Role of Hydrogen Bonding in Azobenzene–Urea Assemblies. Structural Evaluations of Multilayers on Solid Substrates

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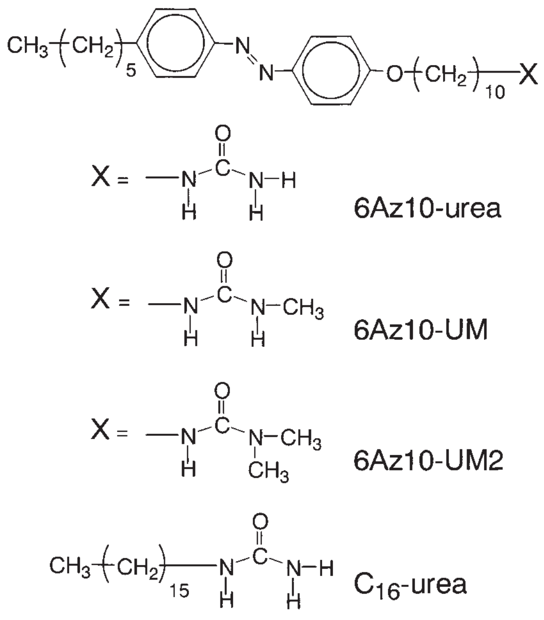
The multilayers of three homologous azobenzene (Az)-containing urea derivatives, having two, one and no hydrogen atom(s) at the terminal nitrogen atom in the urea moiety, and a simple long chain urea (hexadecylurea) were prepared by the Langmuir–Schaefer method. X-ray reflectometry, contact angle measurements of water, and Fourier transform infrared (FTIR) spectroscopy were undertaken to evaluate the layer structure and properties of these multilayered films. Of the four compounds, only the Az amphiphile, having no hydrogen atom at the terminus nitrogen atom, provided a different type of multilayers in terms of the molecular orientation, flexibility of the packing state, and characteristics of the intermolecular hydrogen bonding. The obtained data strongly support the formation of bifurcated hydrogen bonds for compounds having one or two hydrogen atom(s) at the terminus nitrogen of urea. The aspects obtained in this structural study can be exactly correlated with the properties of the Langmuir monolayers floating on water (Seki et al., *Langmuir*, **18**, 5462 (2002).). Based on the X-ray and IR spectroscopic data, plausible models of the packed structure of the urea compounds in the multilayers are proposed.

The urea moiety is frequently utilized as a useful connecting unit via hydrogen bonds in supramolecular organizations.[1–4] The formation of a stranded bifurcated hydrogen bond is the particular feature in the organization of urea compounds. In Langmuir monolayer assemblies, the unique assembling properties of urea-containing amphiphiles have been demonstrated.[5–16] Our efforts have been directed at exploring the photofunctional properties of urea derivatives having an azobenzene (Az) moiety. The crucial role of hydrogen bonding on the packing state and the photoresponsive properties in the Langmuir monolayers of Az–urea derivatives have been demonstrated.[17] The monolayer properties of the mono-methylated Az–urea derivative (6Az10–UM, Scheme 1) resemble those of the mother compound (6Az10–urea); in contrast, the nature of a fully methlylated derivative (6Az10–UM2) becomes completely deviated. These facts are attributable to the difference in the hydrogen-bonding mode between the head groups, i.e., the formation of stranded bifurcated hydrogen bonds for 6Az10–urea and 6Az10–UM, or a stranded-single one (6Az10–UM2). Although the differences are phenomenologically very clear, the experimental justifications of the structure are restricted for films on a water surface, and thus those on a solid substrate should be of particular importance for further understandings.



Scheme 1.

This paper describes the structural characterizations of multilayers of the above compounds on solid substrates, evaluated by means of UV–visible absorption spectroscopy, Fourier transform infrared (FTIR) spectroscopy, X-ray reflectometry, and contact-angle measurements. Besides the three Az–urea compounds, exploration with a simple long chain urea (hexadecylurea) was also conducted to clarify the influence of the Az moiety on the packing state.

