Order–disorder transitions in Langmuir–Blodgett films. II. IR studies of the polymerization of Cd–octadecylfumarate and Cd–octadecylmaleate

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The two isomeric compounds, octadecylfumaric acid and octadecylmaleic acid ($C_{18}H_{37}OCOCH = CHCOOH$) have been synthesized, and Langmuir–Blodgett films of their cadmium salts have been studied by means of transmission and grazing incidence reflection infrared spectroscopy. These measurements provided information about the orientation of molecular segments relative to the substrate surface as well as about the lateral packing of the chains in the unit cell. A structural change of the maleate film was revealed at elevated temperatures. Polymerization of the films was brought about by either UV irradiation or thermal treatment and was followed spectroscopically as a function of exposure time. By comparison with films polymerized on the water surface of a Langmuir trough, it was concluded that the molecular structure is independent of where the polymerization occurs. Interestingly, upon polymerization on the water surface the fumarate undergoes an expansion at constant surface pressure whereas the maleate contracts. A mixture of fumarate and maleate in the ratio of 1 to 3, however, forms a two dimensional solution and preserves its area upon polymerization, a critical feature required for the fabrication of crack free Langmuir–Blodgett films polymerized on solid substrates.

INTRODUCTION

Structural studies of Langmuir–Blodgett (LB) films have revealed both information about the molecular orientation relative to a surface[1–8] and about their intermolecular arrangement in the crystallographic unit cell.[9] However, such films have limited utility because of the lack of in-plane mechanical integrity. In general, this results because of the absence of strong in-plane intermolecular interactions which could strengthen the films. Attempts to circumvent these problems have led to the syntheses[10–16] of novel compounds incorporating reactive groups within the fatty acid backbone of the monolayer components. Upon exposure to UV, electron, or x-ray radiation, polymerization occurs with the resulting polymer backbone usually lying in the plane of the LB film, providing enhanced mechanical stiffness. Polymerized LB films also can exhibit dimensional stability because the thermal expansion coefficient of polymers in a direction parallel to the chain axis can be quite small.

Although the first molecules polymerized in an LB monolayer contained vinyl end groups,[10] the most common systems under investigation are those that contain diacetylene units incorporated into the hydrocarbon backbone.[11–13] It has been shown that a unique aspect of a diacetylene polymerization was that it was topochemically controlled,[11] i.e., polymerization did not occur randomly between adjacent chains but proceeded along a specific crystallographic direction. The attractiveness of such a mechanism lies in the fact that polymerization in an LB film with biaxial orientation could provide 2D films with a high degree of anisotropy, exhibiting, for example, a sizable nonlinear optical coefficient in one particular direction. However, this anisotropic polymerization is not without its drawbacks since examination of reacted films by electron microscopy[15,16] indicated the presence of large cracks and fissures due to the inherent contraction of the monomer film upon exposure to radiation. Hence, diacetylene films have seen restricted use in technological areas where their insulation properties are important. To overcome these shortcomings, the syntheses of new classes of polymerizable molecules have been initiated.[13,14]

Although it has been proposed[17] that LB films have a potential for use in microelectronics and chemical sensors, comparatively very little work has appeared in the literature detailing the molecular structure of such monolayer films. This is primarily due to the lack of nondestructive techniques needed to characterize thin films in the 10–200 Å range. It is only in the past several years, with continued instrumental advances, that studies [8,9,18–22] of monolayers and multilayers ($n < 10$) have begun to appear. Driven by the interest in understanding the relationship between structure and function, researchers have turned towards the use of vibrational spectroscopy in order to determine the orientation of monolayer components relative to a surface and to understand the nature of intermolecular association which is responsible for monolayer stability. Towards this end, infrared reflection at grazing incidence, originally suggested by Greenler,[23] has become extremely useful for the study of LB monolayer assemblies. Recent studies[18,19] have dealt with the comparison of structures obtained from self assembly vs trough assembly, while others[20,21] have reported the characterization of molecular reorganization as LB monolayers are melted at elevated temperatures.

The intention of the present work was to compare the structure and orientation of the molecular components in an LB film before and after polymerization as well as at elevated temperatures. UV and thermal polymerizations of two isomers—octadecylfumarate (ODF) and octadecylmaleate (ODM)—have been investigated to ascertain orientation differences which might be caused by the different configurations of the double bond. Although the former had been previously[24] studied, it was felt that a reinvestigation of ODF, together with its *cis* counterpart (ODM), by using IR

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polarization measurements would be instructive in understanding the mechanism associated with polymerization. In addition, a parallel study of these two materials and their mixtures provided an opportunity to study the macroscopic behavior of polymerizing LB films, both on the water surface and on a solid substrate.

