Vapor Deposition Photopolymerization of Long-Chain Vinyl Compounds: Polymerizability and Molecular Orientation of *n*-Octadecyl Acrylate

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Polymerizability and molecular orientation in the films prepared by vapor deposition photopolymerization of *n*-octadecyl acrylate, in which substrates were irradiated with UV light during deposition, were investigated in comparison with photoinitiated postpolymerization in monomer films prepared by normal vapor deposition (irradiated after deposition). The percentage of the polymer in the films increased with increasing substrate temperature and reached 90% at 20 °C in deposition for 3 h. On the other hand, the percentage was 20% at 20 °C in postpolymerization with irradiation for the same period. The difference in the polymerizability between these two methods was due to the migration of monomers and radicals on substrates during vapor deposition photopolymerization. The molecular orientation in the films was evaluated by polarized FT-IR-ATR measurements. The calculated chain axis tilt angles with respect to the surface normal suggest that the number of methylene units involved in the ordered region is large in the films prepared by vapor deposition photopolymerization since the molecules on substrates have high mobility during deposition.

Introduction

Organic thin films with ordered structure have attracted much attention because of possibilities of their applications to a wide range of functional molecular devices in electronics and optics.[1,2] Although a number of studies have been reported on the concept of molecular devices with thin films, a main problem raised was that thermal, chemical, and mechanical stability of thin films was poor. Polymerization offers an interesting method to improve these properties.[3,4] One representative way to prepare thin films with the desired molecular orientation is the Langmuir–Blodgett (LB) method, by which highly ordered monolayers or multilayers of a number of compounds can be deposited on substrates. To prepare thin polymer films, monomers with functional groups such as unsaturated fatty acids are deposited on substrates and then are polymerized. However, it is difficult to obtain defect-free polymer films by this method since volume change occurs during polymerization. In deposition of preformed polymers, it is sometimes quite difficult to spread it onto the air–water interface to form a condensed monolayer. In addition, disadvantages in the LB method are the difficulty in preparing films with a large surface area and a slow speed to build up multilayers.

The other representative method to prepare thin films is vapor deposition. It is well-known that the molecular orientation of long-chain molecules in deposited films can be controlled by changing the substrate temperature, the deposition rate, the surface energy of the substrate, and so on.[5,6] This method has advantages over the LB method because the films are formed at a high deposition rate and are free from contamination. To prepare thin polymer films having a highly ordered structure by vapor deposition, three kinds of approaches are reported. First, preformed polymers are evaporated directly onto substrates. In this case, degradation such as chain scission often occurs, and hence the molecular weight drastically drops from that of the original. Second, monomer molecules having reactive functional groups are deposited on substrates and then are polymerized. The third approach is vapor deposition polymerization. This method has been developed mainly in a polycondensation system. Two monomers are coevaporated, and a collision of the functions of two monomers occurs during the migration of the monomers and the oligomers on substrates, which leads to polymerization. For example, thin films of polyimide were widely examined with various combinations between acid anhydrides and amines because of its excellent heat resistance and chemical stability[7,8] The polymer chain axes in the film are oriented perpendicularly to the substrate. Usually, polyimide films are prepared through the corresponding poly(amic acid), and annealing is required for imidization. In some cases, reevaporation of monomers and the oligomers takes place during annealing, which causes pinholes in the film.

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In a polyaddition system, vapor deposition polymerization has been studied using plasma or UV light. However, the films are generally amorphous and involve cross-linking, and hence it is difficult to control the molecular orientation in the film.[9] Tamada et al. reported the formation of poly(*n*-octadecyl methacrylate) film by vapor deposition of its monomer in the presence of a red-hot filament.[10] A part of evaporated molecules were decomposed to radicals in vapor phase, and the polymerization was initiated on the substrate. By changing the substrate temperature, the deposition rate, and the filament temperature, the long alkyl side chains oriented perpendicularly to the substrate.

It was reported that vinyl compounds having long alkyl chains were deposited by the LB method and that polymerization proceeded under UV irradiation. The polymerizability was found to be affected by the molecular orientation in the films. As mentioned above, molecular orientation in the films prepared by vapor deposition can be controlled. However, only a few number of vinyl compounds having long alkyl chains have been studied in vapor deposition polymerization with respect to the polymerizability and the molecular orientation.[10,11] We selected vapor deposition photopolymerization, in which substrates were irradiated with UV light during deposition. In this method, since polymerization proceeds simultaneously with deposition, defects caused by volume change during polymerization in monomer films can be avoided, and hence uniform films would be obtainable. The orientation of *n*-alkyl chains in deposited films can be controlled by changing experimental conditions, because this method is based on vapor deposition. In addition, since both radicals and molecules can migrate on substrates during deposition, this method is expected to give us different polymerization behavior and molecular orientation from those found for normal deposition.

In a series of studies, we chose *n*-octadecyl acrylate (ODA) as a monomer. ODA has been studied in LB films since its long alkyl chain and polar ester group promise an oriented structure at the air–water interface. The earliest works on monolayer polymerization of analogous compounds, i.e., *n*-octadecyl methacrylate and *N*-*n*-octadecylacrylamide, were reported by Ringsdorf et al.[12] Fukuda et al. reported the polymerizability of ODA in two types of multilayers.[13-15] ODA transferred at lower pressure showed X-type deposition (head-to-tail arrangement), whereas at higher pressure showed Y-type (head-to-head, tail-to-tail arrangement). From polarized IR measurements, the molecular orientation was found to be uniaxial in the X-type film and biaxial in the Y-type. In γ-ray initiated polymerization, the polymerizability in the X-type film (30% at 20 °C, 1.0 Mrad) was higher than that in the Y-type (10%), suggesting that molecules in the X-type film were packed loosely compared to those in the Y-type and that some rotational freedom was allowed in the former film.[14] Indeed, the conversion in the X-type film reached over 90% in photopolymerization using Xe lamp.[15] They did not report about the molecular orientation in the polymerized films.