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Experimental

Materials. The synthetic procedures for 6Az10–urea, 6Az10–UM, and 6Az10–UM2 were described previously.[14,17]

Hexadecylurea (C_{16}–urea) was synthesized in the same manner starting from heptadecanoic acid (Tokyo Chemical Inc.). Yield: 670 mg (63%), mp: 105–106 °C, IR (KBr): 1651 ($\nu_{C=O}$) and 1556 (δ_{NH}). ^{1}H NMR (δ, $CDCl_3$): 0.88 (3H, t, $J = 7$ Hz, CH_3–), 1.26–1.50 (28H, m, –CH_2–), 3.15 (2H, q, $J = 7$ Hz, $-C\underline{H}_2-NH-$), 4.24 (2H, m, –NH_2) and 4.40 (1H, m, –NH–). Found: C, 71.62; H, 9.67; N, 12.81%, Calcd for $C_{17}H_{36}N_2O_0$: C, 71.83; H, 9.86; N, 12.68%.

Hydrophobilized quartz plates were prepared as follows. Quartz plates were first cleaned by a UV–ozone treatment (Nippon Laser Electronics, NL-UV253), and then subjected to an atmosphere-containing a vapor of 1,1,1,3,3,3-hexamethyldisilazane (HMDS) for 12 h at room temperature. Any excess vapor of HMDS was removed in reduced pressure.

Calcium fluoride (CaF_2) plates (13 × 26 × 1 mm, for transmission) and a Au-evaporated glass plate (10 × 30 mm, for reflection absorption mode) for IR spectroscopy were obtained from OKEN and Nippon Laser Electronics, respectively. These plates were subjected to an ozone treatment before use.

Methods. Langmuir–Schaefer (horizontally lifted) multilayer films were prepared using a Lauda FW1 film balance at 20 °C. The Langmuir monolayers were spread on pure water, as mentioned in previous papers,[14,17] and compressed at a surface pressure of 20 mN m^{-1}. Onto this monolayer, a Teflon compartment frame was placed and the monolayer was lifted. The transferred film was dried by blowing cold air and subjected to the next lifting.

UV–visible absorption spectra were taken on a HP8452A.

The static contact angle of water was measured with a Kyowa Interface CA-X. The films were prepared on a hydrophobic surface treated with HMDS. The lifted films were stored in a dry atmosphere for 1 day before a contact-angle measurement. The contact angle of pure water (Milli-Q grade, pH = 5.8, 18 MΩ cm^{-1}) was measured at 10 s after droplet placing. At least 6 measurements were performed for one sample, and the average value was obtained.

An X-ray analysis in the reflection mode was performed using a Philips PW3050 X'Pert system with a Cu Kα line (0.154 nm) at ambient atmosphere. A specimen was placed horizontally, and the reflected X-ray was detected.

FTIR spectra were taken on a Biorad FTS6000. The DTGS and MCT detector was used for powder samples or solutions and multilayered films, respectively. The sample room was purged with dried air. The frequency resolution was 2 cm^{-1} and the accumulation was made 32–2000 times. For reflection absorption (RA) mode measurements, *p*-polarized light was introduced at an incident angle of 80° from the surface normal.

All procedures were carried out in subdued red light.

Results and Discussion

Film Deposition and UV–Visible Absorption Spectroscopy. The transfer of a monolayer onto a hydrophilic substrate by a vertical dipping method was commonly successful in the case of one layer deposition; however, the feasibility of multilayer deposition was strongly dependent on the compound. The transfer ratios above 2 layers for 6Az10–urea, 6Az10–UM, and 6Az10–UM2 were essentially zero, ca. 0.6, and ca. 1.0, respectively. Only 6Az10–UM2 gave satisfactory transfer ratios. On the other hand, deposition by the horizontal lifting method onto a hydrophobilized surface was commonly applicable to all compounds, providing multilayers having the desired layer numbers.