EXPERIMENTAL

Synthesis of ODF was carried out as follows: Purified octadecanol in ether was added over 3 h to a dry ether solution of furmaryl chloride (three to fourfold molar excess) under argon at 0 °C. The reaction was continued until thin layer chromatography showed no remaining octadecanol (about 1–2 h). The crude product was isolated by hydrolysis in the presence of tetrahydrofuran as a cosolvent and then partitioned between water and ether. After evaporating the ether a tan to brown solid was obtained. The product was purified by flash column chromatography (methylene chloride, ether, ethanol, and acetic acid mixture). The product was obtained after evaporation of solvent at 23 °C in 72% yield as white feathery flakes of mp 91–92 °C (uncorr.).

I.R. (melt, in microns):2.86–4.1 (broad), 3.42, 3.50, 5.75 (strong), 6.09(weak), 6.85, 7.05, 7.80, 7.94, 8.60, and 10.2.

^{1}H NMR($CDCl_3$–DMSO, in ppm relative to TMS): $0.89\delta(t$, 3H), $1.3\delta(s$, 32H), $4.15\delta(t$, 2H), and $6.71\delta(s$, 2H).

The preparation of ODM was carried out as follows: Purified octadecanol was added to an excess (3 M) of maleic anhydride in tetrahydrofuran. The mixture was refluxed until thin layer chromatography showed no remaining alcohol and the product was isolated in a procedure similar to that used for ODF. The product was obtained in 62% yield as white flakes, mp 78.5–80 °C (uncorr.).

I.R. (melt, in microns):2.86–4.1(broad), 3.42, 3.50, 5.78(strong), 5.82(strong), 6.11(weak), 6.82, 7.04, 7.50–8.45, and 8.60.

^{1}H NMR ($CDCl_3$–DMSO, in ppm relative to TMS): $0.87\delta(t$, 3H), $1.3\delta(s$, 32H), $4.13\delta(t$, 2H), and $6.25\delta(s$, 2H).

Both ODF and ODM gave microanalyses in agreement with the molecular formulas (71.7% C, 11.0% H).

The cadmium salt of ODF was prepared as follows: The acid in chloroform (150 mg in 15 ml) was agitated with a solution of cadmium acetate in water (200 mg in 15 ml) and then allowed to stand overnight. The salt which formed at the chloroform–water interface was collected by vacuum filtration and washed with water, methanol, and chloroform. The dull chalky white solid was recrystallized from 8 ml to 1:1:8 chloroform:water:dioxane to yield 123 mg of a shiny white powder. The cadmium salt of ODM was formed similarly. Crystallization from 18 ml of 1:1:8 chloroform:water: dioxane yielded 100 mg of shiny white flakes.

The LB films were prepared on a commercially available film balance (Joyce Loebl), which had been modified by replacing the originally supplied glass trough by a shallower Teflon tank. The enclosure of the whole apparatus was purged with argon to avoid possible oxidation. The subphase was doubly distilled water, containing 2.5×10^{-4} mol/ℓ $CdCl_2$ and NH_4OH to maintain the *p*H around 8. ODF and ODM were both dissolved in chloroform. For the polymerization on the water surface a UV lamp (Spectroline R-51) was used with monochromatic radiation at $\lambda = 254$ nm, the intensity being 1.5 mW/cm^2, uniform over an area of 16×8 cm^2. Under these conditions, the surface pressure of the saturated fatty acid salt, Cd-arachidate, did not change during an hour of UV illumination, indicating no photolysis was occurring. The filter, cutting off at wavelengths shorter than 254 nm, was, however, necessary to avoid photolysis. Otherwise the monolayer area of Cd-arachidate as well as ODF and ODM shrunk steadily with time. Monolayers of the Cd salts of ODF and ODM were transferred as *Y*-type films (head-to-head, tail-to-tail) at a dipping speed of 3 mm/min and a pressure of 30 mN m^{-1}. Substrates were either thallium bromoiodide (KRS-5) for transmission or aluminum coated microscope slides for reflection.

Differential scanning calorimetric (DSC) measurements were made with a DuPont 1090 thermal analyzer using heating rates of 2–10 °C min^{-1}. The transmission temperatures reported correspond to the peak (or trough) positions of the endotherms obtained from a DSC trace.