In this paper we studied the polymerizability and molecular orientation of ODA molecules in films prepared by vapor deposition photopolymerization and compared the results with those found in normally deposited films.

Experimental Section

ODA (Tokyo Kasei) was treated with 1% sodium hydroxide aqueous solution to remove inhibitor and finally recrystallized twice from ethanol. Poly(*n*-octadecyl acrylate) used as a reference was prepared by radical polymerization of ODA in a degassed benzene using AIBN as an initiator at 60 °C. The polymer was purified by repeated precipitation from benzene solution into methanol.

Vacuum deposition was performed in a homemade vacuum chamber having quartz windows. The degree of vacuum in the chamber was kept at (5–8.0 × 10^{-6} Torr. The sample was evaporated from an aluminum furnace at 75 °C. A substrate was placed with an angle of ca. 45° against the directions of the evaporation and irradiation so that UV irradiation could be done during deposition. During vapor deposition photopolymerization the substrate was irradiated with a 150 W Xe lamp, with a condensing lens and a water filter (7 cm), throughout deposition for 3 h. In photoinitiated polymerization of the normally deposited films (postpolymerization), the irradiation was carried out under N_2 atmosphere for 3 h after normal deposition. The thickness of films was ca. 1 μm in the temperature range between −10 and 15 °C, estimated from the intensity of IR absorptions.

Substrates used were ZnSe and NaCl plates. These plates were cleaned before use by sonication in distilled chloroform for 20 min three times.

Infrared spectra were obtained at 18 °C with a resolution of 4 cm^{-1} by using FT-IR spectrometer FIRIS 100 (Fuji Electric) equipped with a DTGS or a liquid nitrogen cooled MCT detector. Interferograms were collected in double precision and Fourier transformed with triangular apodization. Usually 256–512 scans were signal averaged for acceptable signal/noise ratios.

For FT-IR-ATR measurements, a ZnSe plate (25 × 10 × 3mm, 45° parallelepiped) was used as an ATR crystal. A thin film was deposited on one large face of the ZnSe plate and the surface area of the film was 16 × 9 mm. A bench accessory and a wire grid polarizer were used. For the ATR plate used, eight reflections of the IR beam were allowed, and three of them were meaningful for the measurement.

For liquid transmission measurements, a demountable liquid transmission cell with a spacer (0.1 and 0.5 mm) and potassium bromide windows (S. T. Japan Inc.) was used with chloroform as solvent, and the spectra were the results of 1024 coadded scans. Spectra of bulk compounds in transmission were obtained in a potassium bromide pellet.

Results and Discussion

Photoinitiated Polymerization of ODA in the Deposited Films. IR spectra are very informative on the intermolecular environment of the molecules in samples. The transmission spectrum of ODA deposited on a ZnSe plate at −10 °C is shown in Figure 1, and mode assignments of signals are summarized in Table 1 with those for its polymer. The absorptions at 2918 and 2850 cm^{-1} are assigned to the antisymmetric and symmetric CH_2 stretching modes ($\nu_{as}CH_2$ and ν_sCH_2), respectively. All films examined showed the CH_2

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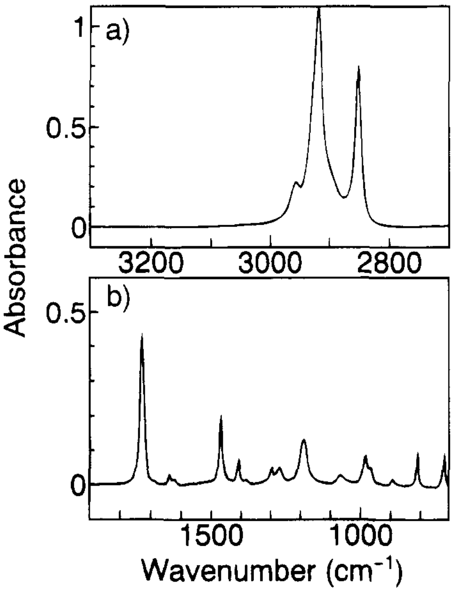

Figure 1. Transmission IR spectra of the ODA film deposited on a ZnSe plate at −10 °C.

Table 1. Infrared Spectra and Mode Assignments for ODA and Its Polymer

frequency		
monomer	polymer	mode[a]
2955	2955	CH_3, asym str
2918	2918	CH_2, asym str
2850	2850	CH_2, sym str
1725	1732	C=O, str
1635–1620		C=C, str
1467	1467	CH_2, scissors def
1408		$=CH_2$, C–H ip def
1298, 1275	1249	C–O–C(ester), asym str
1197	1167	C–O–C(ester), sym str
1065		=CH–, C–H ip def
980		$=CH_2$, C–H op def
890		=CH–, C–H op def
810		$=CH_2$, C–H op def
720	720	CH_2, rocking def

[a] The following symbols are used: str for stretching, def for deformation, ip for in-plane, op for out-of-plane.

stretching modes at the same positions irrespective of experimental conditions. Snyder et al. have shown that the positions of the peak frequencies for the CH_2 stretching modes are sensitive indicators for the extent of the lateral interactions between *n*-alkyl and polymethylene chains.[16,17] The peak positions for the $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ modes of a crystalline polymethylene chain (all-trans zigzag) are 2920 and 2850 cm^{-1}, respectively, whereas those for the liquid state are 2926 and 2856 cm^{-1}. From the peak positions for the CH_2 stretching modes, we may conclude that *n*-alkyl chains in all deposited ODA films are fully extended with all-trans zigzag conformation in a crystalline state, although the progression bands due to the coupled twisting and wagging modes of the CH_2 group in all-trans zigzag chains are not observed between 1150 and 1350 cm^{-1} because of the strong absorptions of the ester group in the same region. The crystallization of *n*-alkyl chains in the deposited ODA films is also supported by the fact that the deposited films are opaque.

