photographs and Dr. N. E. Schlotter (Bell Communications Research) for many helpful discussions.

Registry No. PVF$_2$ (homopolymer), 24937-79-9.

References and Notes

(1) Kepler, R. G.; Anderson, R. A. *CRC Crit. Rev. Solid State Mater. Sci.* **1980**, *9*, 399.
(2) Lovinger, A. J. In "Developments in Crystalline Polymers 1"; Basset, D. C., Ed.; Applied Science: London, 1982.
(3) Hasegawa, R.; Takahashi, Y.; Chatani, Y.; Tadokoro, H. *Polym. J. (Tokyo)* **1972**, *3*, 600.
(4) Yagi, T.; Tatemoto, M.; Sako, J. *Polym. J. (Tokyo)* **1980**, *12*, 209.
(5) Davis, G. T.; Furukawa, T.; Lovinger, A. J.; Broadhurst, M. G. *Macromolecules* **1982**, *15*, 329.
(6) Koizumi, N.; Murata, Y.; Oka, Y. *Jpn. J. Appl. Phys.* **1984**, *23*, L324.
(7) Enomoto, S.; Kawai, Y.; Sugita, M. *J. Polym. Sci., Polym. Phys. Ed.* **1968**, *6*, 861.
(8) Cortili, G.; Zerbi, G. *Spectrochim. Acta, Part A* **1967**, *23A*, 285.
(9) Rabolt, J. F.; Johnson, K. W. *J. Chem. Phys.* **1973**, *59*, 3710.
(10) Kobayashi, M.; Tashiro, K.; Tadokoro, H. *Macromolecules* **1975**, *8*, 158.
(11) Bachmann, M. A.; Koenig, J. L. *J. Chem. Phys.* **1981**, *74*, 5896.
(12) Boerio, F. J.; Koenig, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1971**, *9*, 1517.
(13) Zabel, K.; Schlotter, N. E.; Rabolt, J. F. *Macromolecules* **1983**, *16*, 446.
(14) Wilson, F. C.; Starkweather, H. W., Jr. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 919.
(15) Farmer, B.; Lando, J. B. *J. Macromol. Sci., Phys.* **1975**, *B11*, 89.
(16) Schlotter, N. E.; Rabolt, J. F. *Polymer* **1984**, *25*, 165.
(17) Devlin, G. E.; Davis, J. L.; Chase, L.; Geschwind, S. *Appl. Phys. Lett.* **1971**, *19*, 138.
(18) McGrath, J. C.; Ward, I. M. *Polymer* **1980**, *21*, 855.
(19) Cessac, G. L.; Curro, J. G. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 695.
(20) Snyder, R. G. *J. Mol. Spectrosc.* **1971**, *37*, 353.
(21) Damen, T. C.; Porto, S. P. S.; Tell, B. *Phys. Rev.* **1966**, *142*, 570.
(22) Campos-Vallette, M.; Rey-Lafon, M.; Lagmier, R. *Chem. Phys. Lett.* **1982**, *89*, 189.
(23) Rabolt, J. F. *Polymer* **1981**, *22*, 890.
(24) Rabolt, J. F. *CRC Rev. Solid State Mater. Sci.* **1985**, *12*, 165.
(25) Wang, Y. K.; Waldman, D. A.; Lasch, J. E.; Stein, R. S.; Hsu, S. L. *Macromolecules* **1982**, *15*, 1452.
(26) Snyder, R. G.; Scherer, J. R. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 421.
(27) Fanconi, B.; Rabolt, J. F. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1201.

Orientation of Poly(octadecyl methacrylate) and Poly(octadecyl acrylate) in Langmuir–Blodgett Monolayers Investigated by Polarized Infrared Spectroscopy

Stephen J. Mumby,*[†] J. D. Swalen, and J. F. Rabolt

IBM Almaden Research Center, San Jose, California 95120-6099.

Received November 26, 1985

ABSTRACT: Molecular orientation in Langmuir–Blodgett (L–B) monolayers of poly(octadecyl methacrylate) (PODMA) and poly(octadecyl acrylate) (PODA) has been studied by infrared spectroscopy. Substantial anisotropy between the spectra measured in transmission, and by reflection at grazing incidence, was observed for both these polymers. The carbonyl group was found to be oriented approximately perpendicular to the substrate surface, independent of polymer type and of deposition surface pressure within the range investigated. The long aliphatic ester side groups were also found to be approximately perpendicular to the plane of the monolayer. However, the orientation of these groups was strongly dependent upon the chemical structure of the polymer used and on the surface pressure at transfer. More condensed L–B monolayers of PODA could be formed than was the case for PODMA, in part due to the lower steric hindrance to rotations about backbone bonds in PODA because of the absence of the methyl side group.

