served constancy of the stem length is not unexpected. The decrease in both $\langle A \rangle$ and $\langle B \rangle$ for the copolymer with a 5.0% oxirane content suggests that some incorporation in the crystal core occurs at both T_cs used; however, IEI sequences were not detectable in one sample crystallized at 20 °C. There is on the average an oxirane unit every 20 isoprene units in the random copolymer, which could possible cause some restriction on $\langle A \rangle$. This oxirane content does not affect the melting endotherm when $T_c = 20$ °C but does cause a significant lowering of the endotherm for $T_c = 10$ °C. Before a complete explanation is given for this effect, further study is believed necessary.

For the copolymer with the largest oxirane content (9.8%) crystallized from a mixture of liquids the lower $\langle A \rangle$ is accompanied by a larger $\langle B \rangle$, suggesting enough oxirane unit rejection to affect the fold length. The average number of TPI monomer units between oxirane units in the copolymer with a 9.8% oxirane content is 10, the same as the measured unreacted block length. Evidence for a loss of kinetic control of the crystallization process due to the close spacing of foreign units was observed in the crystallization of a polybutadiene copolymer containing 88.5% trans 1,4, 10% cis 1,4, and 1.5% 1,2 units.[3] $\langle A \rangle$ for that copolymer was 11 ± 1 and $\langle B \rangle$ was 16 ± 1, independent of the conditions used. The amount of oxirane unit rejection from the TPI crystal core is apparently high but is not complete, since a small number of IEI units are probably present.

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Regulation of Supermolecular Structure of Amphiphilic Polymers by Means of the Langmuir–Blodgett Technique

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ABSTRACT: The formation of surface films of poly(vinyl alkylals) at the air/water interface, the transfer of these surface films to solid substrates by means of the Langmuir–Blodgett technique, and the structure of the transferred films have been investigated. Poly(vinyl alkylals) were prepared from atactic poly(vinyl alcohol) (isotactic diad, 53%) and several kinds of *n*-alkyl aldehydes. The spread of dilute benzene solutions (0.01 wt %) of the polymers at the air/water interface, followed by compression of the surface area, gave stable surface films with a limiting area of ~0.3 nm^2/average repeat unit, irrespective of the side-chain length and the degree of polymerization of the starting poly(vinyl alcohol). The surface films could be transferred to several kinds of solid substrates with a transfer ratio of unity to form Y-type built-up films. The thickness of the built-up films was proportional to the number of layers, and single-layer thickness increased with increasing side-chain length. The surface wettability of the built-up films changed alternatingly, depending on whether the number of layers was even or odd. These results indicated that the surface films were monolayers of polymers, with hydrophilic main chains spread over the air/water interface and hydrophobic side chains directed approximately normal to the interface. The transferred films maintained the oriented structure of the monolayers at the interface. If the monolayers were assumed to consist of two-dimensional polymer chains, ^{1}H NMR studies on the stereo structure of the polymers implied that the main chain had two-dimensionally coiled conformations. The results for the limiting area required that the polymer chains be packed very closely.

Introduction

Regulation of supermolecular structures of synthetic polymers is a very important problem, since the properties of the polymers are frequently influenced by their supermolecular structures as well as their molecular structures. The Langmuir–Blodgett (LB) technique is an excellent method for obtaining ultrathin films with a well-defined and controllable molecular assembly, and there has been much interest in LB films because of this molecular assembly.[2] Studies of LB films have been conducted primarily on amphiphilic molecules, such as long-chain fatty acids and dyestuffs with long alkyl chains. However, there has been little study of built-up films consisting of surface films of preformed polymers,[3-12] although a great number of studies have been carried out on the surface films of polymers at the air/water interface.[13] If amphiphilic polymers, spread at the air/water interface, form monolayers which have oriented structures reflecting their amphiphilic nature, and the monolayers are transferred to solid substrates without disrupting the oriented structures, the LB technique will be a promising method for controlling the supermolecular structure of ultrathin films of amphiphilic polymers.

The transfer of surface films of an amphiphilic polymer by the LB technique was first reported by Tredgold et al.,[3] who used poly(1-octadecene-*co*-maleic anhydride). They

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Table I
Reaction Conditions and Characterization of Poly(vinyl alkylals)

	DP of PVA	reaction conditions[a]							
		aldehyde, g	solvent (vol/vol)	amount of solvent, mL	temp, °C	time, h	x^b	T_g,[c] °C	T_d,[d] °C
BuA-PVA	2000	7.0	ethanol/water (7/1)	16	40	15	0.72	60	320
OA-PVA	2000	8.0	chloroform	20	40	15	0.75	25	340
	300	8.0	chloroform	20	40	15	0.75	22	340
	1400	8.0	chloroform	20	40	15	0.79	24	330
	2600	8.0	chloroform	20	40	15	0.79	28	330
	2000	8.0	chloroform	20	35	15	0.70	32	330
	2000	5.0	1,4-dioxane/water (3/1)	200	60	20	0.54	50	360
	2000	1.5	1,4-dioxane/water (9/5)	140	60	20	0.40	58	360
	2000	1.0	1,4-dioxane/water (3/2)	100	60	20	0.34	63	350
DA-PVA	2000	8.0	chloroform	20	40	15	0.74	22	340
DDA-PVA	2000	8.0	chloroform	20	40	15	0.73	13	350
TrDA-PVA	2000	10.0	chloroform	20	40	20	0.78	3	340
TeDA-PVA	2000	10.0	chloroform	20	40	20	0.76	5	350