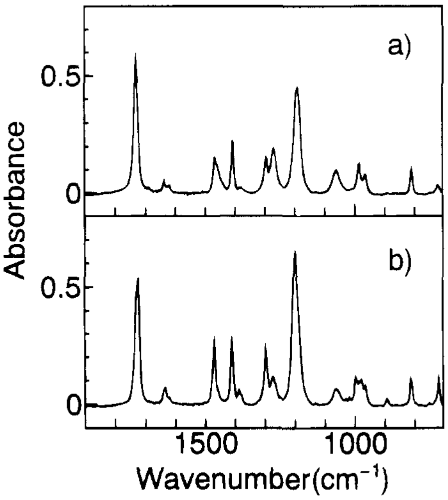

Figure 2. Transmission IR spectra of ODA in a KBr pellet (a) the α-form with the hexagonal packing, (b) the β-form with the triclinic packing obtained by thermal transformation from the α-form.

The absorptions at 1467 and 720 cm^{-1} are assigned to the scissoring and rocking vibration of methylene groups, respectively. These bands are closely correlated with the packing mode of the long alkyl chains. When *n*-alkyl chains are crystallized in a monoclinic or an orthorhombic subcell, these bands should be split into doublet by the crystal field.[18,19] On the other hand, the spectra of the deposited ODA films exhibit single bands of these vibrations, indicating that the hydrocarbon chains in the films are in a triclinic or a hexagonal subcell packing.[18,20]

Three kinds of crystalline modifications were reported for ODA monomer;[21] the α-form with the hexagonal packing is stable at room temperature, and the β-form with the triclinic packing is a stable modification at lower temperature. A metastable form appears transiently in the α to β transition in cooling. The triclinic and hexagonal packing forms can be distinguished by IR spectra. The spectra in Figure 2, parts a and b, correspond to the hexagonal and the triclinic packings, respectively, which were obtained by a successive temperature change of ODA embedded in a KBr pellet. Some characteristic bands show a remarkable change in the shape and intensity on the phase transition. For example, the CH out-of-plane deformation at 980 cm^{-1} and the C=C stretching at 1635 cm^{-1} for the hexagonal packing have distinct shoulders at 964 and 1620 cm^{-1}, respectively (Figure 2a), while these shoulders are observed only with difficulty for the triclinic packing (Figure 2b). The band of the C–O–C asymmetric stretching vibration is observed as doublet at 1296 and 1273 cm^{-1} in both the spectra, while the peak at 1296 cm^{-1} is more intense than that at 1273 cm^{-1} in the spectrum of the triclinic form. The features of these bands of the deposited ODA film (Figure 1b) are quite similar to those of the hexagonally packed molecules. The characteristic features showing the triclinic packing were not observed for all films examined. Therefore, we conclude that the ODA molecules in the films

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deposited in the temperature range between −10 and 20 °C are crystallized in the hexagonal packing.

On the basis of thermal analyses,[21] the α-form was reported to start to transit to the β-form around 0 °C in cooling. However, ODA molecules in the films deposited at −10 °C were crystallized in the hexagonal packing. This behavior may be similar to the fact that the sample obtained by shock crystallization of the melt maintains the α-form for several hours even at a temperature as low as −10 °C.[21]

It is noted here that, although the band features in Figure 1 are quite similar to those in Figure 2a, the relative intensities of the absorptions are quite different from each other. One may consider the possibility that a sort of reactions occurs during deposition. However, this is not likely because the chloroform solution in which the deposited ODA film was dissolved showed the identical IR spectrum with that of ODA. Since ODA molecules in a KBr pellet are randomly oriented, the difference in the intensities between Figures 1b and 2a suggests that ODA molecules in the deposited films have some orientation on the substrate (*vide infra*). In addition, all deposited films of ODA were soluble in methanol, indicating that a part of ODA thermally polymerized in the evaporating boat are not deposited on substrates. Hence, the polymerization discussed below for the normally deposited films (postpolymerization) is initiated only by photochemical process.

The polymerizability of ODA molecules in crystalline samples has been reported with respect to γ-ray-initiated polymerization.[21] In the β-form with the triclinic packing the volume of the CH_2 group in alkyl chains is 23.3 Å^3, whereas that in the α-form with the hexagonal packing is 26.0 Å^3.[21] Since the side chains in poly(*n*-octadecyl acrylate) have a hexagonal packing, polymerization in the α-form proceeded, although some distortion of the side chains may occur in the vicinity of the main chain. On the other hand, polymerization hardly proceeded in the β-form since a large volume expansion is necessary for the polymerization. In addition, the molecules in the α-form are arranged hexagonally in the lamellar structure[22] where some conformational freedom of the functional groups is allowed in a statical sense.[23,24] From these facts the polymerizability in the α-form was enhanced in γ-ray-initiated polymerization. A photoinitiated polymerization is expected to proceed in the deposited film because the ODA molecules in the films are crystallized in the lamellar structure with the hexagonal packing as in the α-form crystal.

