

Odd–Even Effects of Multilayers in Azobenzene–Containing Urea Amphiphiles

Toru Kobayashi[†] and Takahiro Seki^{‡*}[†]Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan^{‡*}Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya, 464-8603, Japan
Fax: +81-52-789-4668, E-mail: tseki@apchem.nagoya-u.ac.jp

Azobenzene-urea amphiphiles show unique aggregation states stemming from the bifurcated hydrogen bonding among urea head groups. So far the odd–even effects originated from the carbon number of spacer are observed for the spreading behavior of Langmuir monolayer on water, for the dynamic Langmuir–Blodgett (LB) deposition process (compressibility and deposition behavior) and for the molecular aggregation on in the monolayer state. This paper deals with multilayers on substrate the carbon parity effects observed in the layer spacing and hydrogen bond strength of multilayer on solid substrate. These are supported by various experimental with multilayers, including the X-ray diffraction measurement and infrared spectroscopic study.

Key words: urea, azobenzene, spacer length, odd–even effect, multilayer

1. INTRODUCTION

Urea derivatives form a hydrogen bonding network between a carbonyl group of one urea unit and two hydrogen atoms of a neighboring one urea unit and two hydrogen atoms of a neighboring one (bifurcated hydrogen bonding). Therefore, this dual hydrogen bond strongly fixes the molecular packing (Figure 1). Long chain urea on Langmuir monolayer also have attracted considerable attention due to their characteristic structure forming abilities derived from this hydrogen bonding.^{1,2} Alkylureas show a distinctive area contraction at a phase transition temperature in the heating process, which can be ascribed to the disruption of the bifurcated hydrogen bonding. Furthermore, an unusual type of Langmuir monolayer is formed from a urea compound.³

A series of azobenzene (Az)-urea derivatives have been performed on the two-dimensional organization by measuring surface pressure–area isotherms, compressibility, and UV–visible absorption spectroscopy. At the air–water interface, when an Az-urea compound having the carbon spacer of 10 (6Az10-urea, see Figure 1) is used, the trans-to-cis photoisomerization is completely impeded despite the fact that the molecular occupying area is larger than those of ordinary Az amphiphiles.⁴ This shows the firm tilted packing state due to the bifurcated hydrogen bonding. This monolayer on a quartz substrate is strongly sensitive to the atmospheric humidity.⁵ Drastic changes in the packing state are observed in response to the humidity changes in a fully reversible manner. Moreover, when the structure of urea group was changed, the role of the hydrogen bond of monolayer on water surface and multilayer on solid substrates is clarified.^{6,7}

In this paper, we report on the marked odd–even effects observed in the Az-urea multilayer assemblies, where the carbon number of the methylene spacer between the urea head and Az moiety is varied (6Az n -urea, n being 3, 4, 5, 6, and 7 in Figure 1). The parity effects are observed for the packing state in a Langmuir monolayer floating on water, compressibility, the deposition behavior in the Langmuir–Blodgett (LB)

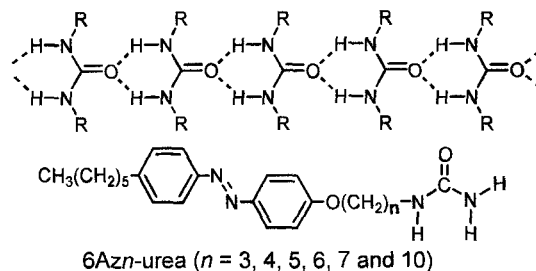


Figure 1. Schematic illustration of the formation of hydrogen bonds of urea containing compounds, and the chemical structure of Az-urea derivatives used in this study.

process, and further the structure of the monolayers on solid substrates. The odd–even effects are widely known in the thermal properties in thermotropic liquid crystals,⁸ but the present effects should be quite unique in that they are observed in Langmuir monolayers floating on a water surface. This paper describes on the structural characterization of the multilayers, which could provide useful information with assembling behavior of Az-urea assemblies.

2. EXPERIMENTAL

The synthetic procedures of materials used in this study were already reported.⁹

Quartz plates were washed with a saturated sodium hydroxide ethanol solution, ethanol, flowing water, and finally pure water (Milli-Q grade, 18 M Ω cm⁻¹, pH = 5.8) under ultrasonic wave treatment. Hydrophobized quartz plates were prepared by treatment with a vapor of 1,1,1,3,3,3-hexamethyldisilazane. For the horizontal lifting procedure, a homemade frame of Teflon sheets (1 mm thickness) was prepared for compartmentalization. The deposition was performed onto the hydrophobic quartz plates prepared in the above manner.