Introduction

The Langmuir–Blodgett (L–B) technique for the deposition of ordered monolayers of amphiphilic molecules on solid substrates has obtained new prominence since the incorporation of L–B films into microelectronic devices. This renaissance has also been inspired by the wide range of other potential technological applications of L–B films[1-3] and by the opportunities to investigate the structure and properties of the molecules in this uniquely ordered environment. However, from the technological standpoint, L–B films of traditionally used amphiphilic materials, such as long-chain fatty acids, are rather fragile, possessing little mechanical or thermal stability or resistance to dissolution. Consequently, efforts have been made to extend the range of materials that may be transferred as monolayers by the L–B technique.[4] Cemel et al[5] first suggested the polymerization of monolayers or multilayers of unsaturated molecules to produce a more robust structure while still retaining the orientation of the monomers. This technique has met with some success; related polymerized liposome structures have been investigated as potential drug carriers[6] and as useful models for cell membranes.[7] However, recent studies[8,9] have revealed that internal stresses, which are frequently generated by polymerization after transfer of the monomer to a substrate, can produce films with large fissures and cracks. One possible means of eliminating this stress is to polymerize a mixture of isomers such that the average area per monomer unit is unchanged after polymerization. This strategy has been adopted by Rabe et al[10] using the two isomers: octadecylfumaric acid and octadecylmaleic acid. In an alternative approach, efforts have been directed toward transferring L–B monolayers of preformed polymers that do not exhibit these inherent stress problems. Structure–property relationships may also

---

[†] Present address: AT&T Bell Laboratories, Room 7C-050, Whippany Road, Whippany, NJ 07981.

0024-9297/86/2219-1054$01.50/0

be more easily investigated with a well-characterized polymeric system as opposed to a system of uncertain structure produced by in situ polymerization. Such structure–property relationships are an important prerequisite to a fuller understanding of these quasi-two-dimensional polymeric systems.

Tredgold and Winter[11,12] were the first to describe the transfer of L–B monolayers of preformed polymers. However, the polymers investigated by these authors were poorly characterized copolymers that had to be hydrolyzed on the surface of the water subphase prior to their transfer to a solid substrate. The principal aim of the investigations by Tredgold et al[11-14] was the development of electronic devices; detailed analysis of the orientation and packing of the polymers in the L–B films was not undertaken. In the work presented here we describe studies of L–B monolayers of well-characterized amphiphilic comblike polymers on the surface of water, their transfer to suitable solid substrates, and their analysis using polarized infrared spectroscopy (IR). In order to obtain information regarding the orientation of the polymer on solid substrates, the transferred films were investigated by both transmission and grazing incidence reflection IR.

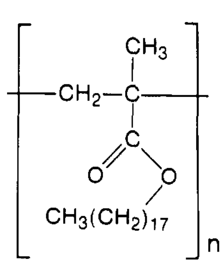
The polymers chosen for the present study were poly(octadecyl methacrylate) (PODMA) and poly(octadecyl acrylate) (PODA). These materials were selected because as well as having the required amphiphilic nature they are also structurally related to the much more widely investigated poly(methyl methacrylate) (PMMA), and the apparent similarities in chemical structure may be utilized in making band assignments. In addition, a considerable amount of work[15-21] on side-chain crystallization in bulk PODMA and PODA has appeared in the literature. X-ray data[19,20] suggest that the side chains of poly(*n*-alkyl acrylates) and poly(*n*-alkyl methacrylates) are extended at right angles to the main chain, thus enhancing the crystallization process but leaving the main chain disordered even in materials that exhibit considerable tacticity. Of interest in the present study are the different crystallization habits of PODMA and PODA that are introduced by the preparation of L–B films. In light of the previously mentioned bulk studies, side-chain organization will certainly be influenced by deposition using the L–B technique such that the resulting structures could be significantly different from those in the bulk.

Structurally, the polymers PODMA and PODA differ only in the replacement of a methyl group by a hydrogen on the carbon backbone in the repeat unit (see Figure 1). However, this small change has a profound effect on the steric hindrance to rotation about bonds in the polymer backbone and produces a much more rigid chain in the case of PODMA. It is also of interest to examine the ramifications of the degree of rigidity of a polymer backbone upon its ability to form well-ordered, closely packed L–B films.

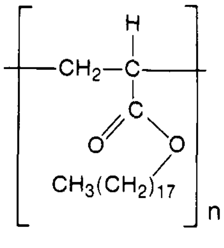
Experimental Section

Substrates for the IR reflection measurements were 1 × 3 in. fused quartz microscope slides, onto one side of which had been evaporated aluminum films approximately 0.2 μm thick. Irtran-2 (38 × 19 × 2 mm) was used as the substrate for transmission measurements. All IR measurements were made with an evacuable IBM IR98 FTIR. Typical spectra were recorded at 2-cm^{-1} resolution, using a Santa Barbara Research MCT detector cooled to liquid nitrogen temperatures. Good signal-to-noise spectra generally required the coaddition of 4000 scans.

For grazing incidence reflection measurements, a standard Harrick reflection accessory was used. Since aluminum has a maximum in the reflectivity ratio, $(R_0 - R)/R_0$, at an angle close to that of silver, the GIR reflection measurements were made at 80–81°, the angle previously[22] determined to be operationally optimal.