The percentage of polymerization was estimated from the integrated intensity change in the absorptions due to the vinyl group (see Table 1). The quantity of $100(A_0 - A_t)/A_0$, where A_0 and A_t are integrated intensities of the band before and after the irradiation, respectively, corresponds to the percentage of polymerization. UV irradiation was carried out for 3 h at the same temperature as at the deposition. The percentages of polymerization were 7 (−10 °C), 24 (8 °C), 16 (15 °C), and 20 (20 °C)%. At 15 °C, the percentage of polymerization increased only by 2% after the irradiation for additional 3 h, indicating that irradiation for 3 h is enough to reach the saturated percentage in the present experiment. These values are comparable with that in the α-form crystal (0.1 Mrad)[21] in γ-ray-initiated polymerization[13] but much smaller than that (90%) in the X-type LB film (90%) in photopolymerization using a 500 W Xe lamp.[15] As expected, the percentage was large at a high temperature. This is owing to thermal motion of molecules, by which functional groups are allowed more rotational freedom. However, the percentage increased only up to 24%, suggesting molecules are packed closely in the film prepared by normal deposition.

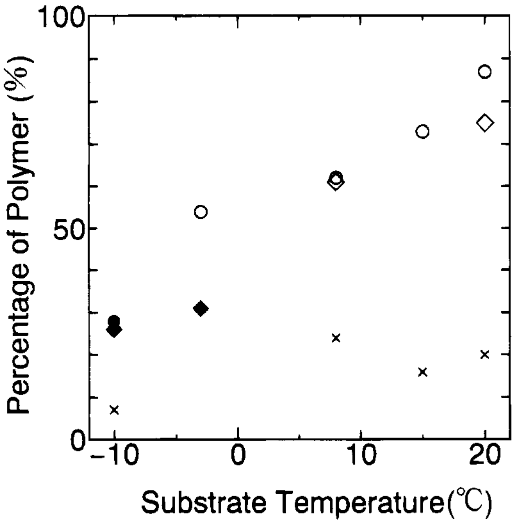

Figure 3. Temperature dependence of the percentage of the polymer in films prepared by vapor deposition photopolymerization; open and closed plots were obtained from cast film and chloroform solution, respectively (see text): (○) on a ZnSe plate, (◇) on a NaCl plate; (×) for postpolymerization on a ZnSe plate for comparison.

Vapor Deposition Photopolymerization of ODA. The percentages of polymerization in vapor deposition photopolymerization are not simply evaluated from the change in the integrated intensities of the absorptions of the vinyl group as in postpolymerization. Because it is quite difficult to obtain ODA monomer films having the same film thickness and molecular orientation as the films prepared by this method, we used the peak intensity ratio of the CH_2 in-plane deformation at 1410 cm^{-1} observed only for the monomer to the CH_2 scissoring deformation at 1467 cm^{-1} common to both the monomer and the polymer for the estimation. Since the films deposited at high substrate temperatures were partially insoluble in chloroform but peeled from the substrate, we measured transmission IR spectra of the films cast from the suspension. When the deposited films were completely dissolved, the chloroform solution was used for IR measurements. A linear relationship of the ratio against the percentage of the polymer was confirmed in separate measurements. The percentages calculated on the basis of this relationship are plotted against the substrate temperature in Figure 3.

The peak positions of the C=O stretching and the C−O−C stretching modes shifted gradually to the

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(22) The molecules in the α-form are layered with head-to-tail arrangement, since the distinct peaks corresponding to the first, second, and third orders of the spacing of 29.7 Å (nearly equal to the length of fully extended molecule) were observed in X-ray powder diffraction patterns in ref 21.

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higher- and lower-frequency regions, respectively, with increasing substrate temperature. These peak shifts indicated an increase in the percentage of the polymer in the deposited films (Table 1). The calculated percentage increases with increasing substrate temperature as expected from the peak shifts (Figure 3). Although the surface properties of ZnSe and NaCl plates are different, no distinct difference is found for the temperature dependence of the percentage of the polymer. It must be noted that the percentages of the polymer in the films prepared by this method are much higher than those in postpolymerization of normally deposited ODA films as seen in Figure 3, although IR spectra showed that long alkyl chains in the films are hexagonally arranged irrespective of the preparation method. Since both radicals produced by UV irradiation and monomers migrate on the substrate surface in vapor deposition photopolymerization, they have much more chance to encounter each other in a suitable configuration for the reaction than in the postpolymerization. Therefore, the large difference in the percentage of the polymer between the vapor deposition photopolymerization and the postpolymerization is attributed to the migration of molecules. Since both the rotation and the migration of the molecules become easier at a higher temperature, the percentage of the polymer increased with increasing substrate temperature.

Desorption of monomers from the deposited films is another factor to be considered. Since the vapor pressure of molecule drastically decreases as the molecular weight increases, the reacted molecules are hard to desorb from substrates. On the other hand, monomers desorb more easily at a higher temperature, and consequently the percentage of the polymer in the resultant film increases at a higher temperature. Although the thickness of the films deposited below 15 °C did not vary remarkably, the thickness at 20 °C dropped to about half of those below 15 °C. Therefore the desorption of monomers is another considerable factor for the percentage near 90% at 20 °C.

As mentioned above, the films deposited at high temperatures were partially insoluble in chloroform and the insoluble portion increased with increasing substrate temperature. This is due to an incidental cross-linking in photopolymerization of ODA. The occurrence of cross-linking was previously reported for photochemical polymerization of methyl acrylate vapor, in which hydrogens on the α-carbon were detached and the branching by means of propiolic ester occurred.[25] The process proposed in the literature seems not to be the main cross-linking reaction in the present results since the carbonyl groups were considered to participate in a cross-linking process as shown below. The well-known photochemistry of poly(*n*-alkyl acrylate)'s and *n*-alkyl acrylate's includes depolymerization, Norrish type I, and type II reactions.[26,27] Since the irradiation was performed using Xe lamp, the carbonyl group in the ester group in addition to the vinyl group was also excited in our experiments and the photochemical reactions at the ester group might take place. To confirm the reaction, the peak intensity ratio of the C=O stretching against the CH_2 scissoring deformation was examined in the IR spectra. The ratio for the monomer embedded in a KBr pellet is ca. 2.4. Although the films deposited at −10 and −3 °C showed the same value irrespective of the substrate used, the ratio decreased with increasing substrate temperature and fell to ca. 1.6 at 20 °C.[28] This result indicates the presence of the photochemical cleavage of the ester group at high temperatures. Any detectable decrease in the ratio was found neither in postpolymerization nor after irradiation to the cast film of poly(*n*-octadecyl acrylate).