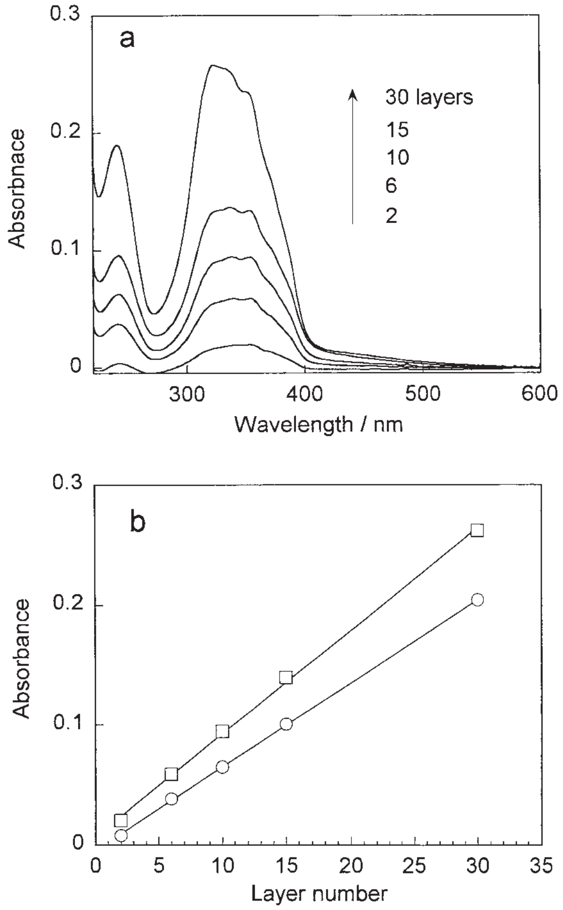

Fig. 1. UV–visible absorption spectra of 6Az10–urea multilayers prepared by horizontal lifting method (a), and absorbance changes of the absorption peaks at 340 nm (squares) and 242 nm (circles) as a function of layer number (b).

Figure 1 shows UV–visible absorption spectra (a) and the absorbance increase at the peak top (b) of transferred layers of 6Az10–urea as a function of the deposition number. As shown, the absorption intensity increased in a proportional fashion with the deposition number, indicating successful depositions as defined multilayers. The transfer ratio by the horizontal lifting method was confirmed to be unity by the following facts. The absorption intensity of 2 layers agreed exactly with that obtained by two single layers obtained by the vertical dipping method (one layer on each side of the substrate). The transfer ratio of the latter method was evaluated to be unity. The absorbance increases at the two peaks were both proportional to the deposition number, indicating that the packing structure was virtually unchanged with an increase in the layer numbers. The proportionality was retained up to 30 layers for 6Az10–urea, but faded for 6Az10–UM and 6Az10–UM2 at 30 layers. Successful deposition was ensured up to 15 layers for the latter two compounds.

The spectral shapes of the multilayers were similar to those

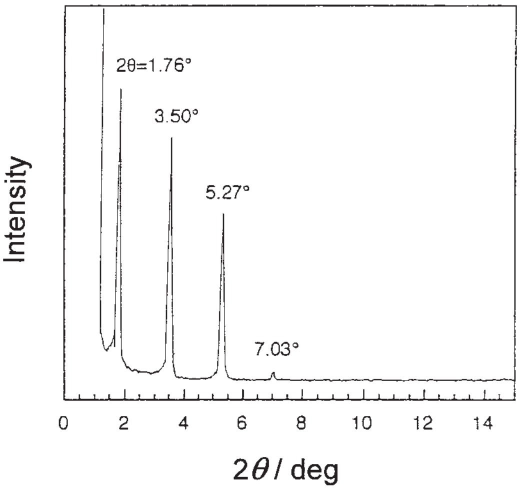

Fig. 2. X-ray diffraction pattern of a 30-layered LB film of 6Az10–urea on a quartz plate.

Table 1. Layer Spacings (*d*) of Multilayers Estimated by X-ray Analysis and Tilt Angles

LB films	Layer spacing /nm	Molecular length[a] /nm	Tilt angle[b] /deg	Layer type
6Az10–urea (30)[c]	5.03	3.64	46	*Y*
6Az10–UM[d] (15)	2.63	3.68	45	*X* or *Z*
6Az10–UM[e] (15)	5.18	3.68	45	*Y*
6Az10–UM2 (15)	5.84	3.68	37	*Y*
C_{16}–urea (15)	3.57	2.56	46	*Y*

a) Estimated from the CPK model. b) Angle from the surface normal. c) Number in the parenthesis shows the layer number. d) Before annealing. e) After annealing at 70 °C for 12 h.

of a Langmuir monolayer on water (see Fig. 3a in Ref. 17), but showed some deviations, indicating that the packing state was slightly modified during the deposition.

X-ray Reflectometry. The layer spacing in the multilayers deposited by the horizontal lifting method on a hydrophbilized quartz plate was evaluated by X-ray reflectometry. Figure 2 shows a typical example of the X-ray diffraction profile for a 30-layered 6Az10–urea LB film. As shown, very sharp diffraction peaks up to higher orders (fourth order in this example) were observed, indicative of the formation of a highly ordered layer structure.