FTIR studies were a combination of grazing incidence reflection (GIR)[25] and transmission spectroscopy. As shown schematically in Fig. 1, the commercially available (Harrick) grazing incidence reflection accessory has been modified in order to heat and irradiate[26] the LB films *in situ* under vacuum. In order to accommodate the high temperature (20–200 °C) measurements, the standard DELRIN block which holds the sample substrate and transfer mirror, was replaced by one made of stainless steel. *In situ* irradiation of the LB films was done with the 254 nm line of the same UV lamp as that used on the LB trough. Irradiation

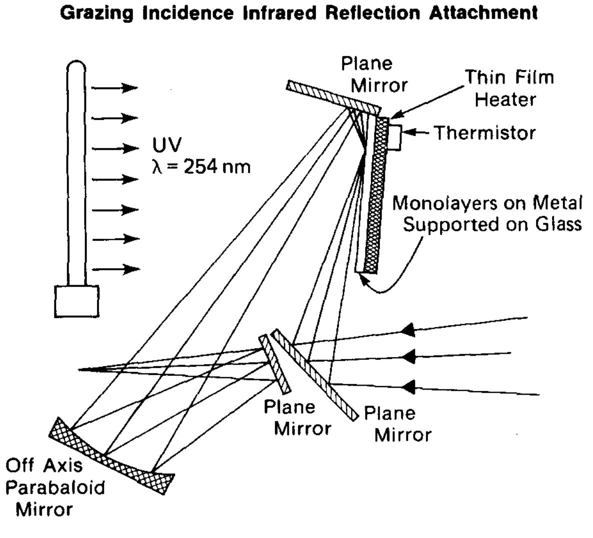

FIG. 1. Schematic of the grazing incidence reflection attachment with sample heater and UV lamp.

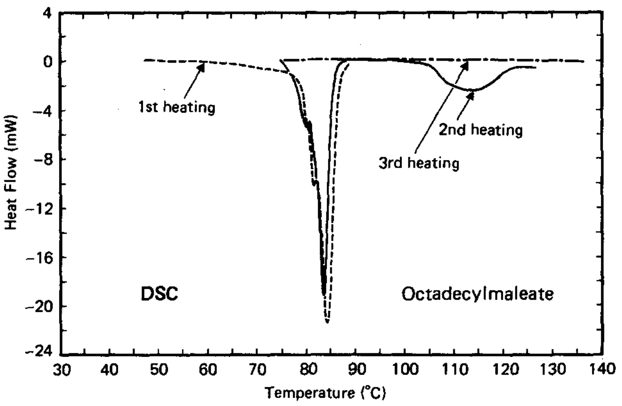

FIG. 2. Differential scanning calorimetry (DSC) thermogram for first and second heating of bulk Cd–octadecylmaleate (Cd–ODM), obtained at a heating rate of 2 °C min^{-1}.

with a 220 nm band under nitrogen, carried out for comparison, gave the same changes in the IR spectra at comparable doses. All spectra were recorded with an IBM IR98 Michelson interferometer at 2 cm^{-1} resolution by a room temperature DTGS (deuterated triglycine sulfate) detector. Spectra with high S/N ratio were obtained through the coaddition of 1000 scans. The spectra are presented as recorded without any analog or digital smoothing.

RESULTS AND DISCUSSION

Thermal analysis

The DSC results obtained from bulk Cd–ODF as crystallized from solution (see the Experimental section) exhibited one endotherm at 118 °C which occurred independent of the heating rate as well as a more complex pattern of peaks at lower temperatures which depends strongly on the heating rate. This latter pattern is entirely absent in a repeated heating cycle. The infrared spectra obtained from the powder before and after heating were identical leading us to conclude that the endotherms present only in the first DSC run are due to a recrystallization of the sample as crystallized from solution. The peak at 118 °C is attributed to melting. For comparison, Cd-arachidate shows one main endotherm at 110 °C, which has been attributed[20] to the melting of the cadmium head group "lattice."

The DSC of bulk Cd–ODM (Fig. 2) gives a rather narrow endotherm at 84 °C, which is reproduced after cooling from 90 °C back to room temperature and is therefore attributed to a structural phase transition. A second broad endotherm occurs around 110 °C. After the Cd–ODM has been heated to 130 °C, neither endotherm remained in a repeated run. Therefore, the endotherm around 110 °C is at least partially attributed to thermally induced polymerization

Langmuir films at the water–air interface

The room temperature isotherms of the cadmium salts of ODF and ODM (Fig. 3) are very similar to the isotherms of the corresponding free acids. At the same pressure, the molecular area of the *cis* (ODM) is larger than for the *trans* (ODF) compound, probably reflecting the larger area occupied by the head group of the *cis* compound. Both isomers could be compressed to a molecular area of 0.20 nm^2 per molecule, approximately the cross section of an extended hydrocarbon chain. The corresponding pressure was about 50 and 60 mN m^{-1}, respectively for the isomers. For comparison, the isotherm of arachidic acid has the same shape with a similar slope but the kink at 0.20 nm^2 per molecule occurs at a pressure of 27 mN m^{-1}. For this material it has been concluded from electron diffraction experiments[27] that the hydrocarbon chains are tilted at pressures below the kink and upright above. However the tilt is not constant over a spot of a few microns. The same interpretation is believed to hold for ODF and ODM, supported by the infrared data given below.

