amphiphiles which undergo large changes of their multilayer spacing^{14}, it is interesting to compare the time dependences of both processes. To ease the comparison, time-dependent changes of the absorbance maximum, of the layer spacing and of the conversion are plotted for **1** in *Figure 9* on the same scale: 0% change corresponds to the initial, monomeric property; 100% change corresponds to the final, polymeric property. The analogous plot for **2** is qualitatively identical. The graph illustrates that the change of the absorbance maximum and the change of the layer spacing occur at different stages of the polymerization: the shift of the absorbance maximum has already ended when the major increase of the layer spacing takes place, i.e. the two processes cannot be directly interdependent.

The u.v. shift represents a change of the environment of the chromophore, which is a part of the reactive hydrophilic head group. In contrast, the increase of the layer spacing represents a rearrangement of the hydrophobic chains. Possibly, the reactive head groups form a sublattice, which is changed continuously during the polymerization. The increasing mismatch between the arrangement of the head groups and the hydrophobic chains starts to deform the monomer lattice, finally forcing a rearrangement of the hydrophobic chains to form the polymer lattice.

Long-term behaviour of the multilayers

The long-term behaviour of LB multilayers of 2-eicosenoic acid was studied by SAXS. No change of the scattering patterns could be detected for monomeric multilayers, when SAXS experiments were performed in a period between 1 h and 6 months after sample

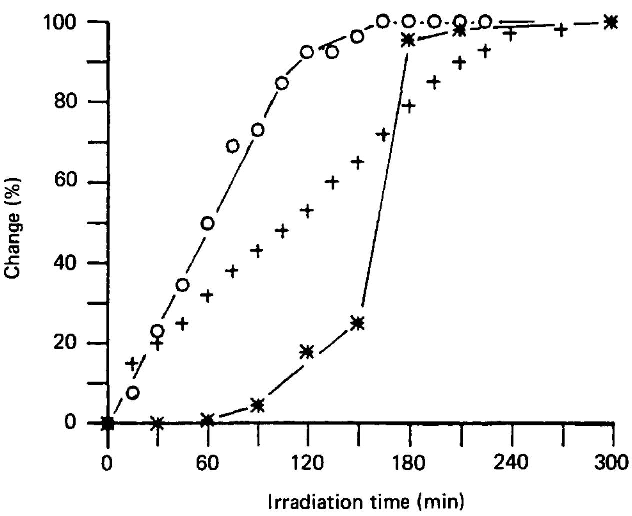

Figure 9 Comparison of the structural changes occurring during the polymerization of 2-eicosenoic acid (**1**) in LB multilayers. Data taken from *Figures 5–7*. 0% change corresponds to the monomeric, 100% change to the polymeric multilayers. Curves: (+) conversion; (○) shift of the absorbance maximum; (*) change of the layer spacing

preparation. In the case of polymeric multilayers, the intensity of the layer reflections was found to increase notably in the first 72 h of storage; the reflection angles, however, were constant.

In the case of partially polymerized multilayers, when multilayer samples are irradiated for 150 min to the onset of the major increase of the layer spacing, the scattering pattern of the samples changes considerably with storage (*Figure 10*). There seems to be only one broad, weak reflection immediately after irradiation, although it cannot be excluded that a second even weaker reflection is hidden in the noise at slightly smaller scattering angle (*Figure 10*, curve A). On storage, two reflections are observed which move slowly towards the reflection angles of the original monomer matrix and of the final polymer matrix respectively with prolonged annealing. The shift of the scattering angles is paralleled by increasing signal intensities (*Figure 10*, curves B–D).

Obviously, phase separation occurs in the partially polymerized multilayers into a 'monomer' phase and a 'polymer' phase. Possibly, monomeric amphiphiles migrate fast enough to enable a concentration or depletion of residual monomers in certain areas. This model would imply a higher mobility of the amphiphiles in the layers than generally assumed. Such a phase separation would correspond to the phase separation of monomeric and polymeric lipids observed in monolayers and liposomes[33,34].