The layer spacing (*d*), estimated by the Bragg's equation, and the tilt angle with respect to the surface normal are summarized in Table 1. The ideally stretched molecular length was estimated with the CPK model. In as-deposit films of 6Az10–urea, 6Az10–UM2, and C_{16}–urea, the layer spacings ($d = 5.03$–5.84 nm) were larger than each molecular length ($d = 3.64$–3.68 nm). On the other hand, the spacing of 6Az10–UM ($d = 2.63$ nm) was exceptional, giving approximately half the length compared to the other urea derivatives. These results indicate that the *Y*-type[18] bilayers are formed for the former LB films, and a polar *Z*- or *X*-type[18] multilayer is formed for the latter in the as-deposited state. After the 6Az10–UM film was annealed at 70 °C for 12 h, this film turned to a *Y*-type LB film (Table 1).

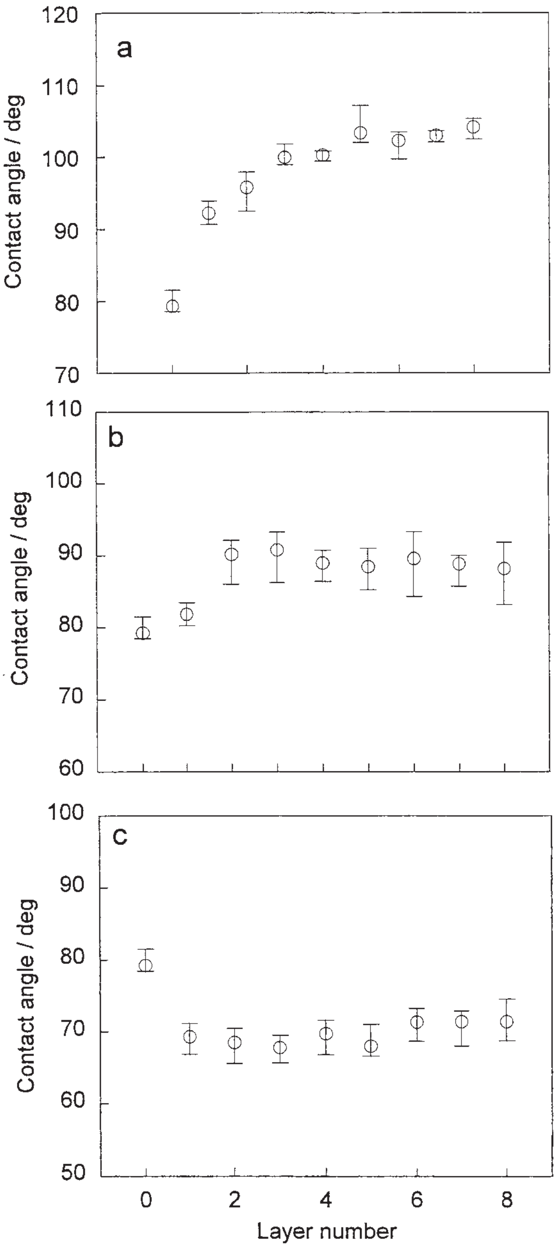

Fig. 3. Static contact angle of pure water on 6Az10–urea (a), 6Az10–UM (b), and 6Az10–UM2 (c) multilayers on a quartz plate hydrophobilized with HMDS as a function of layer number.

When the molecular orientation on water is exactly maintained in the LB films, the deposition by the horizontal lifting method onto the hydrophobic surface should provide the *X*-type multilayers. The X-ray data show that a structural conversion from the polar *X*-type to the thermodynamically stable *Y*-type readily proceeds in the transfer process for most of the urea derivatives, including both Az–ureas and C_{16}–urea. The reason for the exceptional result obtained only for 6Az10–UM is still unclear.

The tilt angles estimated from a comparison between the layer spacing and the molecular length were commonly converged to 45–46° from the surface normal for 6Az10–urea, 6Az10–UM, and C_{16}–urea. This angle was formerly predicted by