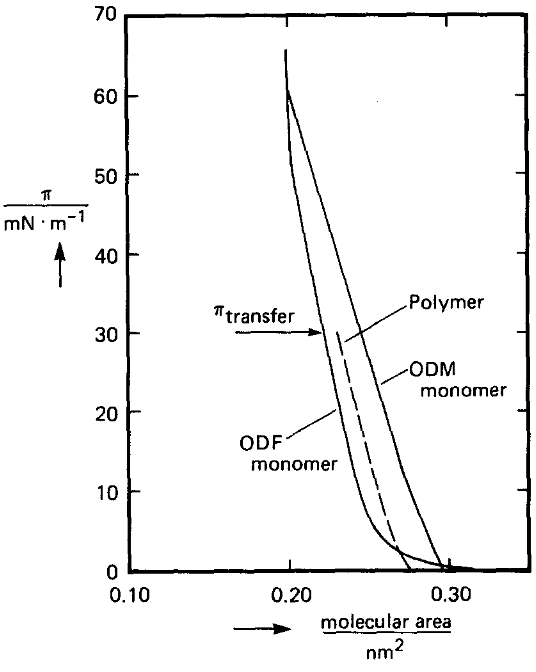

FIG. 3. Surface pressure vs area at room temperature for the monomers of Cd–octadecylfumarate (Cd–ODF) and Cd–octadecylmaleate (Cd–ODM) as well as for the common polymer.

UV polymerization on the water surface resulted in an increase in area for ODF and, interestingly, in an area decrease for ODM. In both cases saturation occurred after approximately half an hour of irradiation. The isotherms of the resulting polymers are identical within experimental error, as shown in Fig. 3.

Mixtures of ODF and ODM with 65%, 50%, and 35% ODF exhibit an area increase upon UV irradiation. An ODF content as low as 25% was necessary to maintain the area constant. Because the expansion observed in pure ODF is smaller than the contraction in pure ODM, one can conclude that the two isomers form a solution rather than phase separate in a monomolecular film. This mixture, therefore, represents a promising example of a film which could be polymerized on a solid substrate without cracking. This would be important for applications using LB films as barriers, since it has been shown[28] that in pure ODF major defects occur upon polymerization.

TABLE I. Band assignments for Cd–octadecylfumarate (Cd–ODF) and Cd–octadecylmaleate (Cd–ODM).

Molecular segment	Mode[a]	Polarization	Frequency in cm^{-1}
	$\nu_a(CH_3)$i.p.	$E\perp$ chain	2962
Aliphatic	$\nu_a(CH_3)$o.p.	$E\parallel$ chain	2954
chain	$\nu_s(CH_3)$	$E\perp$ chain	2931
$-CH_2-$	$\nu_a(CH_2)$	$E\parallel$ chain	2918
	$\nu_s(CH_3)$	$E\perp$ chain	2874
	$\nu_s(CH_2)$	$E\parallel$ chain	2850
	$\delta(CH_2)$	$E\parallel$ chain	1470
	$r(CH_2)$	$E\parallel$ chain	725
Ester	$\nu(C=O)$	$E\parallel C=O$	1720...1730
$-C-O-C-$ ‖ O	$\nu_a(C-O-C)$	$E\parallel$ skeleton	1180
Double bond	$\nu(C=C)$	$E\parallel C=C$	~1650
$-CH=CH-$	$\delta(CH=CH)$	$E\parallel C=C$	1310 for Cd–ODF 1245 for Cd–ODM
Carboxyl	$\nu_a(CO_2^-)$	$E\perp$ bisec.	1540...1565
⋰O $-C$ ⋱O	$\nu_s(CO_2^-)$	$E\parallel$ bisec.	1415...1445

[a] ν_a: asymmetric stretch; ν_s: symmetric stretch; δ: bending; r: rocking; i.p.: in skeletal plane; o.p.: out of skeletal plane.

Langmuir–Blodgett (LB) films on aluminum and KRS-5

The orientation of molecular segments in the LB films was determined by the combination of grazing incidence reflection (GIR) and transmission infrared spectroscopy. In a GIR experiment, the electric field vector, E, is oriented perpendicular to the substrate, whereas in a transmission experiment it is oriented parallel to the substrate. The two spectra together give the average orientation of the change in dipole moment associated with a particular infrared active mode.