Alternatively, a vertical phase separation must be considered, e.g. between the upper and the lower layers of the multilayer due to the slightly different radiation doses. The layers with the higher radiation dose would relax into the polymer matrix, the ones with the lower dose into the monomer matrix, as discussed above for multilayers of octadecyl fumarate (**2**).

Thermal behaviour

Although the thermal behaviour of LB multilayers is of major importance for most of the applications considered, it has been scarcely studied up to now[35–39]. Especially studies on polymeric multilayers are confined to a few reports[10,26,39–43]. We studied the thermal behaviour of monomeric and polymerized LB multilayers of eicosenoic acid (**1**) by SAXS. Eicosenoic acid was chosen because it does not polymerize thermally and is stable at least up to 160°C. D.s.c. traces show only one sharp melting peak at 64°C.

The results of the SAXS experiments are illustrated in *Figures 11* and *12*. When the monomeric multilayers are heated up to 63°C, which is just below the melting point in bulk, no change of the scattering pattern could be detected. The position and intensity of the layer reflections are constant. At 65°C, no layer reflections are observed any more (*Figure 11*). However, if the sample has been kept below 70°C, the layer reflections reappear when the sample is cooled. The reflections appear directly on cooling below 63°C, and are increased in intensity neither by further cooling nor by annealing. Annealing the samples at 70°C for 5 h keeps the positions and intensities of the reappearing reflections unchanged. If the multilayers are heated up to 80°C and then cooled below 64°C, a structural rearrangement takes place: layer reflections of several orders are found, which are shifted to greater scattering angles, i.e. the layer spacing decreases from 3.98 to 3.46 nm. Additional weak reflections are found at the original positions, indicating regions with the original structure still present. The phase separation might be horizontal within the layers, or vertical, e.g. preserving the original structure in the lower layers close to the support. Cyclic heating of the multilayers to increasingly higher temperatures and intermediate cooling to 20°C causes the stepwise loss of the scattering intensities, without changing the scattering pattern. Even after annealing at 120°C, a layer structure is partially reformed on cooling. If the multilayers are annealed at 135°C, no layer reflections are found any more on cooling.

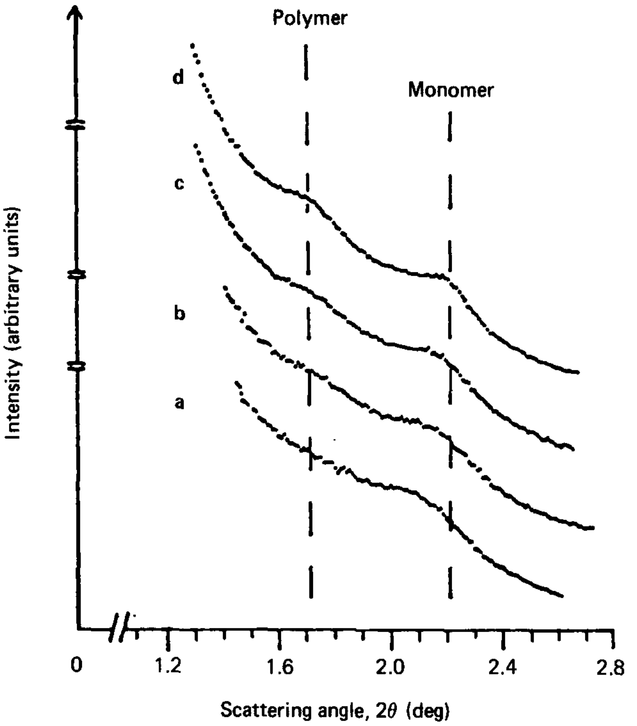

Figure 10 Change of the SAXS diffraction pattern of partially polymerized LB multilayers of 2-eicosenoic acid (**1**) on tempering at 20°C. Multilayers irradiated for 150 min. Tempering time: a, none; b, 1 day; c, 3 days; d, 30 days