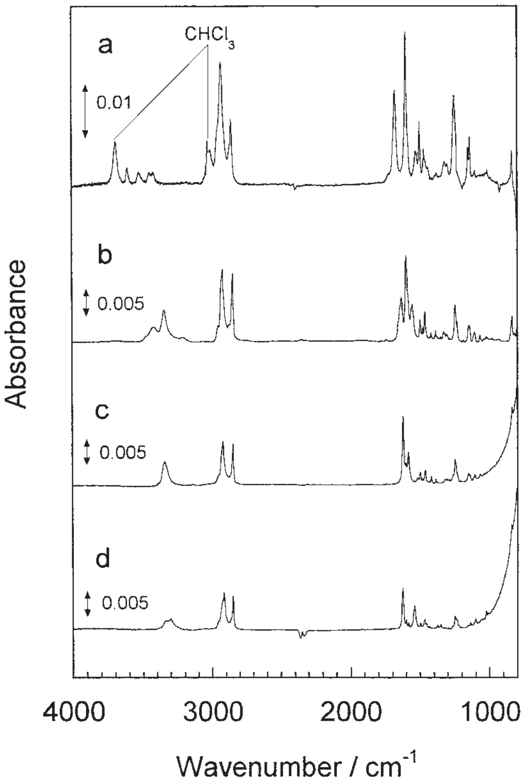

Fig. 4. Transmission infrared spectra of 6Az10–urea in $CHCl_3$ solution (a), 30-layered 6Az10–urea LB film (b), 15-layered 6Az10–UM LB film (c), and 15-layered 6Az10–UM2 LB film (d). Multilayers were prepared on a CaF_2 plate.

Alexander[6] based on the crystal structure of urea derivatives. Interestingly, the introduction of an Az unit in the molecule did not alter the tilt angle at all. This implies that the molecular tilt is firmly fixed by the urea head in the assembly. The more upright orientation (37°) obtained for 6Az10–UM2 implies that the packing state of this compound is more or less similar to that in the α form of a Langmuir monolayer of alkylureas at higher temperatures, in which the bifurcated hydrogen bonds are supposed to be broken.[5–11]

Wettablity of Water. The static contact angles of pure water on multilayered films with increasing layer numbers are indicated in Fig. 3. The contact angle of the bare hydrophobilized surface was ca. 80°. In the case of 6Az10–urea, the contact angle increased with increased layer number. Above 5 layers, the value of the angle became constant around 100° (a). The same tendency was obtained for 6Az10–UM, giving around 90° above 2 layers (b). For 6Az10–UM2, in contrast, the contact angle decreased to ca. 70° after multilayer deposition (c). The followings can be assumed: (1) The hydrophobic long chains are exposed on the topmost surface for 6Az10–urea and 6Az10–UM,[19] showing that the orientation on water is not maintained but a turnover process occurs during deposition. (2) The reduction of the contact angle for only 6Az10–UM2 is unexpected. The polar urea head should be exposed to water at least partially. This may indicate the induction of a turnover by contact with water for measurements. If this is the case, only the 6Az10–UM2 film is sensitive to an environmental change. This is consistent with observations of the flexible packing state of 6Az10–UM2 in the Langmuir monolayer on water.[17]

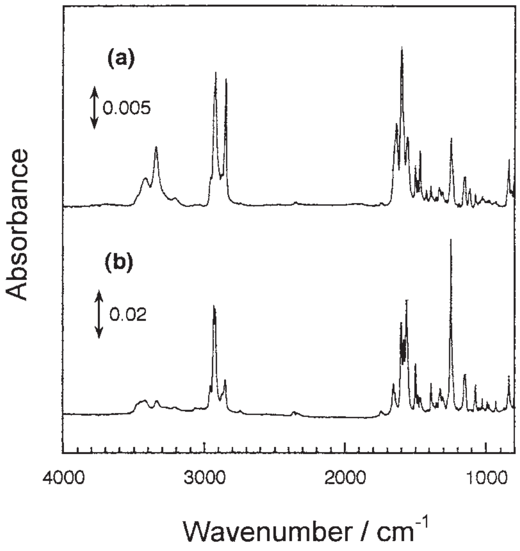

Fig. 5. Infrared transmission (a) and RA (b) spectra of a 30-layered LB film of 6Az10–urea deposited on a CaF_2 plate and a Au evaporated glass substrate, respectively.

Infrared Spectroscopic Study. The transmission IR spectra of the three LB films on a CaF_2 plate are presented in Fig. 4 together with that of 6Az10–urea in $CHCl_3$. In Table 2, band assignments of the IR spectra are summarized for the three Az–urea compounds and C_{16}–urea for comparisons. The table contains data obtained with $CHCl_3$ solutions, LB films, and KBr disks (microcrystals).