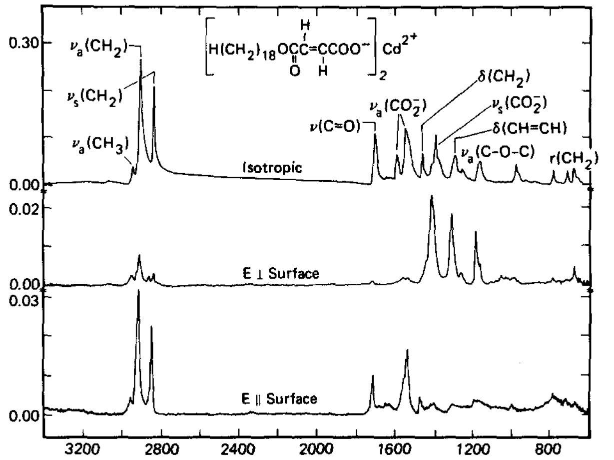

FIG. 4. (a) Transmission spectrum of bulk Cd–octadecylfumarate (Cd–ODF) cast on KBr. (b) Grazing incidence reflection spectrum of a LB film of nine monolayers of Cd–ODF on aluminum. (c) Transmission spectrum of LB film of Cd–ODF, ten monolayers on each side of a KRS-5 substrate.

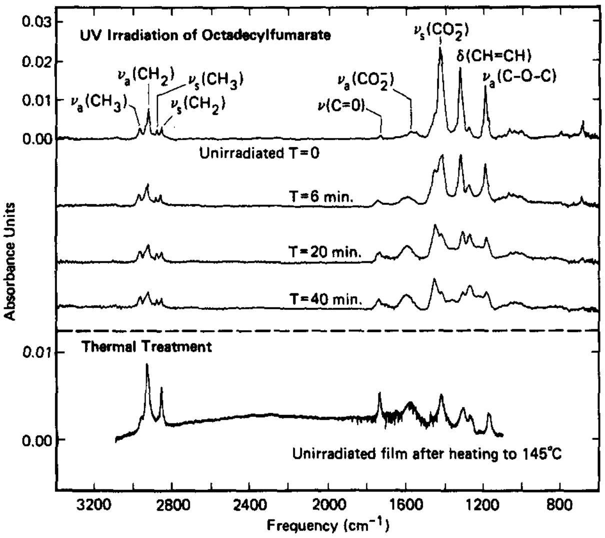

FIG. 5. Grazing incidence reflection spectrum of a LB film of nine monolayers of Cd–ODF on aluminum after (a) 0, 6, 20, and 40 min of UV irradiation or (b) heating to 145 °C and cooling back to room temperature.

In Table I frequencies and polarizations of modes occurring in Cd–ODF and Cd–ODM are given.

Octadecylfumarate (ODF)

In order to obtain an isotropic spectrum of Cd–ODF the bulk salt was cast on KBr from solution. All LB films investigated contained not more than ten monolayers, since for thicker films a different phase was reported from x-ray and electron diffraction studies.[24] Figure 4 gives the absorption spectrum of the bulk sample, the GIR spectrum of nine monolayers on aluminum ($E_\perp$), and the absorption spectrum obtained from 20 monolayers, ten on each side of a KRS-5 substrate ($E_\parallel$). The pronounced differences between the latter two spectra shows the high degree of molecular orientation.

The methylene stretches at 2850 and 2918 cm^{-1} are the dominant bands in the $E_\parallel$ spectrum while they appear with reduced intensity in the $E_\perp$ spectrum, suggesting that the aliphatic tails are oriented with their axes almost normal to the surface. This conclusion is further supported by the absence of CH_2 rocking mode (at 725 cm^{-1}) from the $E_\perp$ spectrum. A slight tilt, however, is present and a more subtle piece of information concerning the orientation of the plane of the hydrocarbon backbone is revealed by the intensity ratio of the asymmetric to the symmetric CH_2 stretching vibration as observed in the $E_\perp$ spectrum. As seen in Fig. 4, this ratio is quite large compared to its counterpart in Cd-arachidate.[9] Considering that the change in dipole moment of the $\nu_a(CH_2)$ mode is perpendicular to the zig–zag plane while that of $\nu_s(CH_2)$ is parallel to the plane, the larger $\nu_a(CH_2)/\nu_s(CH_2)$ ratio indicates that the backbone plane is tilted relative to the surface normal. No evidence has been found in ODF to suggest that this slight planar tilt is anisotropic relative to the dipping direction. As shown in Fig. 5, this intensity ratio decreases with UV irradiation indicating that the tilt is removed with polymerization.