[a] For the reaction of PVA (1.0 g). [b] Mole fraction of alkylalized unit determined by elemental analysis. [c] Glass transition temperature determined by differential scanning calorimetry. [d] Starting temperature of weight loss in air determined by thermogravimetry.

suggested the applicability of the built-up films for microelectronic devices. Mumby et al.[8] determined the molecular orientation of the LB monolayers consisting of poly(octadecyl methacrylate) and poly(octadecyl acrylate) by means of infrared spectroscopy. They demonstrated that carbonyl groups and long aliphatic side groups were oriented approximately perpendicular to the substrate surface, although orientation of the latter groups was strongly dependent upon transfer pressure and the polymer employed.

Our attention has been focused on the applicability of the LB technique to amphiphilic polymers to regulate their supermolecular structures. Poly(vinyl alkylals), prepared from the reaction of poly(vinyl alcohol) (PVA) with alkyl aldehydes, were selected as a model of amphiphilic polymers.[10,11] In previous short communications, it was reported that the surface films of poly(vinyl alkylals) could be transferred to solid substrates by the LB technique to form built-up films.[10] One-layer thickness was influenced by the side-chain length.[10] Surface wettability of the built-up films changed, depending on whether the number of layers was even or odd.[11] These observations seemed to be correlated with the oriented structure of the surface films. The structure of the surface films might depend on the stereoregularity of the starting PVA and the stereo structure of the trisubstituted 1,3-dioxane rings.[11]

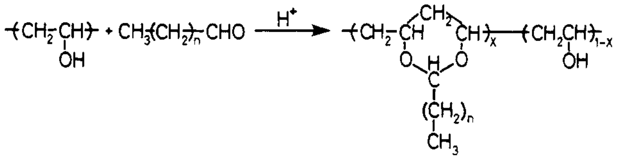
This paper describes in detail the formation of surface films of poly(vinyl alkylals) at the air/water interface and the characterization of the built-up films. Furthermore, the stereo structure of a poly(vinyl alkylal) is determined by ^{1}H NMR spectra, which are compared with those of model compounds. A plausible structure of the monolayer of poly(vinyl alkylals) is proposed based on the stereo structure. The proposed structure interprets well the one-layer thickness, based on the side chain length and the wettability change of the built-up films. The correlation between the results of surface pressure–area (*F–A*) isotherms and the structural model will be discussed.

Experimental Section

Materials. All of the reagents and reaction solvents were purified by conventional methods prior to use. Great care was taken to prevent any contamination of poly(vinyl alkylals) by dust in the course of their syntheses.

Commercially available PVA (Wako Pure Chemical), prepared by radical polymerization of poly(vinyl acetate) followed by hydrolysis (>98 mol %), was used as a starting material for poly(vinyl alkylals). The degree of polymerization (DP) was 2000 unless otherwise noted. Its isotactic diad percentage was shown to be 53% by means of infrared spectroscopy.[14,15]

Scheme I
Synthesis of Poly(vinyl alkylals)



n = 2 (BuA-PVA) n = 10 (DDA-PVA)
6 (OA-PVA) 11 (TrDA-PVA)
8 (DA-PVA) 12 (TeDA-PVA)

Poly(vinyl alkylals) were prepared from PVA and several kinds of alkyl aldehydes in the presence of hydrochloric acid as a catalyst, according to Scheme I. A typical reaction condition is as follows: 1.0 g of PVA and 8.0 g of octaldehyde were added to chloroform (20 mL). After three drops of hydrochloric acid were added, the mixture was allowed to react at 40 °C for 15 h with stirring. The contents became a homogeneous solution as the reaction proceeded. The reaction mixture was then poured into a large excess of methanol containing sodium hydroxide, which was needed for neutralizing the hydrochloric acid, and was recovered by filtration. OA-PVA was reprecipitated 3 times with chloroform/methanol and finally freeze-dried from a benzene solution. Table I summarizes the reaction conditions and characterization of poly(vinyl alkylals) used in this study. The polydispersities (M_w/M_n) of poly(vinyl alkylals) in Table I, determined by GPC using tetrahydrofuran as a carrier solvent, were in the range 2–3, on the basis of a calibration which used narrow-distribution polystyrene standards.[16] Each poly(vinyl alkylal) obtained was amorphous and gave one well-defined glass transition temperature.