(a) Poly(octadecylmethacrylate)



(b) Poly(octadecylacrylate)

Figure 1. Structural repeat units of (a) poly(octadecyl methacrylate) and (b) poly(octadecyl acrylate).

The L–B trough employed in the current investigation was a modified Langmuir Trough 4, obtained from Joyce–Loebl. The large glass tank, which is a part of this apparatus, was replaced with a much shallower (~1 in. deep) Teflon tank. This proved much easier to keep clean, as judged by surface pressure measurements. The tank was filled with water that had been purified, with a Barnstead NANOpure II ultrapure water system fitted with an ORGANICpure oxidation chamber to remove organic impurities.

PODMA (M_W = 321 000 and M_N = 97 200) and PODA (M_W = 23 300 and M_N = 13 000) were secondary standards obtained from Scientific Polymer Products, Inc., Ontario, NY. Both these polymers were atactic. The polymers were spread on the purified water subphase from dilute (0.5–0.05 mg mL^{-1}) solutions in dichloromethane, and the solvent was allowed to evaporate. After several cycles of compressing a monolayer of PODMA or PODA and allowing it to expand, the pressure–area isotherm was found to be completely reproducible for surface pressures up to those approaching the collapse pressure for the respective polymer. It was noted, however, that the collapse pressure was highly dependent upon trace levels of impurities. The more dilute the solution and the longer the time over which the polymer was spread, the more quickly the pressure–area curve became reproducible upon successive compression and expansion cycles.

These comblike polymers could be transferred to solid hydrophilic surfaces as single coherent monolayers upon withdrawal of the substrate from the subphase. Deposition was continuously monitored, and the resulting deposition ratio was always between 0.98 and 1.02 for the L–B films used for spectroscopic studies. The dipping speed was maintained at 2.5 mm min^{-1}. Z-type[23] (transfer on the upstroke only) multilayer structures could also be transferred to IR reflection and transmission substrates. Although Z-type deposition has been reported previously[24,25] for other materials, it has usually been brought about by expanding the Langmuir film, or removing it from the subphase, prior to a downstroke of the substrate. Consequently, it is believed that this is the first observation of the formation of a genuine Z-type L–B multilayer. It was also possible to fabricate X-type[23] (transfer on the downstroke only) assemblies on fused quartz slides that had been alkylated[26] to produce a hydrophobic surface.

Results and Discussion

Pressure–Area Isotherms. Although the molecular weights of PODMA and PODA are substantially different and their polydispersities are large, it has been demon-

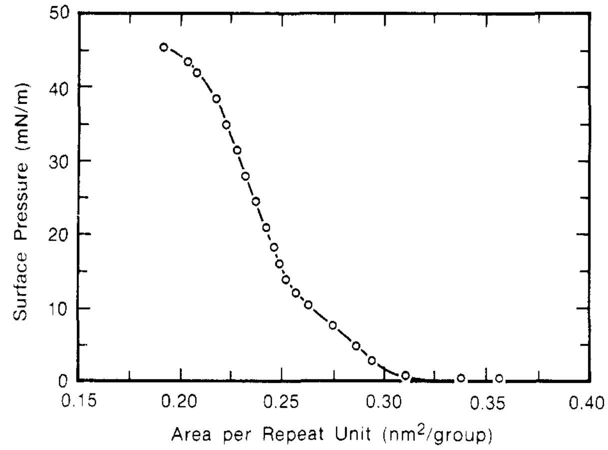


Figure 2. Surface pressure–area curve for poly(octadecyl methacrylate) measured at 20 °C and a compression rate of 0.45×10^{-3} nm^2 s^{-1} repeat unit^{-1}.

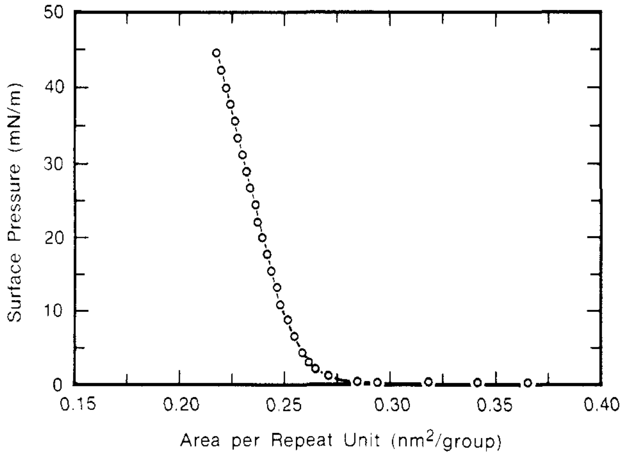


Figure 3. Surface pressure–area curve for poly(octadecyl acrylate) measured at 20 °C and a compression rate of 0.45×10^{-3} nm^2 s^{-1} repeat unit^{-1}.