If Norrish type reactions occur, the radicals expected to produce are $^{\bullet}COOC_{18}H_{37}$, $^{\bullet}C_{18}H_{37}$, and $^{\bullet}OC_{18}H_{37}$.[26] Since many reaction processes can be considered from these radicals, a cross-linking mechanism is very complicated, and we cannot describe what kind of cross-linking occurs in the deposited films. In the IR spectra of the films deposited above 8 °C, a broad absorption newly appeared in the wavenumber region between 1000 and 1100 cm^{-1} which we were unable to assign. The bands at 1780 and 3260 cm^{-1} indicating the formation of the hydroxy group, which were observed for the irradiated poly(*n*-butyl acrylate),[26] were not detected in our experiments. Since insoluble gel portion was found only in vapor deposition photopolymerization at a high temperature, mobility of molecules or segments seems to be required for the cross-linking reaction.

The molecular weight of polymers obtained by the present method is an intriguing matter from the viewpoint of polymer chemistry. In γ-ray-initiated polymerization in the hexagonal form crystal, the molecular weight of the polymer attained over a million.[21] Unfortunately, since an insoluble gel portion was obtained at a high temperature or the amount of the soluble polymer was too small, the molecular weight could not be measured in a general way. Therefore, we have no quantitative information on this matter at present.

Molecular Orientation in Normally Deposited Films. Figure 4a shows geometry of ATR experiments with the directions of infrared beam and polarization. The *z* axis is along the normal to the film or to the ATR plate interface; the *x* axis is along the propagation direction of the beam; the *y* axis is along the direction of the s-polarization. The p-polarization lies in the plane-of-incidence (the *xz* plane) at 45° with each of the two axes. As the infrared beam is totally reflected at the ATR plate/film interface, an evanescent wave decays exponentially in the film. This wave consists of three electric field vectors which interact with the sample film.

When all transition moments of the molecules in the film are uniaxially oriented around the *z* axis (the surface normal) as shown in Figure 4b, the absorbances due to the each electric field component, E_x, E_y, and E_z, are given by[29,30]

$$A_y = {}^1\!/_2 M^2 E_y^{\,2} \sin^2 \phi$$

$$A_x = {}^1\!/_2 M^2 E_x^{\,2} \sin^2 \phi$$

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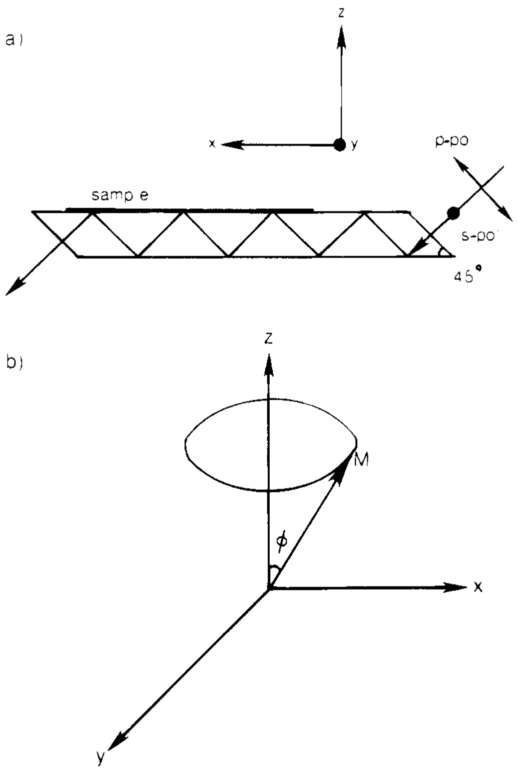

Figure 4. (a) Schematic representation of light undergoing multiple reflections in an ATR plate with experimental geometry and polarization and (b) uniaxial orientation of the transition moment.

$$A_z = M^2 E_z^2 \cos^2 \phi \qquad (1)$$

where ϕ is the angle between the transition moment, M, and the z axis (Figure 4b). The expressions for the electric field components E_x, E_y, and E_z have been evaluated by Harrick.[31] The dichroic ratio in this orientation is therefore

$$D = \frac{A_s}{A_p} = \frac{E_y^2}{E_x^2 + 2E_z^2} \qquad (2)$$

To determine the angle, ϕ, from ATR measurements, we assumed $n_{2x} = n_{2y} = n_{2z}$. Neglecting the dispersion of refractive indices, we fixed the n_1 and n_2 values at 2.40 and 1.50,[29] respectively, throughout the wavenumber region examined.