Strength of Hydrogen Bonding: The spectral shift of the stretching bands of C=O ($\nu_{C=O}$) and N–H (ν_{NH}) provides information about the hydrogen bond formed between the urea heads (N–H···O=C). When a hydrogen bond is formed, the band shifts toward a lower wavenumber.[20,21] As indicated by $\Delta\nu$ ($= \nu_{\text{solution}} - \nu_{\text{LB film}}$) in Table 2, significant shifts were observed for both bands, showing the formation of a hydrogen bond. Among the four urea derivatives, only 6Az10–UM2 exhibited different characters. The frequency shifts were larger and smaller for the ν_{NH} and $\nu_{C=O}$ bands, respectively, compared with the other derivatives. $\Delta\nu$ of ν_{NH} for 6Az10–UM2 and other compounds ranged between 136–173 cm^{-1} and between 103–117 cm^{-1}, respectively. With respect to $\nu_{C=O}$, the shift in the 6Az10–UM2 layer was significantly smaller (12 cm^{-1}) than those for the other compounds, ranging between 30 and 46 cm^{-1}.

It is worth comparing the spectral shape for the multilayers of 6Az10–UM and 6Az10–UM2. The spectral band of ν_{NH} for the 6Az10–UM film gave a sharp single peak, whereas that for 6Az10–UM2 consists of broadened dual peaks. This seems to be somewhat queer, because the former has two N–H bonds at two differently positioned nitrogen atoms of the urea unit, and the latter has only one at the nitrogen. The strength of the hydrogen bonds formed between the two N–H and O=C should be equivalent in the 6Az10–UM film. In contrast, there should be some heterogeneity in the strength of hydrogen bonding in the 6Az10–UM2 film, which is consistent with the flex-

Table 2. IR Frequencies ($\mathrm{cm^{-1}}$) of the Urea Derivatives

Compound	Assignment	$CHCl_3$ soln	Multilayer$^{a)}$	KBr disk	$\Delta\nu^{b)}$
6Az10–urea	ν_{NH}(–NH–)	3453	3345	3346	108
	ν_{as}(–CH_2–)	2931	2924	2923	7
	ν_{s}(–CH_2–)	2858	2849	2848	9
	$\nu_{C=O}$	1680	1634	1636	46
	benzene ring ν_{8a}	1600	1601	1599	
	δ_{NH}(–NH–)		1555	1561	
	benzene ring ν_{19a}	1502	1501	1500	
	$\nu_{Ph–O–C}$	1250	1246	1246	
	benzene δ_{CH}	841	841	843	
6Az10–UM	ν_{NH}(–NH–)	3460	3343	3347	117
	ν_{as}(–CH_2–)	2932	2922	2922	7
	ν_{s}(–CH_2–)	2858	2849	2849	9
	$\nu_{C=O}$	1669	1624	1624	45
	benzene ring ν_{8a}	1600	1605	1603	
	δ_{NH}(–NH–)		1555	1561	
	benzene ring ν_{19a}	1501	1501	1500	
	$\nu_{Ph–O–C}$	1251	1248	1248	
	benzene δ_{CH}	841		842	
6Az10–UM2	ν_{NH}(–NH–)	3477	3341	3311	136
			3304		173
	ν_{as}(–CH_2–)	2931	2919	2919	12
	ν_{s}(–CH_2–)	2858	2851	2852	7
	$\nu_{C=O}$	1641	1628	1630	13
	benzene ring ν_{8a}	1600	1603	1601	
	δ_{NH}(–NH–)		1543	1537	
	benzene ring ν_{19a}	1502	1501	1498	
	$\nu_{Ph–O–C}$	1252	1248	1248	
	benzene δ_{CH}	841		840	
C_{16}–urea	ν_{NH}(–NH–)	3450	3347	3347	103
	ν_{as}(–CH_2–)	2928	2922	2921	6
	ν_{s}(–CH_2–)	2856	2849	2848	7
	$\nu_{C=O}$	1679	1649	1651	30
	δ_{NH}(–NH–)		1555	1557	

a) Transmission on CaF_2 plate. b) $\Delta\nu = \nu_{solution} - \nu_{multilayer}$.

ible nature of the Langmuir film on water[17] and the environmental sensitivity, as postulated by contact-angle measurements. The corresponding bands of the 6Az10–urea film is more complicated, giving at least three bands, as can be seen from spectrum b in Fig. 4. This complexity may reflect the formation of *interlayer* hydrogen bonding through the hydrogen atom that is not used for the intralayer interactions.

All of the above IR data indicate that the mode of the hydrogen bond in the 6Az10–UM2 multilayer differs from that of the others. It is reasonably explained that 6Az10–urea, 6Az10–UM and C_{16}–urea form a bifurcated hydrogen bond, and 6Az10–MU2, which lacks hydrogen at the terminus, forms only a simple (single) hydrogen bond. The frequencies observed with the KBr disk samples mostly agreed with those multilayers. The molecular packing state in the layered films resembles those in the microcrystals.