The isomers of 4,6-dimethyl-2-propyl-1,3-dioxane, model compounds of poly(vinyl alkylals), were synthesized from isomeric mixtures of 2,4-pentanediol (PDO(*M*), Aldrich) and (−)-(2*R*,4*R*)-pentanediol (PDO(*R*), Aldrich) with butyraldehyde (BuA), respectively. PDO(*M*) (5.0 g) and BuA (10.0 g) were dissolved in chloroform (30 mL) and were allowed to react at room temperature for 4 h with stirring in the presence of hydrochloric acid as a catalyst. After the reaction, methanol (20 mL) containing sodium hydroxide for the neutralization was added to the mixture. The products were mixtures of *meso*-(2*s*,4*S*,6*R*)- and D,L-(4*R*,6*R*)-4,6-dimethyl-2-propyl-1,3-dioxane (BuA-PDO(*M*)), which were considered to be model compounds of poly(vinyl alkylals) from atactic PVA: bp 105–108 °C (1.3 × 10^4 Pa (98 Torr)). D,L-(4*R*,6*R*)-4,6-dimethyl-2-propyl-1,3-dioxane (BuA-PDO(*R*)), a model compound of poly(vinyl alkylals) from syndiotactic PVA, was synthesized from PDO(*R*) with BuA. Somewhat severer conditions, that is, 40 °C for 16 h, were required for the synthesis: bp 93–95 °C/ (7.3 × 10^3 Pa (55 Torr)).

***F–A* Isotherms and Transfer of Surface Films to Solid Substrates.** Water was ion-exchanged, filtered (activated

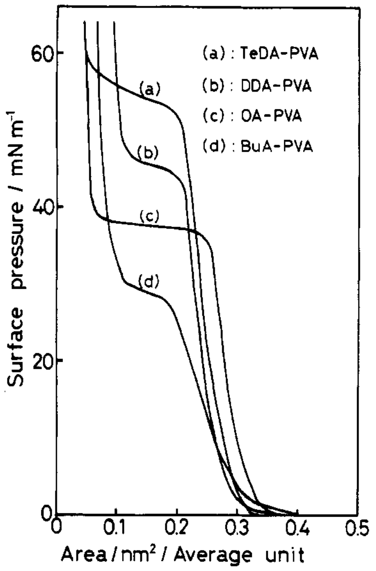


Figure 1. *F–A* isotherms of poly(vinyl alkylals) (x = 0.72–0.78) at the air/water interface.

charcoal and membrane filter), and distilled twice in dual-stage quartz stills. Benzene was purified by distillation. All of the glasswares used for the preparation of surface films were etched by concentrated KOH–ethanol solutions and washed sufficiently with purified water.

Benzene solutions of poly(vinyl alkylals) (0.01 wt %) were dropped on the surface of water (10–11 °C) in a commercially available Langmuir trough (Lauda film balance), which was set in a clean booth. The solutions spread out on the surfaces immediately. After evaporation of the solvent, *F–A* isotherms were recorded with a compression speed in the range 0.5–2.5 cm/min. In this range, the change in a *F–A* isotherm with the compression speed was negligible.

The solid substrates to which the surface films were transferred in this study were Si and Al. Si wafers were etched by HF aqueous solutions and then washed thoroughly with water. Al (99.999%) was evaporated on glass plates under vacuum ($<6.7 \times 10^{-3}$ Pa), and the resulting Al-evaporated glass plates were used as Al substrates (sheet resistance of Al layer ~15 Ω). The surface films of poly(vinyl alkylals) were transferred to the substrates by the following method. The surface films of poly(vinyl alkylals) were first compressed to appropriate pressures. While keeping the pressures constant, the substrates were vertically taken up and down with a speed of 0.5–2.5 cm/min across the surface films. The first layer was only transferred in a down mode for the Si substrates and in an up mode for the Al substrates; however, after the second layer, the surface films could be transferred both in an up and a down mode to form Y-type built-up films of up to several hundred layers. In order to obtain built-up films with an even number of layers on Al substrates (see Figures 4 and 5), the substrates were set in the water subphase after a down stroke, the remaining surface films were cleaned by an aspirator, and then the substrates were taken up.

Measurements. Thicknesses of the built-up films of poly(vinyl alkylals) were measured by ellipsometry (Shimazu EP-10). The wavelength of the incident light from a He–Ne laser was 632.8 nm. Substrates for the built-up films were Si wafers.

Capacitance of the built-up films was measured for the cell configuration of Al/film/Al. The surface films were transferred onto Al substrates. Upper Al electrodes (0.15 ± 0.02 cm^2) were vacuum-evaporated through a metal mask. Before the evaporation of the upper electrodes, the built-up films were kept in silica gel filled desiccators for at least 5 days. The cell capacitance was measured with an impedance analyzer (Yokogawa–Hewlett-Packard 4192A) at 1 kHz and an oscillation level of 10 mV under dry N_2 atmosphere.

Surface wettability of the built-up films on Al substrates was estimated by measuring the contact angles of water (Erma G-I) at 23 °C. Water drops (10 μL) were placed on the surfaces from a microsyringe, and the contact angles were measured 1 min after placing the drops on the surfaces.

Table II
Results of Limiting Area of Poly(vinyl alkylals) Found in *F–A* Isotherms

	DP of PVA	x[a]	limiting area m^2/mg	 nm^2/average repeat unit
BuA-PVA	2000	0.72	1.58	0.30
OA-PVA	2000	0.75	1.16	0.31
	300	0.75	1.16	0.31
	1400	0.79	1.15	0.32
	2600	0.79	1.15	0.32
	2000	0.70	1.13	0.29
	2000	0.54	1.19	0.25
	2000	0.40	1.01	0.18
	2000	0.34	1.03	0.17
DA-PVA	2000	0.74	1.00	0.30
DDA-PVA	2000	0.73	0.86	0.28
TrDA-PVA	2000	0.78	0.82	0.30
TeDA-PVA	2000	0.76	0.76	0.29

[a] Mole fraction of alkylalized unit.