UV–visible absorption spectra were taken on a HP8452A.

The static contact angle of water was measured with a

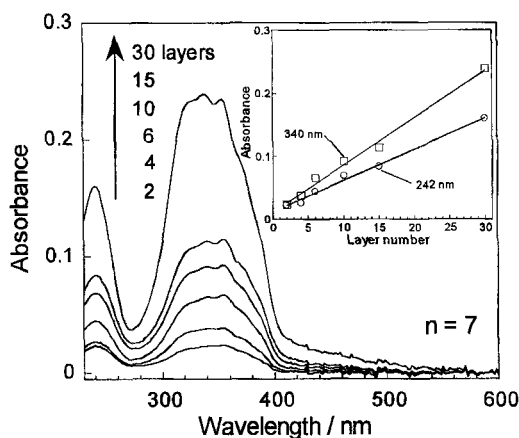


Figure 2. UV-visible absorption spectra of multilayers of 6Az7-urea at various deposition numbers. The inset shows absorbances at the two band peaks as a function of deposition number.

Kyowa Interface CA-X. The lifted films were stored in a dry atmosphere for 1 day before a contact angle measurement. The contact angle of pure water was measured at 10 s after droplet placing. At least 7 measurements were performed for one sample, and the average value was obtained.

All films of 30 layers spectra were taken on a PW3050 X'Pert system (Philips) using a $\text{CuK}\alpha$ radiation (40 KV, 30 mA). The diffraction intensity profiles were measured between 1° and 40° in the $2\theta/\theta$ -scan mode with steps at room temperature.

Fourier transform infrared (FT-IR) spectra were recorded on a Biorad FTS6000 spectrometer equipped with deuterated tri-glycine sulfate (DTGS) and mercury cadmium tellide (MCT) detectors. Transmission spectra of KBr disk pellets and films were measured. The films of 30-layered 6Az n -urea were prepared by the horizontal lifting method on a CaF_2 plate. The spectra were obtained by integration of 64–2000 scans at a resolution of 2 cm^{-1} .

3. RESULTS AND DISCUSSION

3.1. Multilayer Deposition.

For precise structural evaluation of the monolayer by X-ray analysis and IR spectroscopy, preparation of LB films in the multilayered state is desirable. First, the vertical dipping method onto the hydrophilic plate was attempted for the preparation of multilayers. In this procedure, the first layer was satisfactorily transferred as stated on hydrophilic plate,¹⁰ however, the second layer was readily peeled off in the downstroke dipping process. The multilayer deposition was unsuccessful.

We next applied the horizontal lifting procedure (Langmuir-Schaefer method). The 6Az n -urea monolayer was compressed to a surface pressure of 20 mN m^{-1} , the film was compartmentalized by a Teflon frame, then a hydrophobic quartz plate was attached to the monolayer and lifted. In this method, multilayer deposition could be performed at least up to 30 layers. UV-visible absorption spectra were taken at each step in order to confirm the transfer state, and representative