The thermal behaviour of polymerized multilayers of **1** is exhibited in *Figure 12*. While heating up to 40°C does not change the scattering pattern, already at 45°C all scattering reflections are lost. Obviously, the 'melting point' of the polymerized multilayer structure is lower compared to that of the monomeric layers. This result corresponds to thermal studies on monomeric and polymerized LB multilayers of cadmium octadecyl fumarate by grazing-incidence i.r. spectroscopy[39,41]. It can be related to the decrease of the phase transition temperature of polymerized liposomes[44,45]. The direct covalent binding of the hydrophobic chains to the polymer backbone interferes with efficient packing of the chains, thus lowering the transition temperature[46]. This is particularly true for vinyl monomers, as the length of the repeat unit is small compared to the diameter of the hydrocarbon chain.

On cooling the polymeric multilayers to 20°C the original scattering pattern reappears, with increased intensity (*Figure 12*). In contrast to the monomeric multilayers, the scattering pattern evolves not directly on cooling, but is increased with decreased temperatures and increasing annealing time at low temperature. Cyclic

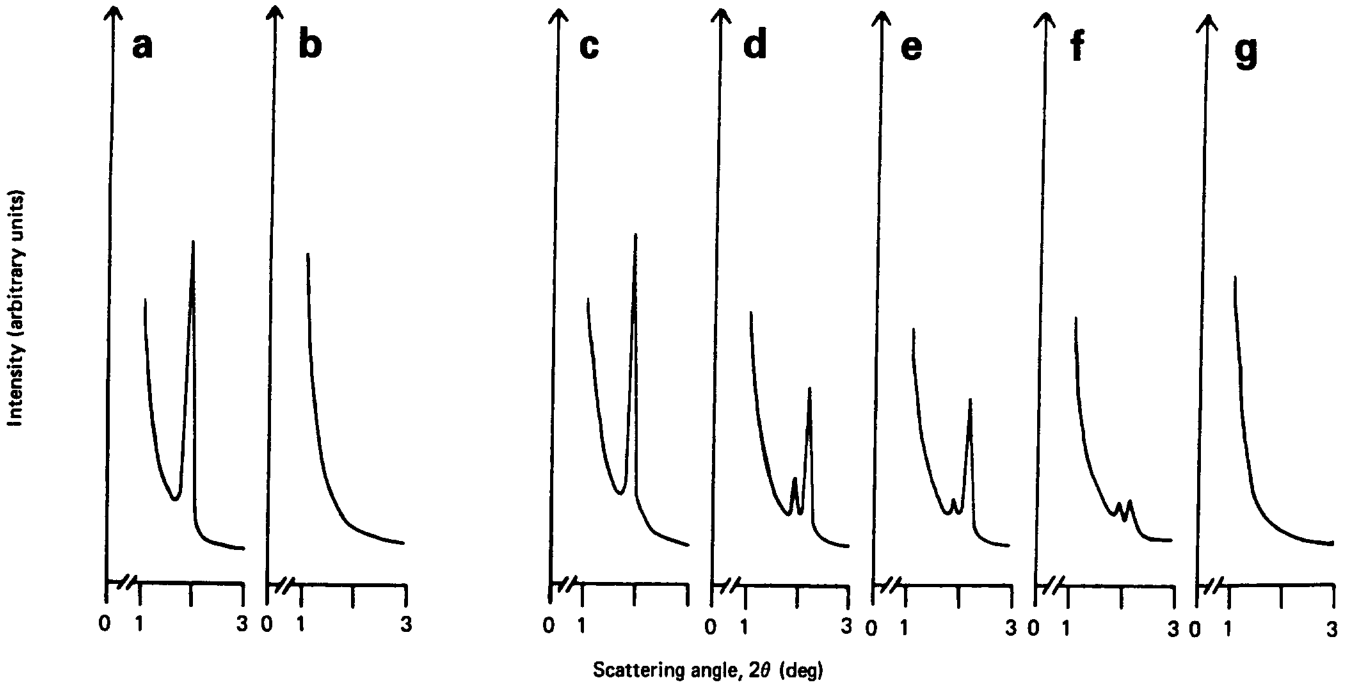

Figure 11 SAXS diffraction patterns of monomeric LB multilayers of 2-eicosenoic acid (**1**): (a) 60°C; (b) 65°C; (c) 20°C, sample tempered at 70°C; (d) 20°C, sample tempered at 90°C: (e) 20°C, sampled tempered at 105°C; (f) 20°C, sample tempered at 120°C; (g) 20°C, sample tempered at 135°C

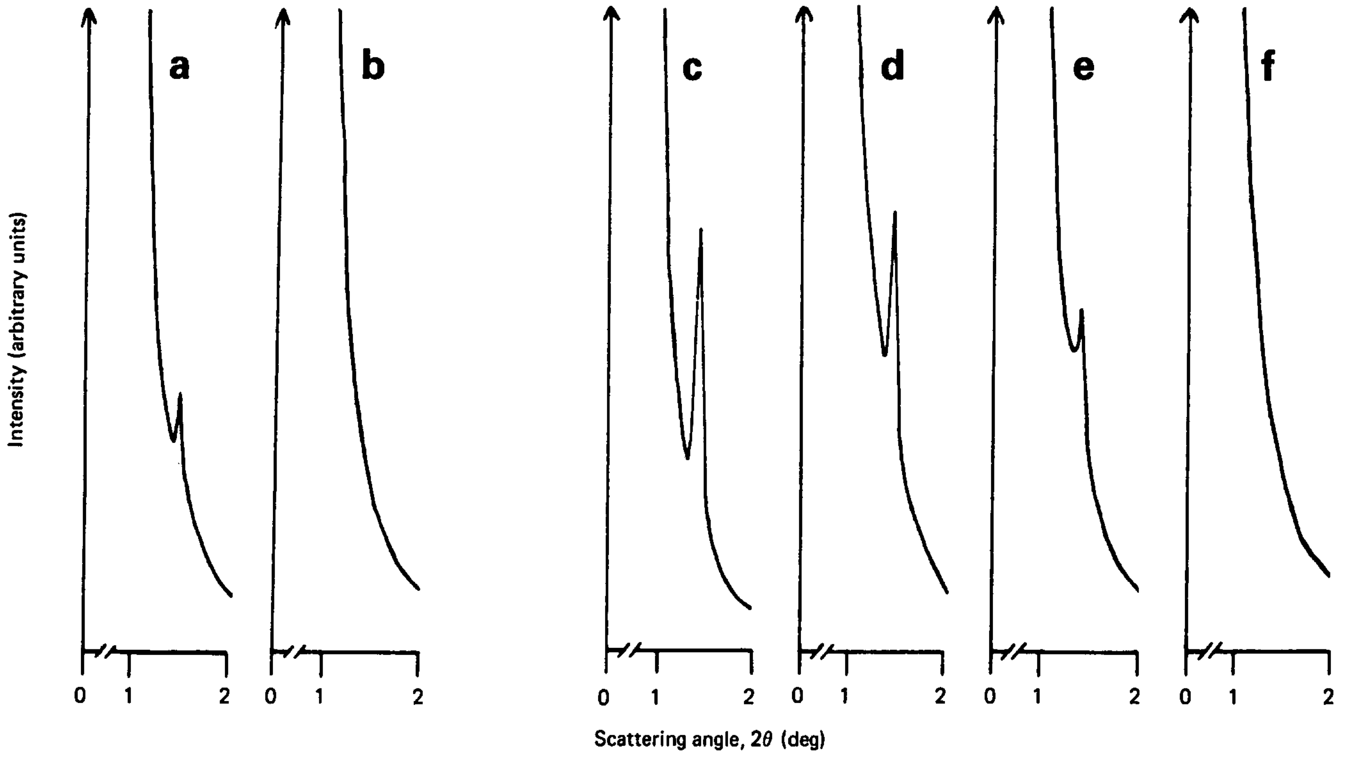

Figure 12 SAXS diffraction patterns of polymerized LB multilayers of 2-eicosenoic acid (**1**): (a) 20°C; (b) 50°C; (c) 20°C, sample tempered at 50°C; (d) 20°C, sample tempered at 80°C; (e) 20°C, sample tempered at 100°C; (f) 20°C, sample tempered at 110°C