^{1}H NMR spectra (JEOL GX270) were measured at 70 °C for poly(vinyl alkylals) and at room temperature for the model compounds in $CDCl_3$ with an internal standard of tetramethylsilane.

Results and Discussion

***F–A* Isotherms.** Figure 1 shows *F–A* isotherms of poly(vinyl alkylals) with a mole fraction of alkylalized unit (x) of 0.72–0.78. As the area was compressed, the surface pressure first increased steeply, reached a plateau region, and then increased again, for all of the *F–A* isotherms in Figure 1. The latter increase in the surface pressure corresponded to a collapse of the surface films, which could also be confirmed with the naked eye. The surface pressures which gave the plateau region increased with increasing side-chain length. When the area was compressed again after compression of the area to the plateau region and expansion of the area to the zero surface pressure area, the resulting *F–A* isotherms were the same as the initial ones.[16] Thus, the plateau region seems to correspond to the conformational changes of the polymers, which depend on the balance of hydrophilicity and hydrophobicity of the polymers. The former increase in the surface pressure corresponded to the formation of condensed surface films. It should be noted that the limiting areas, estimated by extrapolating the steepest region to zero surface pressure, were 0.28–0.31 nm^2/average repeat unit, irrespective of the side-chain length (Table II). The effect of the molecular weight of the polymer on the limiting area was investigated by using OA-PVAs (x = 0.75–0.79), prepared from PVAs with different DP (300, 1400, and 2600), as shown in Table II. The limiting areas of 0.31–0.32 nm^2 were constant independent of the molecular weight and were consistent with the area of OA-PVA obtained from PVA (DP = 2000). These results mean that the molecular dimensions of the condensed surface films are determined neither by the side-chain length nor by the molecular weight of the polymer, but rather by the main chain structure.

Figure 2 shows *F–A* isotherms of OA-PVAs having different x values. The limiting area decreased with decreasing x, as is expected by the assumption that the area of the vinyl alcohol unit must be smaller than that of the alkylalized unit. However, the decrease in the limiting area was much larger than that in x when $x < 0.54$. If the limiting area of the vinyl alcohol unit is simply assumed to be 0.12 nm^2,[17] that of the alkylalized unit is calculated to be 0.34–0.37 nm^2 for all of the poly(vinyl alkylals) with x = 0.54–0.79 in Table II. The same calculation for the OA-PVAs with x = 0.40 and 0.34 gives the limiting areas of 0.26 and 0.25 nm^2, respectively. These values are much

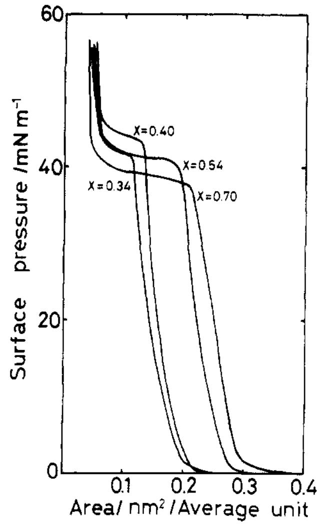


Figure 2. F–A isotherms of OA-PVAs with x = 0.34–0.70.

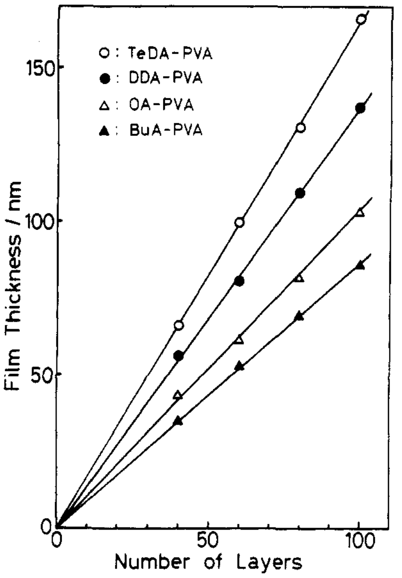


Figure 3. Film thickness of built-up films of poly(vinyl alkylals) (x = 0.72–0.78) as a function of number of layers.

smaller than those of the others. This fact, in turn, led us to perform the calculation of the limiting area of the vinyl alcohol unit, assuming that the limiting area of the alkylalized unit was 0.34–0.37 nm^2. The limiting areas of the vinyl alcohol unit are found to be between 0.05 and 0.07 nm^2. This calculation seems to be more plausible, since the vinyl alcohol unit is more hydrophilic than the alkylalized unit and is likely to slip into water. Thus, the condensed surface films of OA-PVAs with x = 0.40 and 0.34 are not strictly monolayers and seem to have a structure in which the sequence of vinyl alcohol units slips into water as a loop. In contrast, in the condensed surface films of the other poly(vinyl alkylals), the polymer main chains may be packed very closely to form monolayers, where the main chain and the side-chain function as hydrophilic and hydrophobic groups, respectively.

Characterization of Built-Up Films. The surface films of poly(vinyl alkylals) could be transferred to the substrates with a transfer ratio of unity within experimental error, when the surface pressures were set appropriately[18] and the polymers with x = 0.70–0.79 in Table I were used.