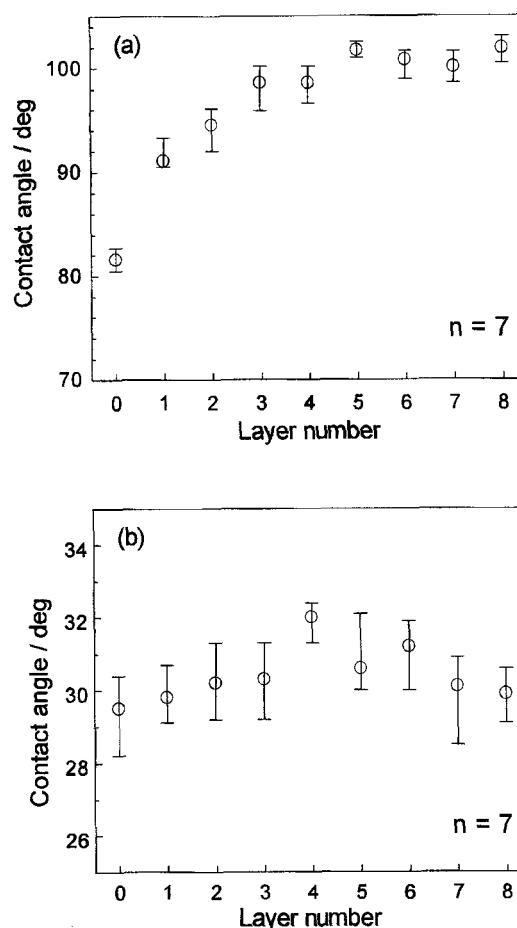


Figure 3. Static contact angles for pure water (a) and hexadecane (b) of 6Az7-urea monolayer on a hydrophobic quartz plates as a function of layer number.

data were depicted in Figure 2 for 6Az7-urea. Essentially the same data were obtained for the other series ($n = 3, 4, 5,$ and 6). In the multilayered films, the aggregation state of Az became somewhat multifarious. The π - π^* absorption band gave multiple peaks around 320–350 nm. Also, the peaks at shorter wavelengths became more dominant with the increase in deposition number. As shown in the inset, the absorbances at the band peaks (340 nm and 242 nm) were proportional to the deposition number, indicative of successful deposition at good transfer ratios and proper multilayer formation. The absorbance of a 2-layered film prepared by the horizontal lifting method exactly agreed with that of two single layered films on both sides obtained by the vertical lifting procedure in which the transfer ratio can be correctly evaluated. This fact further justifies the successful deposition in the horizontal lifting method.

3.2. Contact Angle

The result of the static contact angle of 6Az7-urea is shown in Figure 3. The static contact angle of pure water before transfer showed $81 \pm 1^\circ$. When one layer was transferred, the static contact angle of pure water showed the value exceeding 90° . About 5 layers, the contact angle of pure water was fixed at values around

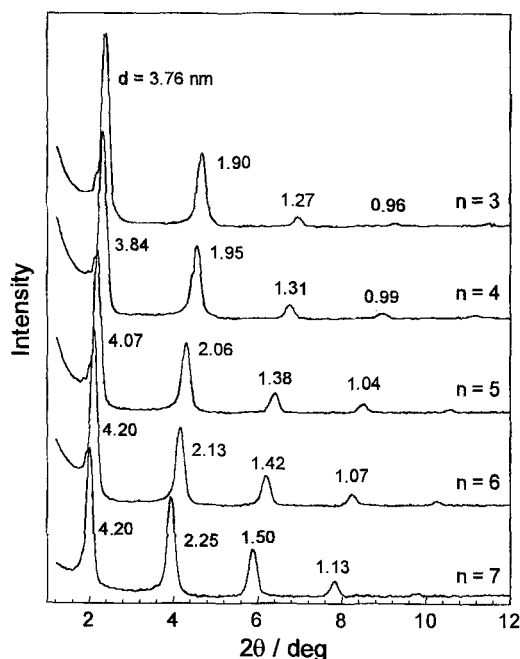


Figure 4. X-ray diffraction pattern profiles of multilayers (30 layers) of 6AzN-urea on a quartz plate.

100°. The static contact angle of hexadecane ranged $30 \pm 2^\circ$. These facts show that when multilayers are produced by the horizontal lifting method Y-type (head-to-tail) multilayer films are formed. The alkyl chains are positioned at the topmost surface and the bilayer structure is formed in the inner part.

3.3. X-ray Diffraction measurements.

The characteristic layer spacing and ordering of the multilayers were examined by X-ray diffraction analysis. Small-angle regions of the X-ray diagrams for 30-layered 6AzN-urea LB films gave a series of sharp reflection peaks up to fifth order, as shown in Figure 4. These results indicate that the highly ordered multilayered structure is obtained in all cases.