As seen in Fig. 4, there is a considerable amount of orientation information about other parts of the ODF molecules. The C = O stretching vibration is very intense in the $E_{\parallel}$ spectrum but vanishes in the $E_{\perp}$ spectrum indicating that the C = O bond lies parallel to the substrate. Similarly, the asymmetric C–O–C skeletal stretching vibration appears predominantly in the $E_{\perp}$ spectrum suggesting that this part of the molecule, like the hydrocarbon tail, is almost perpendicular to the surface. The C = C stretching vibration found in the 1650 cm^{-1} region is weak in the infrared; however, the mode involving in-plane bending of the hydrogens attached to it[29] is found at 1310 cm^{-1} and has considerable intensity. It is absent from the spectrum when $E_{\parallel}$ surface indicating that the double bond is oriented normal to the surface.

The asymmetric and symmetric CO_2^- stretching vibrations due to the head group are found at ~ 1540 and ~ 1430 cm^{-1}, respectively. Particularly for the bulk sample as crystallized from solution there is a fine structure to these rather broad bands which is probably due to different headgroup configurations. As can be seen in Fig. 4, the $\nu_a(CO_2^-)$ appears much stronger when $E_{\parallel}$ surface while $\nu_s(CO_2^-)$ is observed mainly in the $E_{\perp}$ spectrum. This indicates that the head group is oriented perpendicular to the surface similar to that found for Cd-arachidate.[9,20]

The absence of pronounced twisting and progression bands in the $E_{\perp}$ spectrum as well as the fact that the $\delta(CH_2)$ and the $r(CH_2)$ bands did not exhibit pronounced splittings (see Table I) indicate that Cd–ODF does not crystallize in the orthorhombic subcell as observed for Cd-arachidate.[9] This may be due to the fact that the monolayers were not transferred in the fully condensed state above 50 mN m^{-1} or that the steric hindrance due to the bulkier head group prevents the close packing associated with the orthorhombic subcell.

After UV irradiation the GIR spectra in Fig. 5 show a considerable reduction in the intensity of the $\delta(CH = CH)$ vibration which does not appear in the transmission spectrum (not given here). This loss of absorption is due to polymerization rather than a simple dimerization since no indications of an IR absorption between 900 and 1000 cm^{-1}, due to a C_4 ring,[30] are observed. During polymerization, the intensity of the methylene stretch is further reduced, indicating that the aliphatic chains are now even more upright. After 40 min of UV irradiation the CH stretch region resembles very much that of Cd-arachidate[9] as mentioned previously. The ester group is, on the average, more tilted now since the carbonyl stretch absorbs more in $E_{\perp}$ and less in $E_{\parallel}$. The same increase in average tilt can be concluded for the carboxyl group, since the ratio of the symmetrical and the asymmetrical absorption peaks decreases for $E_{\perp}$ and increases for $E_{\parallel}$ during polymerization.

It should be noted that monolayers polymerized on the water surface and subsequently transferred to the substrate give the same IR spectra, indicating that the molecular structure is independent of where the polymerization occurs. The observation that the polymerization rate is comparable at 220 and 254 nm although the double bond is reported[24,28] to absorb in the vicinity of 210 nm indicates that the polymerization is not initiated by a direct excitation of the double bond and might in turn explain the comparatively long polymerization times.

Heating the monomeric film on the solid substrate to 145 °C and cooling it subsequently to room temperature gives qualitatively the same spectrum as observed upon UV irradiation, indicating that polymerization has occurred. However, the vibrations of the methylene and carbonyl stretches show a large increase in intensity in the $E_{\perp}$ spectrum as shown in the bottom panel of Fig. 5. The different relative intensities for the thermally polymerized film reflect chain disorder, due to the melting, which occurs simultaneously at these temperatures and which results in a polymerized film with "frozen in" disorder.

The heating of the UV polymerized film revealed its reduced thermal stability compared to the monomeric or a Cd-arachidate film. While the chain as well as the head group orientation of the latter two were only little affected by heating it to 90 °C, the polymer was irreversibly disordered at this temperature. Apparently the nature of packing of the hydrocarbon tails into a unit cell contributes significantly to its thermal stability. At this point it should be noted that generally the half-widths of the absorption bands increased upon polymerization, e.g., in transmission the half-width of the asymmetric methylene stretching vibration increases from 14 cm^{-1} for the monomer to 21 cm^{-1} for the polymer. The same broadening is observed at elevated temperatures and may reflect the loss of order within the unit cell or the increase in molecular motion which can occur in the absence of a close packed unit cell.