Conformations of Alkyl Chains: From the frequencies of the asymmetric (ν_{as}) and symmetric (ν_{s}) stretching bands of the methylene chain of the LB films, it is indicated that the conformations are mostly inclined to the trans-zigzag state; however, a certain number of gauche conformers should be involved.[22–25] The peak positions of the ν_{s}(–CH_2–) band for the LB films were 2849–2851 $\mathrm{cm^{-1}}$, which almost coincide with those observed for lipid bilayers in a crystalline state. With respect to ν_{as}(–CH_2–), the frequencies ranged between 2919 and 2924 $\mathrm{cm^{-1}}$, indicative of the involvement of *gauche* conformers. Thus, the alkyl chains are not closely packed in the *all-trans-zigzag* state, but contain some disordered parts. The disorder of alkyl chains does not necessarily indicate a disruption of the well-ordered layer structure, as described in the X-ray analysis.

Molecular Orientations and Packing State: The IR spectra were compared between the transmission and RA modes (Fig. 5). The transition moments in the planar and perpendicular directions to the surface are emphasized in the transmission and RA modes, respectively.[26,27] The directions of the transition moments of each bond are displayed in Fig. 6. In both spectra, the C–H stretching bands were observed in comparable intensities, indicating that the long alkyl chains are tilted as in accord with the X-ray data. A noticeable feature in these vibration bands is that the intensity of the ν_{s}(–CH_2–) band was more enhanced in the transmission mode than that in the RA mode.

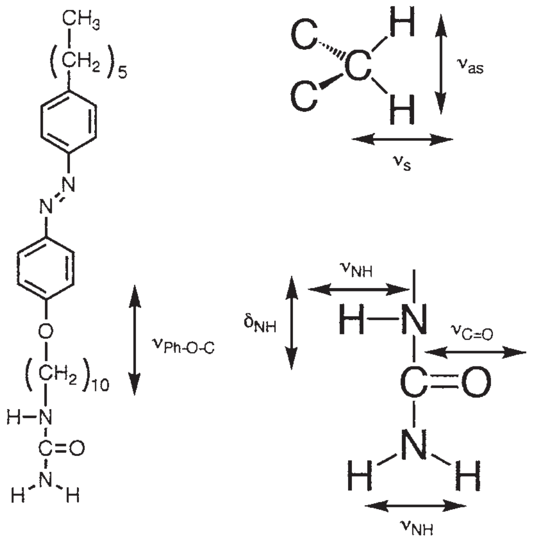

Fig. 6. Direction of transition moment of each IR signals from 6Az10–urea.

This should show that the zigzag plane of the tilt alkyl chain is arranged preferentially parallel to the substrate plane. This observation is very similar to the packing state of a LB film consisting of a long-chain acrylamide derivative investigated by Miyashita et al.[28] Essentially the same tendency in the transmission and RA spectra was obtained for C_{16}–urea, indicating that the molecular tilt and the packing state of the alkyl chain is unchanged by introducing an Az unit.

The intensities of the stretching vibrations of N–H (3345 cm^{-1}) and C=O (1634 cm^{-1}) were significantly smaller in the RA spectrum compared with those taken in the transmission mode. Therefore, these bands are preferentially oriented parallel to the substrate plane. In other words, the plane of the urea moiety lies flatly parallel to the substrate. On the other hand, the ester bond connecting the phenyl and alkyl groups (ϕ–O–) at 1246 cm^{-1} was emphasized in the RA mode. The Az moiety should be in a more upright orientation.

The plausible molecular orientation models of 6Az10–urea and C_{16}–urea are displayed in Fig. 7 based on the all results including IR and X-ray data.

Summary

Structural evaluations of multilayered films of Az–urea amphiphiles were carried out by UV–visible absorption spectroscopy, X-ray reflectivity, surface wettability, and IR spectroscopy. All data indicated the importance of the mode of intermolecular hydrogen bonding. Among the four urea derivatives examined, the hydrogen atom at the terminal nitrogen is missing only in 6Az10–UM2. This very subtle structural difference leads to critical influences on the molecular packing state. The following facts strongly support the formation of a bifurcated hydrogen bond for the rest of the urea derivatives having hydrogen atom(s) at the terminus. (i) The molecular tilt is strongly fixed between 45–46° from the surface normal for both systems with and without Az. The only exception was 6Az10–UM2, which adopts a more upright orientation (37°). (ii) The ν_{NH} band of 6Az10–UM exhibits a sharp single peak, despite the fact that this head group has two hydrogen atoms at the terminal and amide linkage, showing an equivalent character of the two