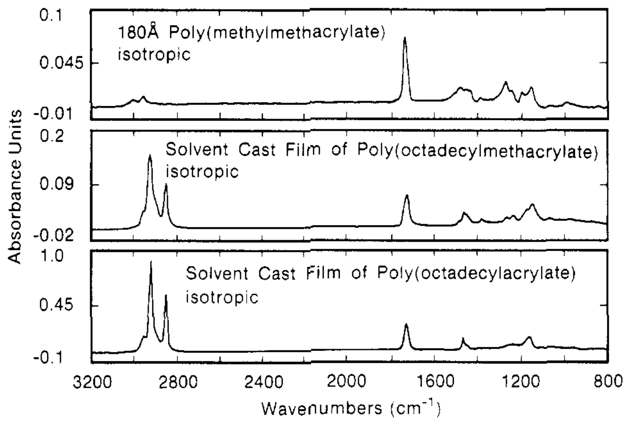


Figure 4. Infrared spectra of isotropic films of poly(methyl methacrylate), poly(octadecyl methacrylate), and poly(octadecyl acrylate) measured in transmission.

strated[27] that pressure–area curves for surface films of these high polymers do not show any appreciably dependence on molecular weight under the usual experimental conditions (surface pressure above 0.2 mN m^{-1}) and provided the molecular weight is large enough (>2000). Consequently, surface pressures are plotted in Figures 2 and 3 as a function of the area occupied per monomer unit, and interpretation of the isotherms will be made in terms of differences between the chemical structure between PODMA and PODA rather than in terms of differences in molecular weight.

The pressure–area curves for PODMA and PODA, shown in Figures 2 and 3, respectively, were measured at 20 °C and at a compression rate of 0.45×10^{-3} nm^2 s^{-1} per repeat unit. The isotherm of PODMA is in good agreement with that measured in a much earlier study by Crisp.[28] In the isotherm of PODMA (Figure 2), it is observed that there are two distinct regions in which the surface pressure rises approximately linearly with reduction of surface area. The linear rise in the less condensed regime is interpreted as resulting from trying to force the backbone of the polymer into a closely packed, quasi-two-dimensional structure against considerable steric hindrance. The second, and steeper, rise of surface pressure apparent upon reducing the surface area still further is attributed to interactions between the long aliphatic side chains of the polymer molecules. In the phase corresponding to this steeper rise, the long side chains are believed to be approximately perpendicular to the surface of the water, but although they interact with one another they are not close enough to form an ordered crystalline lattice. The cross sectional area of a saturated aliphatic chain in a close-packed Langmuir film in the solid phase is ~0.20 nm,^{2} as exemplified by arachidic acid.[29] In Figure 2, it is seen that the smallest stable area per repeat unit, which is attained immediately preceding collapse, is ~0.22 nm,^{2} some 10% in excess of the optimum packing area. Thus, these measurements of the pressure–area isotherm of a monolayer of PODMA indicate that the polymer Langmuir film becomes unstable and undergoes collapse before the optimum crystalline packing of the aliphatic side chains can be achieved.

The pressure–area isotherm for PODA, shown in Figure 3, differs substantially from that for PODMA. On compression of a monolayer of PODA, the first rise in surface pressure occurs at an area per repeat unit where the side chains are expected to be entering the liquid phase.[23] No distinct contribution to a rise in surface pressure is observed in the regime where compression of the polymer backbone is thought to be dominant. This is to be expected, since rotations about bonds in the polymer backbone are sterically less hindered for acrylates, as compared with methacrylates, due to the absence of the methyl side group. This lower degree of steric hindrance in PODA also allows the aliphatic side chains to be compressed to smaller surface areas prior to collapse than is the case for PODMA. The minimum stable area per repeat unit for PODA was found to be ~0.21 nm^2, which is only ~5% greater than the optimum packing area.

Infrared Spectroscopy. Shown in Figure 4 are three spectra of isotropic films of PMMA, PODMA, and PODA. The C–H stretching regions of the spectra of PODMA and PODA are dominated by the asymmetric and symmetric C–H stretching in the long ester side groups. The antisymmetric and symmetric C–H bands occur at 2922 and 2851 cm^{-1} in PODMA, and at 2918 and 2850 cm^{-1} in PODA, respectively. The shoulder at ~2955 cm^{-1} results[30,31] from asymmetric stretching of C–H bonds in the terminal methyl group of the long aliphatic side chains and of the vinyl C–H bonds; plus, in the spectrum of PODMA, an additional contribution arises from the C–H stretching of the vinyl methyl group. These latter assignments were made by comparison with previous[30,31] results obtained for PMMA. Several absorption bands in the spectrum of PODMA are indicative of the presence of the methyl group that distinguishes PODMA from PODA. The most noticeable of these bands, which arises from the methyl bending mode of the C–CH_3 group, occurs at 1384 cm^{-1} and contains contributions from both the –CH_3 side chain and