The thickness of built-up film was proportional to the number of layers (N), as shown in a previous communication[10] (Figure 3). At a given N, the film thickness increased with increasing side-chain length. Single-layer thicknesses were 0.85, 1.05, 1.40, and 1.65 nm for BuA-PVA, OA-PVA, DDA-PVA, and TeDA-PVA, respectively. The effect of the molecular weight on the film thickness of OA-PVAs was checked. However, the relations between the film thickness and N were identical. These facts mean that the side-chain length is strongly reflected by the one-layer thickness, while the limiting areas of these polymers at the air/water interface are identical. Figure 4 shows the relation between the reciprocal of capacitance and N for the built-up films of BuA-PVA and OA-PVA. The capacitances could be measured from monolayers and were almost temperature-independent in the range 145–293 K irrespective of N for both of the built-up films. The reciprocal of capacitance was proportional to N. This means that the one-layer thickness is constant. In both of the relations definite intercepts are seen; these are attributable to the layer of Al_2O_3 on the Al substrates. On the assumption that the relative dielectric constant of Al_2O_3 is 8,[19] the thickness of the Al_2O_3 layer was calculated to be 3.5–4.5 nm. Both film thickness and capacitance measurements indicate that the one-layer thickness of each built-up film is constant over a wide range of N.

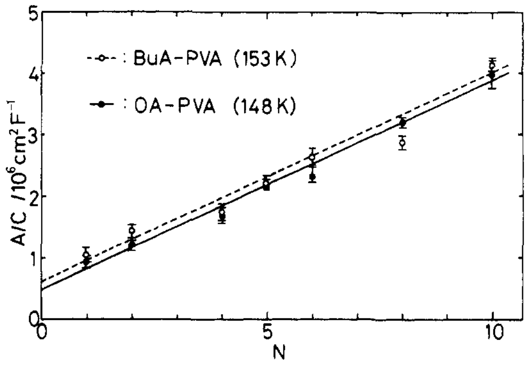


Figure 4. Relationship between reciprocal capacitance and number of layers for built-up films of BuA-PVA (x = 0.72) and OA-PVA (x = 0.70).

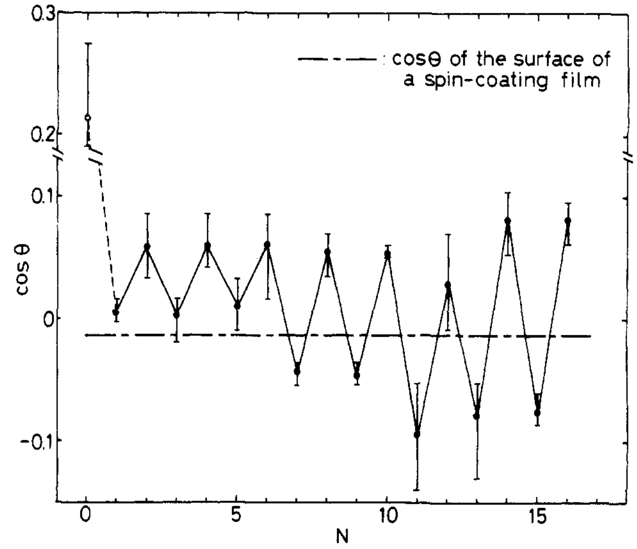


Figure 5. Wettability of the surfaces of built-up films of OA-PVA (x = 0.70) as a function of number of layers.

The wettability for the surfaces of the built-up films of OA-PVA is shown in Figure 5 and is cited from ref 11. The wettability changed alternatingly and was higher when N was even than when N was odd. Since the first layer was transferred in an up mode for the Al substrates, this change is consistent with the transfer if we assume that the side alkyl chains are oriented approximately normal to the

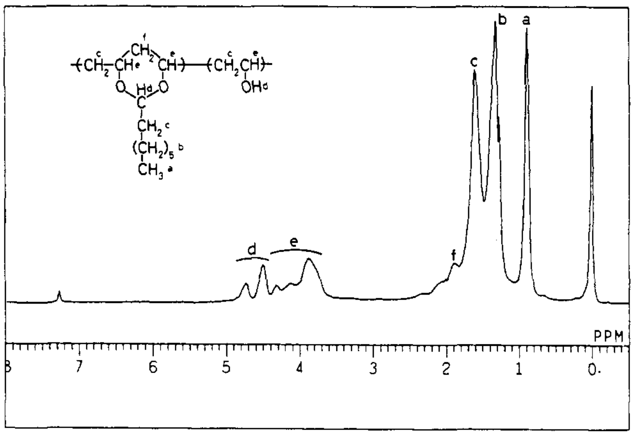


Figure 6. ^{1}H NMR spectrum of OA-PVA (x = 0.70).