Figure 5 shows the polarized transmission spectra of the ODA film deposited on a ZnSe plate at −10 °C. The solid and dotted lines refer to the orientation of the electric vectors parallel to the x and y axes (Figure 4a), respectively. Since the two spectra are identical, the molecules in the deposited film are randomly oriented in the xy plane. All films prepared in this work also showed the same transmission spectra irrespective of polarization direction. In Figure 6 is shown the polarized ATR-IR spectra of the same film. The intensities of the asymmetric and symmetric CH_2 stretching modes at 2918 and 2850 cm^{-1} and the CH_2 scissoring deformation mode at 1467 cm^{-1} are stronger in the p-polarized spectrum, whereas those of the C=O stretching mode at 1726 cm^{-1}, the asymmetric C−O−C stretching mode at 1298 and 1273 cm^{-1}, the symmetric C−O−C stretching mode at 1197 cm^{-1}, and modes for the vinyl group at 1635−1620, 1408, 1065, and 980 cm^{-1} are stronger in the s-polarized spectrum. From the results of polarized transmission and ATR spectra, it may be concluded that the molecules are uniaxially oriented with respect to the z axis in the film. Since each molecule cannot orient in a random position in a crystalline state, the deposited films are composed of many crystallites oriented randomly around the z axis. The directions of the transition moments for characteristic modes are given in Table 2.[32,33] Here, the direction of the transition moment for the symmetric C−O−C stretching (the ester band) is not assigned due to the complex coupling of other modes with this stretching,[34] but the direction of this band should be correlated with that of the C=O stretching because the five atoms in the ester group in poly(methyl methacrylate) films form a rigid planner

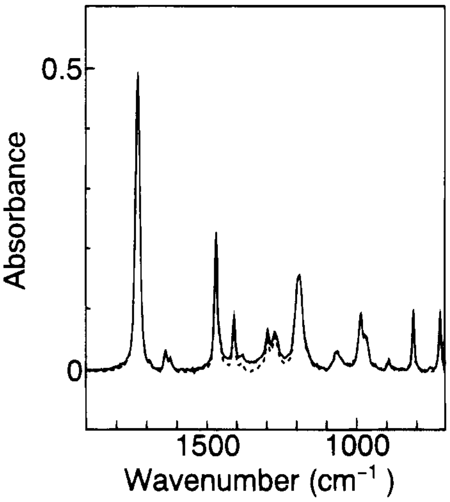

Figure 5. Polarized IR transmission spectra of ODA deposited on a ZnSe plate at −10 °C. Solid and dotted lines refer to the orientation of the electric vectors parallel to the x and y axes of the ZnSe plate, respectively.

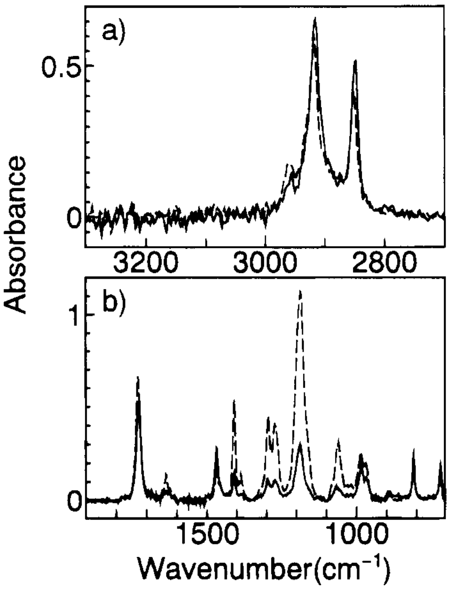

Figure 6. Polarized ATR-IR spectra of ODA molecules deposited on a ZnSe plate at −10 °C. Solid and broken lines refer to p- and s-polarized incidence, respectively.

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Table 2. Directions of Selected Transition Moments (M)[a]

mode[b] (in order of decreasing frequency)	direction of M relative to molecular coordinate[c]
CH_3, asym str	⊥ ccc backbone plane
CH_2, asym str	⊥ chain axis
CH_2, sym str	⊥ chain axis, ip ccc backbone ∥ H−C−H plane, bisecting HCH angle
C=O, str	∥ C=O bond
CH_2, scissoring def	⊥ chain axis, ip ccc backbone ∥ H−C−H plane,bisecting HCH angle
$=CH_2$, CH_2 op def	⊥ $C=CH_2$ plane

[a] From refs 32 and 33. [b] See Table 1 for details. [c] ∥, parallel; ⊥, perpendicular; ip, in-plane; op, out-of-plane.

Table 3. Mode and Calculated Transition Moment Orientation for ODA Molecules in the Deposited Films

	ϕ, angle of M from the surface normal (deg)								
temp[a] (°C)	ν_{as}-(CH_3)	ν_{as}-(CH_2)	ν_s-(CH_2)	ν-(C=O)	δ-(CH)[b]	ν-(COC)[c]	δ-(CH)[d]	γ[e]	γ'[e]
−10	69	65	63	71	60	81	71	39	41
8	70	62	61	70	62	80	74	43	43
15	73	63	61	69	62	81	73	41	43
20	72	64	62	70	62	80	71	39	42

[a] The substrate temperature. [b] CH_2 scissoring deformation at 1467 cm^{-1}. [c] Symmetric stretching at 1197 cm^{-1}. [d] $=CH_2$, C−H out-of-plane deformation at 980 cm^{-1}. [e] The chain axis tilt angle from the surface normal.

configuration.[35] In the evaluation of molecular orientation in films containing polymers, we neglect the one CH_2 group per repeating unit in the main chain since there are 17 CH_2 groups in the side chain.

The angles of the transition moments for the characteristic bands with respect to the z axis are listed in Table 3 for the molecules in the normally deposited films. In ATR analysis as the direction of the transition moment becomes parallel to the film surface, the accuracy of its estimated angle increases.[36] In the calculated angle region, we estimated the error in the dichroic ratio to be less than 0.01 in IR measurements. Such an error in the dichroic ratio corresponds to the error of only ca. 0.2° in ϕ. Therefore, the estimated angles should provide clear information about molecular orientation. However, films prepared under the same conditions reproduced the dichroic ratio with the error less than 0.1, corresponding to the error of ca. 2° in ϕ. The angles listed in the tables are therefore representative results at each substrate temperature.