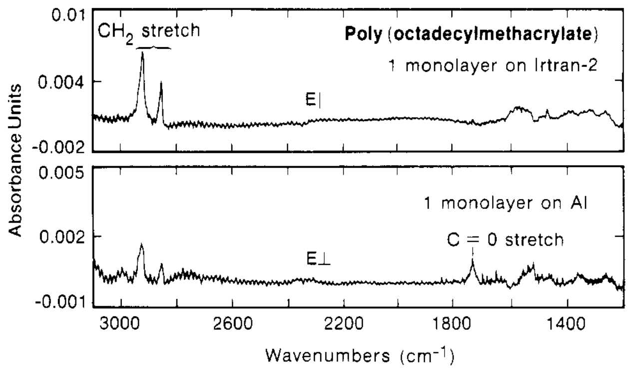


Figure 5. Polarized infrared spectra of a single monolayer of poly(octadecyl methacrylate) obtained with (a) E parallel to the surface (transmission), and (b) E perpendicular to the surface (grazing incidence reflection).

the $-CH_3$ end group of the octadecyl chain. This band is approximately twice as intense in the spectrum of PODMA as the corresponding band in the spectrum of PODA, which only has a contribution from the terminal methyl group. A common feature of all three spectra is the strong C=O stretching vibration at ~1736 cm^{-1}. It will be principally this band, together with the bands corresponding to the asymmetric and symmetric C–H stretching vibrations in the ester side chain, which will be used to probe the orientation of the polymer molecules in the L–B monolayers.

Grazing incidence reflection (GIR) IR spectroscopy, complemented by standard transmission measurements, is a powerful technique with which to probe the orientation of molecules in ordered films, such as L–B monolayers. The use of GIR gives a preferential selection[32] of the polarization component perpendicular to the metal surface. In the case of anisotropic films, this gives rise to a polarized IR spectrum that contains bands whose transition dipole moments have some component along the direction of the electric field. In a standard transmission measurement the electric field of the incident beam is parallel to the substrate surface. Thus, by comparing the relative intensities of bands in a GIR spectrum with those measured in transmission, information regarding the orientation of selected parts of a molecule can be obtained. Such a comparison may be made of the two spectra presented in Figure 5. These spectra are of a single monolayer of PODMA transferred to solid substrates by the L–B technique at a constant surface pressure of 20 mN m^{-1}. Such a monolayer has a thickness of ~30 Å. The upper spectrum in this figure was measured in transmission, whereas the lower spectrum was recorded by reflection at grazing incidence. Significant band intensity variations are noticeable between these spectra. In particular, the C=O stretching vibration at 1736 cm^{-1} shows considerable anisotropic character, indicating that the change in dipole moment of the C=O bond is primarily perpendicular to the surface. Likewise, bands attributable to the $-CH_2-$ stretching vibrations are much less intense in the reflection experiment, indicating that the hydrocarbon tails are also oriented primarily perpendicular to the surface.

To examine spectroscopically the orientation of the PODMA molecules in the two distinct regimes of the pressure–area isotherm, L–B monolayers were transferred to reflection substrates at different surface pressures. The C–H and C=O stretching regions of the spectra of two of these L–B monolayers are shown in Figure 6. The monolayers from which these spectra were recorded were transferred maintaining a constant surface pressure of 6 mN m^{-1} (upper spectrum) and 20mN m^{-1} (lower spectrum), respectively. These surface pressures correspond to the approximate midpoints of each of the linear portions of the pressure–area isotherm for PODMA. Upon inspection, it is clear that the intensity of the C=O absorption at 1736 cm^{-1} is similar in both spectra, indicating that the orientation of the C=O bond does not change significantly between the two regimes. At a surface pressure of 20mN m^{-1}, the spectra in Figure 5 show that the aliphatic side chains are approximately perpendicular to the surface, as attested by the relatively weak absorptions of the C–H bonds in the reflection spectrum. In the reflection spectrum of the film transferred at 6 mN m^{-1}, however, both the symmetric and antisymmetric C–H stretching bands are now considerably more intense. This indicates that at a surface pressure of 6 mN m^{-1} the ester side chains are tilted substantially away from the normal to the surface.

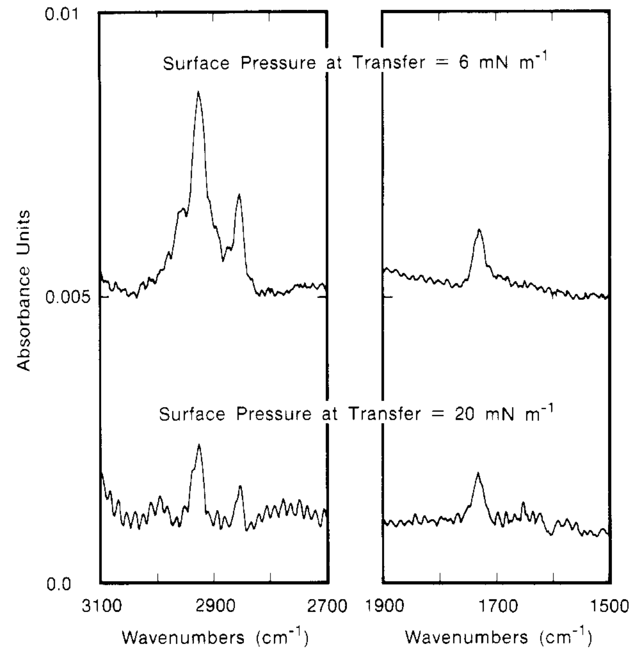


Figure 6. Grazing incidence reflection infrared spectra of monolayers of poly(octadecyl methacrylate) obtained from L–B films transferred at 6 mN m^{-1} (upper spectrum) and 20 mN m^{-1} (lower spectrum).