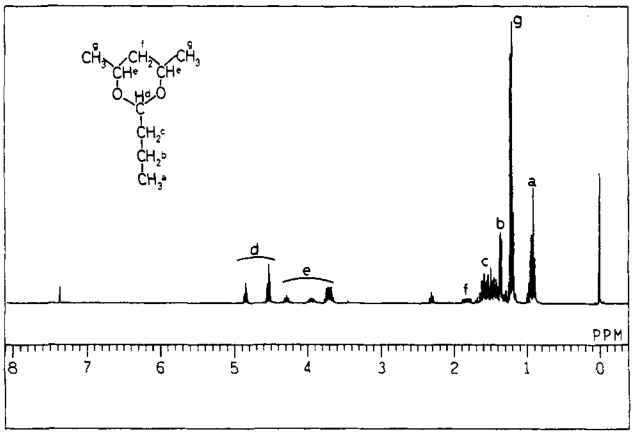
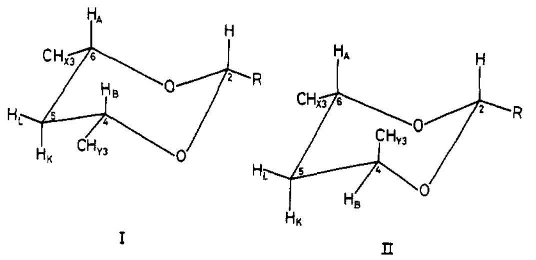


Figure 7. ^{1}H NMR spectrum of isomeric mixtures of 4,6-dimethyl-2-propyl-1,3-dioxane.

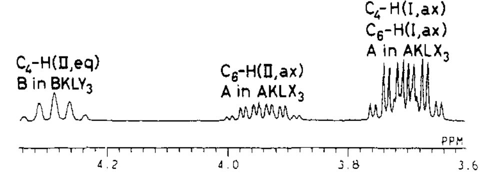
air/water interface. This behavior contrasts with the wettability of the built-up films of barium stearate: the wettability was independent of N and was constant at cos $\theta \simeq -0.1$. The surface wettability of a spin-coating film lay between the values for the built-up films of even and odd N values when N was larger than 6. The reason for the anomaly of wettability for $N \leq 5$ is still not clear; however, some effect of the substrate on the wettability might appear for low numbers of layers. The alternating change strongly suggests a layered structure of the built-up films and some structural anisotropy along the film thickness.

The above characteristics of the built-up films can be interpreted as follows: the condensed surface films of poly(vinyl alkylals) have an oriented structure, due to their amphiphilic nature; these surface monolayers are transferred to the substrates without disrupting the oriented structure. Thus, the application of the LB technique to the amphiphilic polymers has proved to be a method for controlling the supermolecular structure of the ultrathin films.

Stereo Structure of Poly(vinyl alkylals). Since we used atactic PVA as a starting material of poly(vinyl alkylals), the structure of the surface films and built-up films is influenced by the stereo structure of the trisubstituted 1,3-dioxane rings. Figures 6 and 7 show ^{1}H NMR spectra of OA-PVA and BuA-PDO(M), respectively. Each proton of both compounds was assigned as shown in the figures. Since BuA-PDO(M) is a model compound of poly(vinyl alkylals) from atactic PVA, the two NMR spectra matched each other well. Our attention was focused on the methine protons at the 4- and 6-carbons in the 1,3-dioxane rings, designated by e in Figures 6 and 7, which reflected well the stereo structure of 1,3-dioxane rings. The NMR spectra of the methine protons at the 4- and 6-carbons of BuA-PDO(M) and BuA-PDO(R) are shown in (a) and (b) of Figure 8, respectively, together with the possible stereo structures (I and II) of BuA-PDO. Studies[20] on the stereo structures of 2,4,6-trimethyl-1,3-dioxane by ^{1}H NMR have excluded the possibilities of (i) axial substitution of the methyl group at the 2-carbon, (ii) the boat forms of the 1,3-dioxane ring, and (iii) the exchange between two chair forms at least in the temperature range from −77 to 150 °C. Since BuA-PDO has a more bulky propyl group at the 2-carbon, the above possibilities can also be excluded. Thus, the possible stereo structures of BuA-PDO are limited to the forms I and II. BuA-PDO(R) has the structure of form II, where protons A and B are axial and equatorial protons, respectively, and the two are not equivalent. From the position and shape of the signals, the signals at around 3.94 and 4.29 ppm are assigned to the axial proton A in the AKLX$_3$ system and to the equatorial proton B in the BKLY$_3$ system, respectively.[20] In the spectrum of BuA-PDO(M), the other signals appeared at around 3.70 ppm. These signals are assigned to the axial protons A and B in the form I, where the two protons are equivalent. The line shapes and relative intensities due to each proton coincided well with the calculated spectra.[20]



(a) BuA-PDO(M)



(b) BuA-PDO(R)

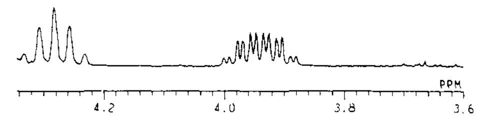


Figure 8. Stereo structures and ^{1}H NMR spectra of 4,6-dimethyl-2-propyl-1,3-dioxane: (a) from mixtures of meso and racemic forms of 2,4-pentanediol; (b) from the racemic form of 2,4-pentanediol.