The angle for the C=O stretching is 71°, indicating that the C=O bonds are relatively parallel to the surface. This is quite different feature from that in the LB film of ODA, in which the C=O bonds are preferentially perpendicular to the surface.[37] The different orientation should be attributable to the difference in the surface properties. The orientation of the C=O bonds in the LB films is dominated by the interaction at the air−water interface and the polar C=O bonds direct along the normal to the interface. Since the surface of a ZnSe plate is not hydrophilic, the same interaction as that at the air−water interface is not expected.

The orientation of the C=C group is complicated since the existence of two peaks at 1635 and 1620 cm^{-1} for the C=C stretching vibration indicate that there are transoid and cisoid conformations of the double bonds in the $H_2C{=}CHC({=}O)O-$ group.[21] However, since the modes for the vinyl group (Table 1) are observed more strongly in the s-polarized spectrum compared with the p-polarized one (Figure 6b), the C=C bonds are considered to lie in the xy plane. The angle for the mode at 980 cm^{-1}, for which the direction of the transition moment is perpendicular to the C=C bond, is 71° (Table 3) at −10 °C. In addition, the direction of the transition moment for the C=C stretching mode is parallel to the C=C bond, and the calculated angle for this mode at 1635 cm^{-1} is 89°. From these angles and the space-filling model of ODA, we suppose that the C=C bond is almost perpendicular to both the z and the chain axes.

The directions of the transition moments for the asymmetric and symmetric CH_2 stretching are perpendicular to the chain axis and the angles for these modes are 65° and 63°, respectively. Takenaka et al. proposed a method to calculate the chain axis tilt angle, γ, using the tilt angles of two transition moments.[38,39] For an orthogonal system of the chain and two transition moments, γ can be evaluated by

$$\cos^2 \phi_1 + \cos^2 \phi_2 + \cos^2 \gamma = 1 \tag{3}$$

The asymmetric and symmetric CH_2 stretching vibrations are good candidates for the two transition moments, because these vibrations are known to be pure modes which do not mix with other modes.[39,40] The average chain axis tilt angles (γ) calculated using eq 3 are also listed in Table 3. At −10 °C, the chain axes of the molecules in the deposited film are tipped away from the z axis by 39°. This angle is larger than that for cadmium stearate in the LB film[38] but comparable with those for ω-tricosenoic acid in the vacuum-deposited film,[11] lauric acid adsorbed on a Ge plate,[39] and azobenzene-containing long fatty acids in the LB film.[23] The tilt angles of the transition moments of both the C=O stretching and the CH_2 out-of-plane deformation of the $=CH_2$ group are 71°. The molecular orientation of ODA from these results are schematically illustrated in Figure 7.

It is important to note here that this result is an average orientation. The chain group mode frequencies should be generally unaffected by small differences in interchain interactions and changes in orientation with respect to the surface. Therefore line shapes do not give us any information on the distributions of orientation. It is a possibility that the data could be rationalized by invoking some fortuitous combination of *gauche*-CH_2 group interactions along occasional twisted chains with a very high proportion of chains having a fully extended trans zigzag conformation and with orientation closely normal to the surface.[33] In such a case, the chain axis tilt angles calculated from IR measurements should be larger than the actual angles in the films.

Although it is well-known that the chain axes of n-paraffins and long-chain alkyl fatty acids in the deposited film tend to orient along the surface normal with increasing substrate temperature,[5,6] the chain axis

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(36) Maoz, R.; Sagiv, J. *J. Colloid Interface Sci.* **1984**, *100*, 465.

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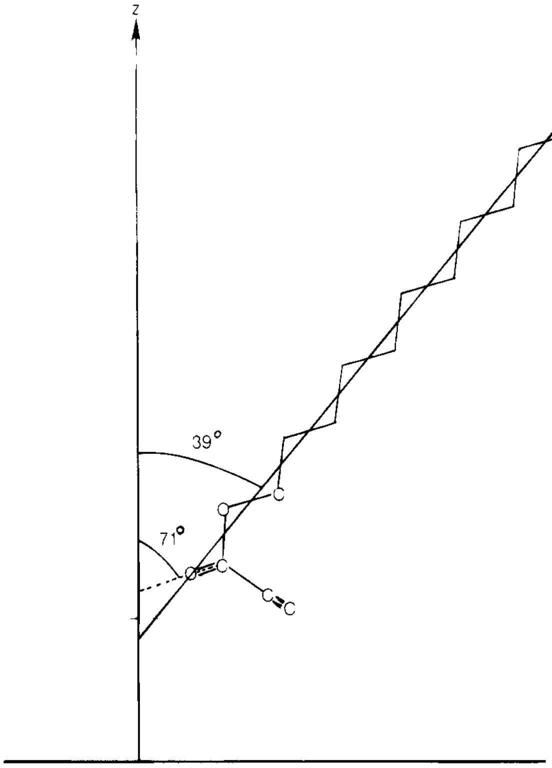

Figure 7. Schematic illustration of the molecular orientation of *n*-octadecyl acrylate in the film deposited on ZnSe plate at −10 °C.

tilt angle in the present films is almost independent of the substrate temperature. Even at a temperature of the substrate as low as −10 °C, ODA molecules orient with their alkyl chain axis tilt angle of 39°. We cannot mention at the present stage whether it is the nature of ODA to orient with the chain axis tilt angle of ca. 40° on a ZnSe surface or whether the temperature range we examined is too narrow to observe the orientational change.