heating of the polymeric multilayers to increasingly higher temperatures and intermediate cooling to 20°C results in a stepwise loss of scattering intensity. Opposite to the monomeric multilayers, no change of the scattering pattern is observed. As long as the polymeric layers are kept below 110°C, the layer structure is partially reformed on cooling. If the samples are heated up to 110°C, no layer reflections are found any more on cooling.

According to the described thermal behaviour of monomeric and polymeric multilayers of **1**, the layers are capable of partial reorganization after 'melting' within a limited temperature range. The 'melting' of the layer structure should correspond to a melting of the hydrocarbon chains. As discussed above, a sublattice of the hydrophilic head groups might be considered, the melting point of which is much higher. Its preserved structure enables the ordered reorganization of the recrystallizing hydrocarbon chains. A similar model has been proposed previously[39].

It should be noted that the scattering pattern of the polymeric multilayers disappears at lower temperatures compared to the monomeric ones. That means the loss cannot be mainly due to thermodesorption processes, which seem to be important for the thermal decomposition of multilayers of fatty acid salts[43]. The polymeric multilayers would desorb at much higher temperatures than the monomeric ones, which is opposite to the observed behaviour.

CONCLUSIONS

The u.v. irradiation of 2-eicosenoic acid (**1**) and octadecyl fumarate (**2**) was found to yield polymers in LB multilayers. Although the photopolymerizations are performed in air, no photo-oxidation takes place. This may be due to the tight packing of the hydrophobic chains, which prevents a fast, interfering oxygen diffusion. In the course of the polymerization, structural changes of the hydrophobic regions as well of the hydrophilic regions, in which the reactive moieties are incorporated, occur. However, both processes do not occur in parallel, but as different stages of the polymerization. The change of the hydrophilic region, in which the polymerization takes place, is the faster process. The rearrangement of the hydrophobic changes may be caused by an increasing mismatch of the proposed head-group sublattice and the chain sublattice. The increasing mismatch may be responsible as well for the phase separation into polymeric and monomeric domains, which is observed in partially polymerized multilayers on storage. This might imply a much higher mobility of the amphiphiles in the solid multilayers than generally assumed. Thermal studies showed that eicosenoic acid is able to reorganize in the original layer structure when heated above the melting point of the multilayer structure and recooled, within a limited temperature range. This result supports the model of the head-group sublattice, the preserved structure of which enables the observed reorganization of the molten hydrophobic chains on cooling.

The observations that the polymeric multilayer structure melts below the monomeric one, that the polymerizations are connected with substantial structural changes and that defects can be induced during the polymerizations underline the basic problems involved in the polymerization of vinyl monomers in LB multilayers. They can be referred to the discrepancy between the rather large cross-section of the hydrocarbon chains and the rather small vinyl repeat unit: the formation of the polymer backbone interferes with the necessary packing of the hydrophobic chains[46]. Thus, monomers yielding polymeric backbones with longer repeat units such as diynes[13,17,47–49], dienes[13,14,32,50–52] or ethylene oxides[53] seem to be more favourable to prepare high-quality polymeric LB multilayers. Alternatively, amphiphiles suited for four-centre polymerization[54] or amphiphiles containing flexible spacer groups[46] should be chosen. The use of prepolymerized amphiphiles[46,55,56] has to be considered too, which is however severely restricted concerning ease, speed and quality of the multilayer preparation.

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