Figure 9 shows the stereo structures of trisubstituted 1,3-dioxane rings in poly(vinyl alkylals) and the ^{1}H NMR spectrum of OA-PVA. Form I is cis-4,6-substituted 1,3-dioxane formed from isotactic diads in the starting PVA, and form II is trans-4,6-substituted 1,3-dioxane formed from syndiotactic diads. The comparison of this spectrum with those of the monomer analogues enabled us to assign these protons, as shown in the figure. The relative composition of structures I and II in octalized units of OA-PVA is ca. 7:3. Thus, the overall composition of OA-PVA can be represented by Scheme II. Since the isotactic diad percentage of the starting PVA is 53%, the composition in Scheme II indicates that most of the isotactic diads are octalized to form cis-4,6-substituted 1,3-dioxane rings. This result corresponds to the fact that the reaction rate

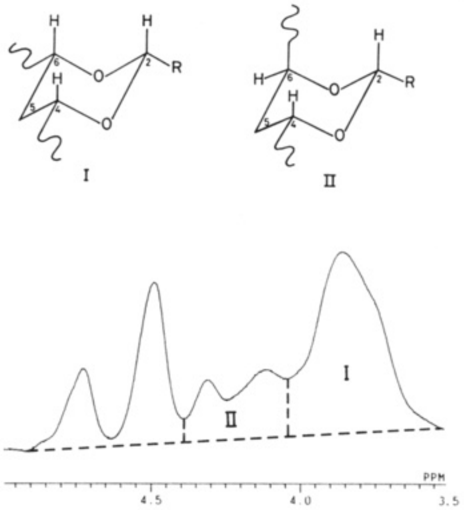


Figure 9. Stereo structures and ^{1}H NMR spectrum of OA-PVA (x = 0.70).

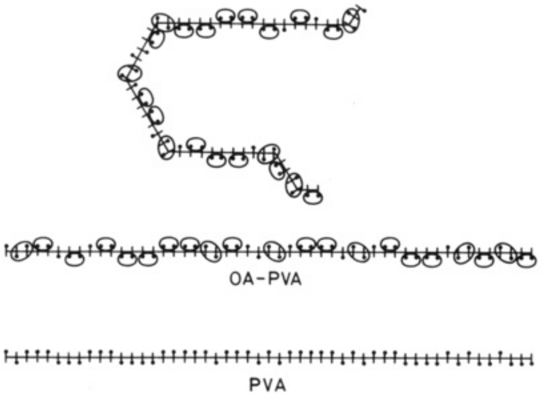
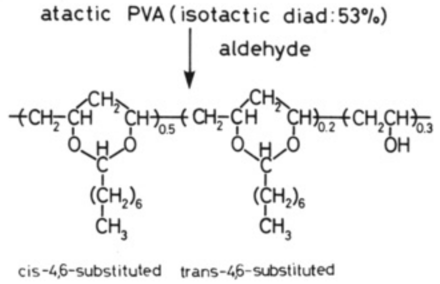


Figure 10. Schematic diagram for structures of atactic PVA (isotactic diad, 53%) and OA-PVA (x = 0.70).

Scheme II
Structure of OA-PVA (x = 0.70) from Atactic PVA (Isotactic Diad, 53%)



for the formation of cis-4,6-substituted 1,3-dioxane rings is much faster than that of trans-4,6-substituted ones.[21]

Molecular Structure for Monolayers. On the basis of the results of the F–A isotherms, the characteristics of the built-up films, and the stereo structure, a plausible molecular structure can be presented. Figure 10 shows a schematic diagram for the main chain structures of atactic PVA and OA-PVA with the composition in Scheme II. We assume that the main chains are spread in the plane parallel to the substrate or subphase surface and that the side chains are collected in one side of the space divided by the plane and are oriented approximately normal to the plane. On these assumptions, there are not so many conformational degrees of freedom for poly(vinyl alkylals), especially for their main chains. In the sequence of alkylalized units from isotactic diads and vinyl alcohol units, a straight stretched main chain, having a trans-zigzag conformation normal to the plane, is probable. The main chain has to bend at the junctions between alkylalized units from an isotactic diad and a syndiotactic diad. Thus, the overall main chains seem to have a two-dimensional coiled conformation, as shown in the upper diagram of Figure 10. Figure 11 shows a space-filling molecular model for BuA-PVA. This model represents well the one-layer thickness, which increases with increasing side-chain length, and the wettability change with N.