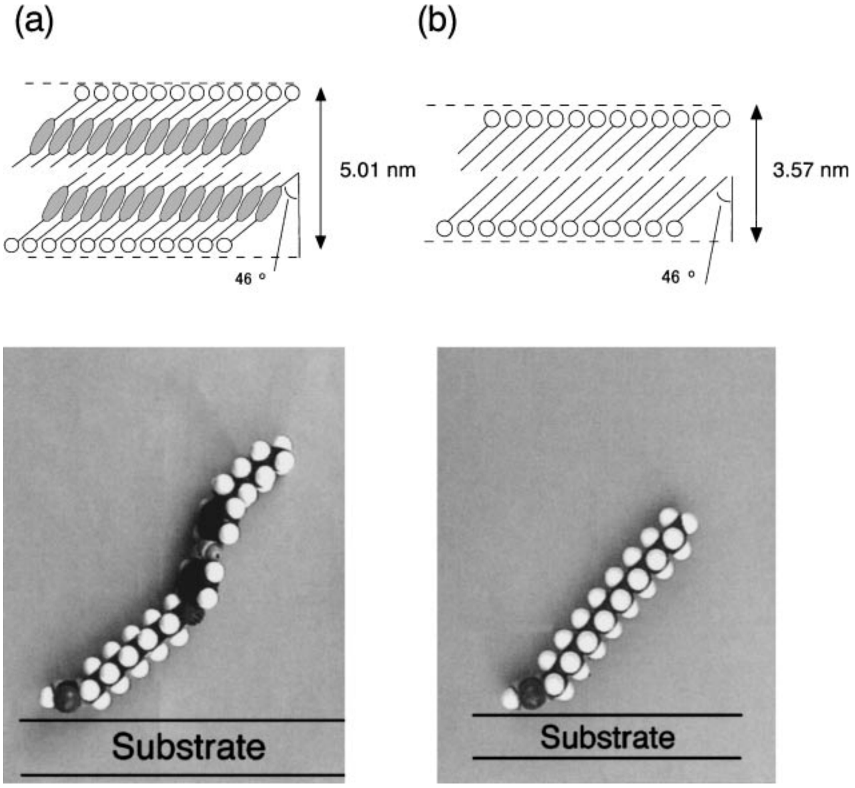

Fig. 7. Schematic illustrations of the layer structure and plausible orientations expressed by the CPK model for 6Az10–urea (a) and C_{16}–urea (b) in the multilayers based on the X-ray and IR spectroscopic data.

N–H bonds. (iii) The frequency shifts of the $\nu_{C=O}$ band due to the formation of an intermolecular hydrogen bond commonly range from 30 cm^{-1} to 46 cm^{-1}, whereas only a significantly small shift is observed (13 cm^{-1}) for 6Az10–UM2. The larger shift indicates stronger hydrogen-bond formation. Also, (iv) a structural turnover upon contact with water may occur only in the case of 6Az10–UM2, as shown from the contact-angle measurements, indicative of the labile character of the film. The strong influence of interactions at the urea moiety on the molecular packing may explain the involvement of gauche conformers in the alkyl chains, as indicated by IR spectroscopy. The alkyl chains may be distorted by the requirement from the head-group packing.

There still remains an unsolved problem as to whether the hydrogen-bonding mode is identical or not between the floating Langmuir monolayer and the deposited multilayers on the solid substrate. In fact, the spectral feature of the Az unit shows minor, but meaningful, deviations between the Langmuir monolayer and deposited multilayers. Nevertheless, the difference in the packing behavior of 6Az10–UM2 from that of the rest compounds is evident in both layer systems. All results, including the Langmuir monolayers on water[17] and multilayers on the solid substrate in the present study, can be consistently understood by the hydrogen-bond mode.

The previous paper[17] and this report clearly show the crucial role of the hydrogen bond, affecting the various properties in the monolayer of an Az–urea amphiphile. It is stressed that a very subtle modification in the molecular structure, namely the presence or absence of *one* hydrogen atom at the terminus, leads to critical influences in the packing structure and resulting photoreactivity of the Az unit. Surprisingly, all or no control in the photoreactivity is achieved by this modification in the Langmuir monolayer systems;[17] also, the structural features of the multilayer are essentially modified accordingly. The knowledge obtained in this work may provide many ideas for the design of molecular functional materials and also for bio-related aspects.

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