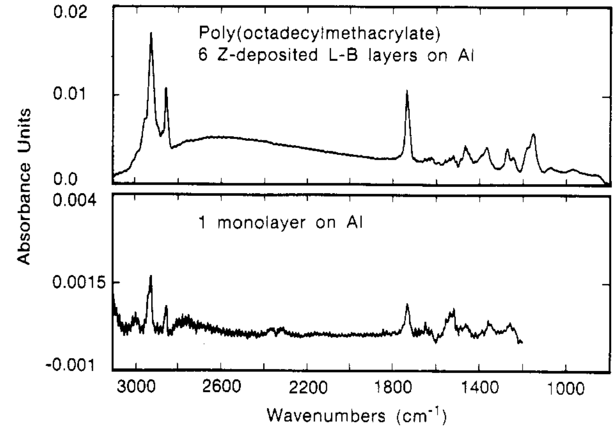


Figure 7. Grazing incidence reflection infrared spectra of L–B films of poly(octadecyl methacrylate), deposited at 20 °C and surface pressure of 20mN m^{-1}. The upper spectrum corresponds to six Z-deposited layers and the lower spectrum is that of a single monolayer.

Builtup Z-type multilayers of either PODMA or PODA could be fabricated on hydrophilic surfaces. Up to six L–B monolayers have been transferred to substrates in the current investigations. Attempts to transfer additional

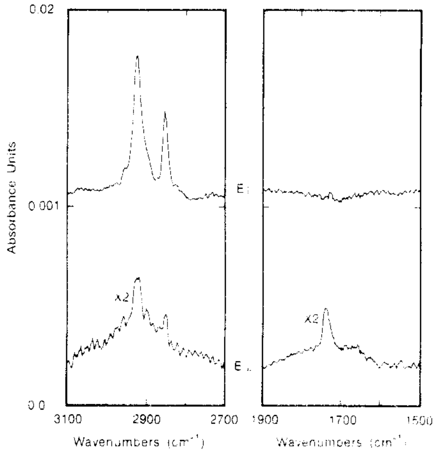


Figure 8. Structurally significant regions of the polarized infrared spectra of a single monolayer of poly(octadecyl acrylate) obtained with (a) *E* parallel to the surface (transmission), and (b) *E* perpendicular to the surface (grazing incidence reflection).

monolayers proved less successful, as indicated by a diminishing deposition ratio. A question arises as to whether or not the order found in a single monolayer is maintained in each of the repeating layers of a multilayer assembly. Shown in Figure 7 are two grazing incidence IR spectra of L–B films of PODMA deposited at 20 °C, while maintaining a constant surface pressure of 20 mN m^{-1}. The upper spectrum in Figure 7 is of a multilayer structure comprised of six Z-deposited layers, and the lower spectrum was obtained from a single monolayer. The ratio of the integrated intensity of any band in the monolayer spectrum to that of the corresponding band in the multilayer spectrum is approximately the same for all absorption bands. With the assumption that the electric field is constant up to 2000 Å from the surface, this ratio is expected to be 1:6. A somewhat higher value was found here, but since this ratio was approximately constant for all corresponding bands in the two spectra, the apparent discrepancy is attributed to slight changes in the instrumental conditions rather than a difference in the orientation of the molecules in the multilayer as compared to the monolayer. Thus, we conclude that the orientation in the single monolayer is replicated throughout the multilayer structure.

Comparison of pressure–area isotherms of PODMA and PODA earlier in this work has shown that PODA could be compressed into a more compact monolayer on a water surface than PODMA. It is of interest to determine if this more condensed structure is retained on transferring a monolayer of PODA to a solid substrate and whether this increase in packing efficiency can be discerned by polarized IR spectroscopy. Shown in Figure 8 are the structurally significant regions of two spectra of a single monolayer of PODA transferred to solid substrates at 20 °C and a surface pressure of 20 mN m^{-1}. The upper spectrum was measured in transmission and the lower spectrum was recorded by reflection at grazing incidence. A large degree of anisotropy is apparent between these spectra. Comparison of either the transmission or reflection spectrum in Figure 8 with the spectrum measured under identical conditions for PODMA (Figure 5) shows that the absolute magnitude of the C=O stretching vibration is identical, within experimental error. However, there are differences between the magnitudes of the C–H stretching bands for PODMA and PODA. Those of PODA are stronger in transmission and weaker in reflection. The ratio of the sum of the integrated intensities of the asymmetric and symmetric C–H stretching modes measured in reflection to this sum measured in transmission is ~1:4 for PODMA; this ratio increases to ~1:5.5 for PODA. Thus, it would appear from these spectroscopic results that, although the orientation of the carbonyl group is approximately the same for PODMA and PODA, the long ester side chains are more perpendicular to the substrate surface in monolayers of PODA.