Molecular Orientation after Postpolymerization. The chain axis tilt angle after postpolymerization, γ', are listed in the far right column in Table 3. The chain axis tilt angle increased by ca. 2° after the polymerization. It is reasonable to consider that the increase is due to an increase in the conformational disorder of the alkyl chain. To polymerize in the same plane of the lamellar structure, the molecules must change more or less their positions.[41] This change might cause a distortion in the ordered structure of the molecules. Although the side chains in poly(*n*-octadecyl acrylate) are crystallized in a highly ordered structure, a part of the side chains in the vicinity of the main chain are known to be in a disordered phase with a random displacement of the side chain crystallites.[42,43] The same random displacement may occur after the polymerization.

Molecular Orientation in Films Prepared by Vapor Deposition Photopolymerization. The molecular orientation in the films prepared by vapor deposition photopolymerization was also evaluated, and the calculated angles (ϕ) of the transition moments are listed in Table 4 with the chain axis tilt angle γ. The angles for the transition moments are close to those for the ODA molecules in the normally deposited films. The chain axis tilt angles, γ, are between 42 and 45°. The γ values are slightly larger than those for the normally deposited film at the same temperature. The increase in γ is considered to be due to the existence of the polymer in the film, where a part of methylene groups in the side chains are disordered.[44] The aforementioned cross-linking may also disturb the orientation.

Table 4. Mode and Calculated Transition Moment Orientation for ODA Molecules in the Films Deposited under Irradiation

	ϕ, angle of M from the surface normal (deg)						
temp[a] (°C)	ν_{as}-(CH$_3$)	ν_{as}-(CH$_2$)	ν_s-(CH$_2$)	ν-(C=O)	δ-(CH)[b]	ν-(COC)[c]	γ[d]
−10	69	62	59	69	60	83	45
−3	70	63	59	71	59	79	43
8	73	63	60	71	62	78	42
15	73	62	60	72	61	80	44
20	70	65	62	72	63	79	39

[a] The substrate temperature. [b] CH$_2$ scissoring deformation at 1467 cm^{-1}. [c] Symmetric stretching. [d] The chain axis tilt angle from the surface normal.

Interestingly, although the percentages of the polymer in the films are much higher in vapor deposition photopolymerization than in postpolymerization (Figure 3), the chain axis tilt angles are almost the same. These results may indicate that the number of methylene groups of the side chains included in the ordered region is larger in vapor deposition photopolymerization than in postpolymerization, and the position of cross-linking is located in the region near the main chain.

Concerning the side-chain crystallization of poly(*n*-octadecyl acrylate), Jordan et al. proposed the number of methylene group in the ordered region to be 8−9 from thermodynamic studies[45] and also reported that the number of methylene units increased at the crystallization in the presence of methanol, which solvated the polar carbonyl groups of the main chains and increased the main-chain mobility. In vapor deposition photopolymerization process, the molecules migrate and react each other on the surface. The crystallization of the side chains and the reaction are associated with each other or the reaction occurs faster. That is, in vapor deposition photopolymerization the main chains as well as the side chains have higher mobility than those in postpolymerization. Hence, it is possible that a large number of methylene units in chains enter the crystalline region during vapor deposition photopolymerization process.

Another plausible possibility of increasing the number of methylene unit in the ordered crystalline phase is that the degree of polymerization might be small. As the main chain was getting longer, a larger number of methylene groups might be needed as spacer in order to adjust for the density difference between the hex-

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(41) After postpolymerization, the molecules seem to keep the layered structure with head-to-tail arrangement, since polymerization proceeds in each layer and polymerized samples showed the same crystalline characteristics in IR spectra as those observed for monomer films.

(42) Plate, N. A.; Shibaev, V. P.; Petrukhin, B. S.; Aubor, Y. A.; Kargin, V. A. *J. Poly. Sci., Part A* **1971**, *9*, 2291.

(43) Hsieh, H. W. S.; Post, B.; Morawetz, H. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1241.

(44) In low percentage of polymer region, the molecules would have a similar layered structure to that in normally deposited films. In high percentage of polymer region, the layered structure could change, since an interdigitation of side chains between two neighboring main chains was proposed in ref 43.

(45) Jordan, Jr., E. F.; Feldeisen, D. W.; Wrigley, A. N. *J. Polym. Sci., Part A1* **1971**, *9*, 1835.

agonally packed side chains and the steric requirements forced on the side chains by fixing them to the polymer backbone.[46] Therefore, if the degree of polymerization was low, a higher number of methylene units were permitted to enter the crystal lattice.

In vapor deposition photopolymerization, the percentage of the polymer in the film increased with increasing substrate temperature. However, γ did not increase as expected. This result is not typical for vapor deposition photopolymerization, since, in the case of *n*-octadecyl methacrylate γ increased from 32° to 39° with increasing temperature from −20 to 15 °C, while the percentage of the polymer increased from 36 to 90%.[47] The crystallinity of the side chains seems to increase with increasing substrate temperature because the mobility increases. In fact, although all films were opaque, the films prepared at a higher temperature were more turbid. The improvement in the crystallinity may compensate the increment in γ as expected from an increase in the percentage of the polymer in the film.

Annealing is known to improve the crystallinity of the polymer. Thus the film prepared at 15 °C by the present method was annealed at 30 °C for 6 h, which is just below the melting point of ODA monomer. The γ decreased from 42° to 30° after annealing, suggesting that some rearrangement of *n*-alkyl chains occurred.

In conclusion, we found that vapor deposition photopolymerization was a useful method to prepare thin polymer films with high molecular orientation. This method has an advantage over postpolymerization of monomer films because the percentage of the polymer significantly increased.

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[47] Orihashi, Y.; Taniguchi, I.; Kawakami, N.; Itaya, A., manuscript in preparation.