The tilt angle of the 6AzN-urea molecules in the layer was evaluated from the layer spacing and the molecular length estimated from the Corey–Pauling–Koltun (CPK) model. The estimated tilt angles at each carbon number are summarized in Figure 5. Since the tilt angles from the normal were smaller for the odd number series the 6AzN-urea molecules having an odd numbered carbon spacer leads to more upright orientation with respect to the substrate plane. This tendency is again in agreement with the data of molecular occupying area in the Langmuir monolayers, and also with those of the absorption spectra.⁹

3.4. Infrared Spectroscopy.

FT-IR spectroscopy provides useful information on the state of hydrogen bonds. Figure 6 exhibits the IR spectra of 30 layered multilayers on a CaF₂ substrate for the five films in the range of 1700–1200 cm⁻¹. The IR bands of ring C–C stretch (ν_{9a}), C=O stretching vibration band, and N–H (–NH–) deformation were observed at 1645–1635 and 1545–1570 cm⁻¹, respectively. Figure 7 shows the absorption frequen-

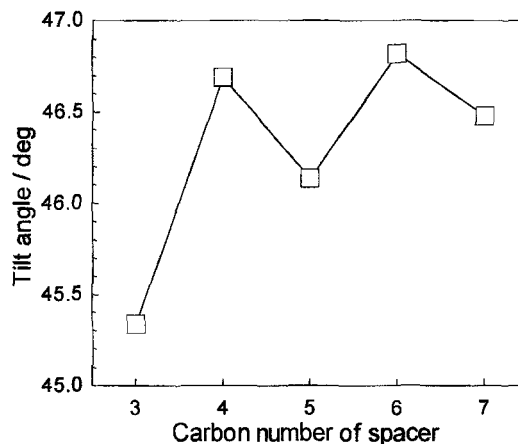


Figure 5. The molecular tilt angle in the multilayers of 6AzN-urea as a function of the carbon number of the alkylene spacer. The tilt angles were determined by comparisons between the layer spacing (X-ray) and molecular length (CPK model).

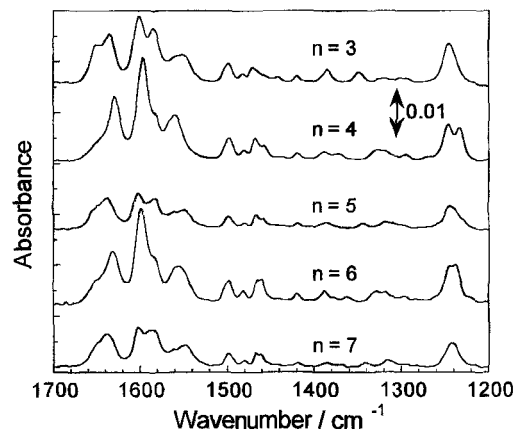


Figure 6. Transmission infrared spectra of multilayers of 6AzN-urea (30 layers) on a CaF₂ plate. The spectral region of 1700–1200 cm⁻¹ is indicated.

cies of these bands versus the spacer chain length (*n*). As indicated, clear odd–even alternations were obtained. In the peak intensity of ring C–C stretch vibration, the even-numbered series gave stronger absorption. This behavior indicates that the molecular tilt of the even-numbered series is greater, which is consistent with the data earlier. Because the bond energy of C=O is weakened by hydrogen bond formation, the absorption frequencies of the stretching vibration of these functional groups ($\nu_{C=O}$) should shift to lower wavenumbers when a stronger hydrogen bond is formed. On the other hand, the absorption frequency of the N–H deformation band (δ_{N-H}) increases with the hydrogen bond formation due to the larger energy required for the deformation of N–H bond strained hard by the hydrogen bonding. The IR spectral data show systematic shifts to relatively lower frequencies for $\nu_{C=O}$ band and higher frequencies for δ_{N-H} when the even-numbered derivatives are employed. Hence, the intermolecular hydrogen bonding becomes stronger for the 6AzN-urea derivatives having an even numbered carbon spacer than

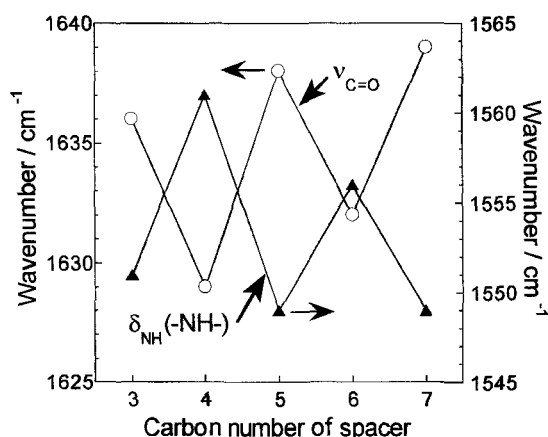


Figure 7. Band frequencies of typical infrared absorption bands as a function of the carbon number of the alkylene spacer of 6Az_n-urea multilayers deposited on a CaF₂ plate. The two symbols show the peak positions corresponding to the C=O stretching and N-H deformation modes.