Octadecylmaleate (ODM)

The polarized IR spectra of Cd–ODM monolayers shown in Fig. 6 are quite different from those of Cd–ODF previously discussed. It becomes immediately apparent upon inspection of the CH stretching region (2800–3000 cm^{-1}) that the band intensities are similar in both $E_{\parallel}$ and $E_{\perp}$ spectra. This indicates that the aliphatic chain is considerably tilted relative to the surface normal as would be expected from the conformational constraints imposed by a *cis* double bond. This is further supported by the presence of the CH_2 bending vibration at $\sim 1470\ \text{cm}^{-1}$ in both $E_{\perp}$ and $E_{\parallel}$. A

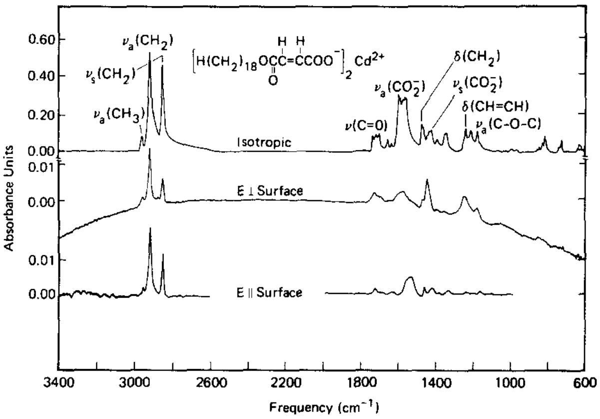

FIG. 6. (a) Transmission spectrum of bulk Cd–octadecylmaleate (Cd–ODM) cast on KBr. (b) Grazing incidence reflection spectrum of a LB film of seven monolayers of Cd–ODM on aluminum. (c) Transmission spectrum of LB films of Cd–ODM, ten monolayers on each side of a KRS-5 substrate.

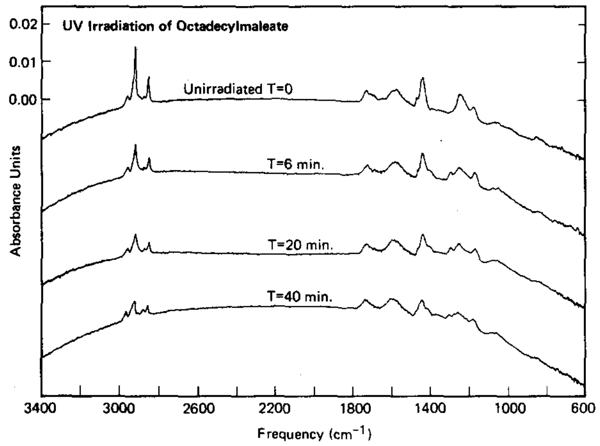

FIG. 7. Grazing incidence reflection spectra of a LB film of seven monolayers of Cd–ODM on aluminum after 0, 6, 20, and 40 min of UV irradiation.

tilt of the aliphatic chain with respect to the substrate is consistent with the fact that the molecular area on the water surface at the transfer pressure of 30 mN m^{-1} is approximately 10% larger for the *cis* compound (ODM) than for the *trans* (ODF) analog.

It is interesting to note that there are three components to the $\nu(C = O)$ stretching vibration, whereas previously in ODF there was only a single band in this region. In both $E_{\parallel}$ and $E_{\perp}$ spectra, only the highest frequency component remains after polymerization. It is believed that the lower frequency components result from a resonance interaction between C = O and C = C groups giving rise to band splitting. In any case, it does appear that the ester bridging group is also tilted relative to the surface normal.

The $\nu_a(CO_2^-)$ and the $\nu_s(CO_2^-)$ are partially obscured by other bands in their vicinity but the intensity of the former is much greater in the spectrum with $E_{\perp}$ than it is in Cd–ODF. Likewise, there also appears to be a greater contribution of the $\nu_s(CO_2^-)$ to the $E_{\parallel}$ spectrum suggesting that the head group does not lie completely perpendicular to the surface as was found for Cd–ODF. Thus, it appears as if in the case of Cd–ODM, the *cis* double bond causes a tilting of the entire molecule: aliphatic tail, bridging ester group, and head group.

The effects of polymerizing Cd–ODM by UV irradiation are quite dramatic as shown in Fig. 7. In addition to the gradual disappearance of the $\delta(CH = CH)$ band around 1245 cm^{-1} with polymerization, there is a dramatic change in intensity of the $\nu_a(CH_2)$ and the $\nu_s(CH_2)$ in the 2800–3000 cm^{-1} region. As discussed previously, exposure of Cd-arachidate to UV radiation for similar amounts of time did not indicate that degradation occurred. Thus, the change in intensity in the CH stretching region must be due to changes in the molecular orientation of the Cd–ODM as polymerization proceeds. This would then indicate that as the *cis* double bond becomes saturated, the aliphatic tails reorient normal to the surface. This would also explain the contraction of the Cd–ODM monolayers upon polymerization as indicated in the pressure-area curves shown in Fig. 3. Another interesting observation can be made by comparing the $E_{\perp}$ spectra of Cd–ODF and Cd–ODM after 40 min (see Figs. 5 and 7) exposure to UV radiation. The two spectra are identical as expected, since both monomers polymerize to the same polymer having the same orientation of aliphatic side chains (Fig. 8). Hence there is no longer any distinction between *cis* and *trans* isomers.