Conclusions

It has been demonstrated that stable monolayers of PODMA and PODA may be formed on a water subphase and transferred to solid substrates by means of the L–B technique. Z-type multilayer films can also be transferred to hydrophilic substrates. It is believed that this is the first time genuine Z-type deposition has been observed for L–B films. Single L–B monolayers of these polymers, which are ~30 Å thick, have been investigated by transmission and grazing incidence reflection IR. From the polarized IR spectra obtained with these techniques, orientation of the carbonyl groups and long ester side chains have been studied. The carbonyl groups and ester side chains were found to be approximately perpendicular to the substrate for both PODMA and PODA. The orientation of the former group was little affected by the transfer surface pressure, whereas the precise deposition of the aliphatic chains was strongly dependent upon the transfer pressure and the polymer employed.

Overlap of the backbone C–H stretching bands with the C–H stretching bands of the alkyl tail has prevented a study of the orientation of the polymer backbone in the L–B monolayer. It would be of great interest to investigate the topography of the polymer chain in the monolayer and to determine the extent of overlap that occurs between neighboring chains. However, since the area per repeat unit for these polymers is only ~5–10 % greater than the optimum packing area, it seems unlikely that chain overlapping occurs with any great frequency. A detailed spectroscopic investigation of the orientation of the polymer backbone is currently in progress using partially deuterated PODMA specially synthesized for this purpose.

Acknowledgment. We thank Dr Jürgen P. Rabe for many useful discussions. This work was, in part, supported by the Army Research Office Contract No. DAAG-29-83-K-0100.

References and Notes

(1) Roberts, G. G.; Vincett, P. S.; Barlow, W. A. *Phys. Technol.* **1981**, *12*, 69–87.
(2) Munn, R. W. *Chem. Br.* **1984**, 518–524.
(3) Vincett, P. S.; Roberts, G. G. *Thin Solid Films* **1980**, *68*, 135–171.
(4) Vincett, P. S.; Barlow, W. A.; Boyle, F. T.; Finney, J. A. *Thin Solid Films* **1979**, *60*, 265–277.
(5) Cemel, A.; Fort, T.; Lando, J. B. *J. Polym. Sci., Part A-1* **1972**, *10*, 2061–2083.
(6) Gregoriadis, G., Allison, A. C., Ed. *Liposomes in Biological Systems*; Wiley: New York, 1980.
(7) Hupfer, B., Ringsdorf, H. *Polymeric Monolayers and Liposomes as Models for Biomembranes and Cells*; *ACS Symp. Ser.*; *No. 175*, American Chemical Society: Washington, DC, 1981.
(8) Lieser, G.; Tieke, B.; Wegner, G. *Thin Solid Films* **1980**, *68*, 77–90.
(9) Sarkar, M.; Lando, J. B. *Thin Solid Films* **1983**, *99*, 119–126.
(10) Rabe, J. P.; Rabolt, J. F.; Brown, C. A.; Swalen, J. D. *Thin Solid Films*, in press.
(11) Tredgold, R. H.; Winter, C. S. *J. Phys. D.* **1982**, *15*, L55–L58.
(12) Tredgold, R. H.; Winter, C. S. *Thin Solid Films* **1983**, *99*, 81–85.
(13) Winter, C. S.; Tredgold, R. H. *IEE Proceedings* **1983**, *130*, 256–259.
(14) Winter, C. S.; Tredgold, R. H.; Hodge, P.; Khoshdel, E. *IEE Proc.* **1984**, *131*, 125–128.

(15) Kaufman, H. S.; Sacher, A.; Alfrey, T., Jr.; Fankuchen, I. *J. Am. Chem. Soc.* **1948**, *70*, 3147.
(16) Overberger, C. G.; Arond, L. H.; Wiley, R. H.; Garrett, R. R. *J. Polym. Sci.* **1951**, *7*, 431.
(17) Port, W. S.; Hansen, J. E.; Jordand, E. F., Jr.; Dietz, T. J.; Swern, D. *J. Polym. Sci.* **1951**, *7*, 207.
(18) Greenberg, S. A.; Alfrey, T. *J. Am. Chem. Soc.* **1954**, *76*, 6280.
(19) Plate, N. A.; Shibaev, V. P.; Petrukhin, B. S.; Zubov, Y. A.; Kargin, V. A. *J. Polym. Sci., Polym. Chem. Ed.* **1971**, *9*, 2291.
(20) Hsieh, H. W. S.; Post, B.; Morawetz, H. *J. Polym. Sci. Polym. Phys. Ed.* **1976**, *14*, 1241.
(21) Jones, A. T. *Makromol. Chem.* **1974**, *71*, 1.
(22) Rabolt, J.; Jurich, M.; Swalen, J. D. *Appl. Spectrosc.*, in press.
(23) Gaines, G. L. *Insoluble Monolayers at Liquid-Gas Interfaces*; Interscience: New York, 1966.
(24) Baker, S.; Petty, M. C.; Roberts, G. G.; Twigg, M. V. *Thin Solid Films* **1983**, *99*, 53-59.
(25) Baker, S.; Roberts, G. G.; Petty, M. C. *IEE Proc.* **1983**, *130*, 260-263.
(26) Sagiv, J. *J. Am. Chem. Soc.* **1980**, *102*, 92-98.
(27) Crisp, D. J. In *Surface Phenomena in Chemistry and Biology*; Danielli, Pankhurst, Riddiford, Eds.; Pergamon: London, 1958; p 23.
(28) Crisp, D. J. *J. Colloid Sci.* **1946**, *1*, 161-184.
(29) Nutting, G. C.; Harkins, W. D. *J. Am. Chem. Soc.* **1939**, *61*, 1180-1187.
(30) Dirlikov, S.; Koenig, J. *Appl. Spectrosc.* **1979**, *33*, 551-555.
(31) Dirlikov, S.; Koenig, J. *Appl. Spectrosc.* **1979**, *33*, 555-561.
(32) Greenler, R. G. *J. Chem. Phys.* **1966**, *44*, 310-315.