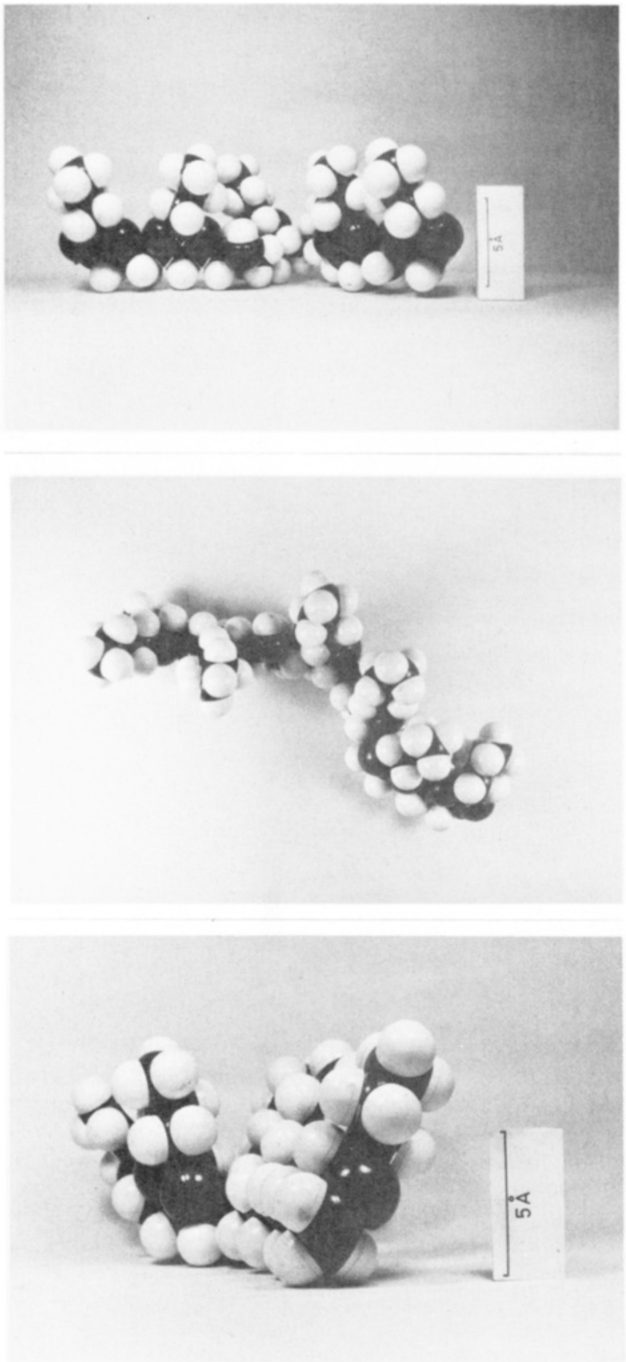


Figure 11. Space-filling models of BuA-PVA.

A remaining point is the correlation between the limiting area in F–A isotherms and the packing of the two-dimensional chains. We cannot deny the possibilities of the overlaps of the main chain in one layer of the polymer. However, the one-layer thickness measured suggests that this possibility is low. If so, the results of the limiting area ($\sim$0.3 nm^2/average repeat unit), which do not depend on the side-chain length and the molecular weight, imply that the two-dimensional chains are packed very closely. The problem of the packing of two-dimensional polymer chains is very interesting, and comparisons with normal polymer solids will be helpful. It is still not clear that the packing of two-dimensional chains in one-layer is either islandlike or intertwined. These questions should be clarified in the future.

Registry No. 4,6-Dimethyl-2-propyl-1,3-dioxane, 5406-35-9.

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Photoinitiated Thermal Degradation of Polymers. 1. Elementary Processes of Degradation of Polystyrene

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ABSTRACT: Elementary processes of thermal degradation of polystyrene were studied at 160–270 °C by using a photoinitiation method with benzophenone derivatives. All the relative kinetic rate constants in thermal degradation of polystyrene except that for initiation were obtained by this new method. By putting the activation energy for depropagation ΔE_d = 24 kcal/mol, the activation energies for chain transfer (ΔE_f = 8 kcal/mol), back biting (ΔE_b = 12 kcal/mol), β-scission (ΔE_β = 24 kcal/mol), and termination (ΔE_t = 50 kcal/mol) were determined. The temperature range of the main-chain scission can be lowered from 300–320 °C of the usual thermal degradation condition to 160–200 °C of the photoinitiated case and the temperature range of monomer formation from over 300 °C to 230–250 °C. The ratio of trimer to monomer formed increases with decreasing temperature of the thermal degradation and becomes about a half at 230 °C.

Introduction

The thermal degradation of polystyrene has been a subject of study for many years.[1-4] At 270–300 °C, random main-chain scission[5,6] resulting in the decrease in molecular weight occurs due to the initiation by the thermal scission of the main-chain bonds and in some cases weak links such as head-to-head linkages, chain branches, chain end allylic bonds, and peroxide linkages.[7-9] At temperatures above 300 °C volatile products containing monomer and oligomers are formed[6,10-12] in addition to the random main-chain scission, and the half-weight-loss temperature after 30 min was reported to be 360 °C[1] for polystyrene in the absence of air.

A linear relationship between the half-weight-loss temperature after 30 min and the bond dissociation energy of the weakest bond in the main chain for various polymers[1,3] has shown that the initial step of the thermal degradation is the bond scission of the main chain into radicals and it has the highest activation energy. All the subsequent elementary reactions such as chain transfer, β-scission, etc, have much lower activation energies, and therefore it has been difficult to analyze clearly these elementary reactions at the thermal degradation temperatures.

The present series of work is based on the idea that if we replace this thermal initiation by a photochemical one, we would control the reaction temperature easily. In other words, by controlling the rate of radical production with photoinitiator and by carrying out the decomposition over a wide temperature range, we can observe rather easily the elementary reactions other than initiation. We can also avoid the difficulty of analyzing the kinetic data due to the possible contribution of the weak links to the degradation. Furthermore the photoinitiation method may be used in industry for recovery of degradation product, because the degradation temperature can be lowered and the species of the degradation products may be varied by changing the decomposition temperature. Photoinitiation may be carried out easily by using hydrogen abstraction with benzophenone derivatives. The photoinitiation mechanism of benzophenone for polystyrene degradation has already been clarified in solution.[13] In the present series of work, benzophenone derivatives with four or six

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