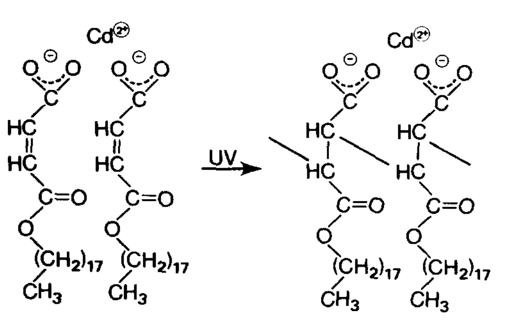

FIG. 8. Schematic, showing the change in bonding with polymerization of Cd–ODM. The polymerization of Cd–ODF follows in a similar manner.

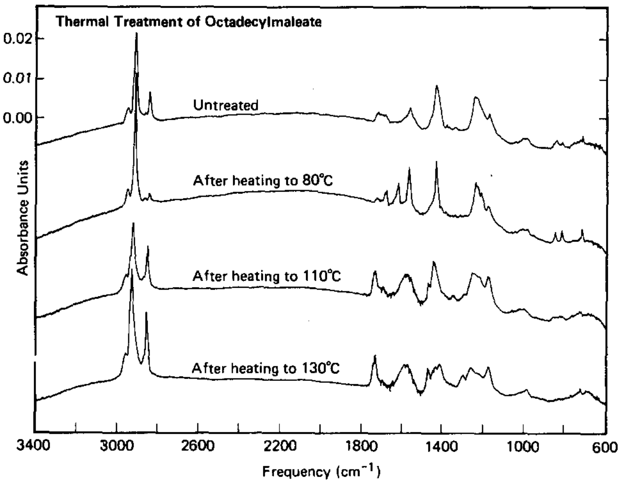

FIG. 9. Grazing incidence reflection spectra of a LB film of nine monolayers of Cd–ODM on aluminum at room temperature, not thermally treated as well as after heating it to 80, 110, and 130 °C, respectively.

Thermal treatment of Cd–ODM has a dramatic effect at temperatures well below the melting point as shown in Fig. 9. A significant change in all parts of the spectrum was observed after the LB film was heated to 80 °C. In addition to the sharp features found in the 1500–1800 cm^{-1} region, there is a dramatic change in the ratio $\nu_a(CH_2)/\nu_s(CH_2)$. As discussed previously, this indicates that the aliphatic tails are arranged with their chain axes and zig–zag planes parallel to the surface. This is most likely due to the recrystallization of the monomeric Cd–ODM film. It may correspond to the endotherm observed at 84 °C in the DSC of Cd–ODM. Subsequent heating to 110 and 130 °C results in a spectrum very similar to thermally polymerized Cd–ODF (Fig. 5) indicating that the end product of the thermal treatment is the same for both isomers, as would be expected. As discussed previously for ODF, the difference in relative band intensities between UV irradiated Cd–ODM and that obtained from thermal polymerization reflects the fact that, in the latter, orientational disorder[20] is accompanying polymerization resulting in a polymer with considerably less order.

CONCLUSIONS

The orientation of Cd–ODF and Cd–ODM monolayer components has been studied by polarized IR measurements with both grazing incidence reflection and transmission techniques. It was found that the Cd–ODF molecules are oriented almost normal to the substrate while the Cd–ODM is considerably tilted relative to the surface reflecting the conformational constraints imposed by the *cis* double bond. At elevated temperatures a structural change occurred in the monomeric maleate film which may be attributed to three dimensional recrystallization. After UV polymerization, there is a striking similarity in the spectra indicating that the resulting polymers are identical and independent of the nature of the starting isomer. A substantial reorientation of the molecules was observed resulting in an alignment of the aliphatic tails normal to the surface. The comparison with the IR spectra of thermally polymerized Cd–ODF and Cd–ODM indicated that the resulting polymer was similar but, in contrast to that obtained from UV polymerization, it was obvious that a considerable amount of orientational disorder has been introduced by the thermal treatment. It was concluded that this resulted from thermally induced disorder occurring simultaneously during polymerization and causing a significant amount of structural disorder in the polymer. A UV polymerized fumarate film exhibited a reduced structural stability upon heating as compared to the monomeric form or Cd-arachidate, reflecting the importance of unit cell structure for thermal stability. Interestingly a mixture of fumarate and maleate in the ratio of 1 to 3 was found to preserve its area upon polymerization. This is believed to be a promising example of a film which could be polymerized on a solid substrate without cracking.

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