Laser Raman Optical-Wave-Guide Study of Mono- and Multilayer Langmuir–Blodgett Films of Poly(diacetylenes) Containing a Carboxylic Acid Group

Ryszard Burzynski, Paras N. Prasad,* James Biegajski, and David A. Cadenhead

Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14214. Received September 30, 1985

ABSTRACT: Coherent mono- and multilayer polymer films of the 11-8 diacetylenic fatty acid $CH_3(CH_2)_{11}C\equiv CC\equiv C(CH_2)_8COOH$ were formed by the Langmuir–Blodgett technique. The films thus formed were characterized by traditional force–area isotherms while on a pure water subphase. Molecular organization in both mono- and multilayer films was investigated by the resonance Raman optical-wave-guide method. Our results show that the molecular organizations in both the monolayer and multilayer films are the same and also show no dependence on the nature of the substrate. Furthermore, both monolayer and multilayer films can be prepared in either blue or red forms. The study of the Raman spectral change as a function of the blue-to-red polymer-form conversion reveals that the phase transformation involves a two-phase heterogeneous process.

Introduction

Diacetylenes have received considerable attention because of their ability to form highly ordered polymers by topochemical polymerization in the solid state.[1] Poly(diacetylenes) are highly conjugated linear polymers that exhibit anisotropic optical properties as well as strong third-order nonlinear interactions. Potential applications of poly(diacetylenes) as ultrathin resins, as protective coatings, or as integrated optical devices have been discussed.[2-6]

One special group of diacetylenes has the general formula

$$C_mH_{2m+1}—C\equiv C—C\equiv C—(CH_2)_n—COOH$$

These amphiphilic diacetylenes form traditional mono- and multilayer Langmuir–Blodgett (abbreviated as L–B) films. Photopolymerizations have been observed in these L–B films to produce highly oriented polymer films.[7-9] It has been reported that the polymers formed in the L–B films are initially in a blue (nonfluorescing) form but subsequently transform to a red form that is highly fluorescent.[10,11] The exact nature of this transformation is not established, although it is agreed that the π-electron conjugation in the red form is reduced.

All past studies of structural characterization have dealt with multilayer films. Only very recently, a surface-enhanced Raman scattering study of monolayer L–B films of a poly(diacetylene) with $m = 12$ and $n = 8$ in the above formula has been reported.[12] This work reports that the polymer in a monolayer L–B film deposited on silver is of a different form than that in multilayer films and in a bulk state. These authors attribute this difference as being due to a more delocalized backbone when more than one layer is deposited.

In the present paper, we report the structural studies of mono- and multilayer L–B films of a specific poly(diacetylene) with $m = 12$ and $n = 8$ by using the technique of Raman optical wave guide. The Raman optical-wave-guide technique has successfully been used in the vibrational study of many polymer films.[13] The technique does not rely on any specific enhancement from the surface of the substrate, such as is the case when the film is deposited on silver. In addition, the study of poly(diacetylene) films in an optical-wave-guide system is also of interest from the point of view of its application in integrated optical devices. These films are deposited on several different kinds of optical wave guides to examine the effect of the substrate. Mono- and multilayer films are compared to investigate if indeed the monolayer structure is different from that of multilayer L–B films. Finally, we discuss the formation of both blue and red forms in monolayer and multilayer L–B films.

Experimental Section

L–B Experiments. The diacetylenic fatty acid used in this study was $CH_3(CH_2)_{11}C\equiv CC\equiv C(CH_2)_8COOH$. From here on the monomer will be abbreviated as 11-8 DA and the corresponding polymer as 11-8 PDA. It was obtained from Dr. D. Chapman (Royal Free Hospital, School of Medicine, London, England) and was used without further purification. Prior to L–B film formation, bulk material was stored in a dark container at about 0 °C to avoid polymerization and thermal decomposition. The water used for the subphase was first distilled and subsequently filtered to remove trace organics and ions. This water of resistivity more than 15 MΩ cm was then quadruply distilled, first from a slightly

0024-9297/86/2219-1059$01.50/0