those having an odd numbered one. Similar carbon parity on the amide absorption bands has been reported for the cast films of Az containing amphiphiles.¹¹

The C-H antisymmetric stretching peaks are positioned at 2926–2934 cm⁻¹. For this band, no odd-even nature was observed; instead, the molecule having the longer spacer showed an absorption band at the higher wavenumber. In any case, the alkyl chains are not in a highly crystalline trans-zigzag state but are relatively disordered.^{12,13} As discussed above, the appearance of the odd-even nature is frequently explained by the trans-zigzag packing of the alkyl chain adopt parallel (even number) or bent (odd number) directions. The disordered conformation of the alkyl chain observed here may be somewhat conflicting. Two explanations can be possible in this regard. (i) Only the tail part of Az is disordered, whereas the spacer part is highly crystallized. Each molecule has both alkyl tail and alkylene spacer, and the IR spectrum provides the overall signals. (ii) The periodic effects are attained as the result of interdependence between the urea and Az parts even if the spacer chain is in such a disordered state. This situation may be similar to that in fluid liquid crystal materials where the periodic alterations are often observed in the nematic to isotropic phase transition temperature.⁸ If the latter is the case, the effects are derived from a strong cooperativity of the molecular assemblies.

4. CONCLUSION

This paper proposed unique odd-even effects

observed in 6Az_n-urea assemblies, where *n* denotes the carbon number of the methylene spacer between the urea and Az moieties (*n* = 3, 4, 5, 6, and 7). A number of periodic effects with increasing *n* are observed in multilayers on the substrate. The effects should be the consequence of the formation of bifurcated hydrogen bonds between urea head groups since the other hydrophilic head group, carboxylic acid or alcohol, does not lead to such effects.

ACKNOWLEDGMENT

We thank Prof. K. Ichimura of the Tokyo University of Science, Prof. M. Nakagawa of the Chemical Resources Laboratory at the Tokyo Institute of Technology, and Dr. S. Nagano of Nagoya University for helpful comments and discussions. We also thank Dr. Saiki of the Tokyo Institute of Technology for X-ray measurements.

REFERENCE

- 1 J. Glazer and A. E. Alexander, *Trans. Faraday Soc.*, **47**, 401 (1951).
- 2 M. Shimizu, M. Yoshida, K. Ichimura, N. Suzuki, and T. Kato, *Colloids and Surf., A: Physicochem. Eng. Aspects*, **102**, 69 (1995).
- 3 Q. Huo, S. Russev, T. Hasegawa, J. Nishijo, J. Umemura, G. Puccetti, K. C. Russell, and R. M. Reblanc, *J. Am. Chem. Soc.*, **122**, 7890 (2000).
- 4 T. Seki, T. Fukuchi, and K. Ichimura, *Bull. Chem. Soc. Jpn.*, **71**, 2807 (1998).
- 5 T. Seki, T. Fukuchi, and K. Ichimura, *Langmuir*, **16**, 3564 (2000).
- 6 T. Seki, T. Fukuchi, and K. Ichimura, *Langmuir*, **18**, 5462 (2002).
- 7 T. Seki, T. Fukuchi, T. Kobayashi, and K. Ichimura, *Bull. Chem. Soc. Jpn.*, in press.
- 8 For example, D. Demus, in *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Gray, H. -W Spiess and V. Vill, Vol. 1, Wiley-VCH, Weinheim, 1998, pp. 133-187, and references therein.
- 9 T. Kobayashi, T. Seki, and K. Ichimura, *Chem. Commun.*, 1193 (2000).
- 10 T. Kobayashi, T. Seki, and K. Ichimura, *Trans. Mater. Res. Soc. Jpn.*, **26**, 487 (2001).
- 11 N. Yamada, K. Okuyama, T. Serizawa, M. Kawasaki, and S. Oshima, *J. Chem. Soc., Perkin Trans. 2*, 2707 (1996).
- 12 T. Kajiyama, Y. Oishi, M. Uchida, Y. Tanimoto, and H. Kozuru, *Langmuir*, **8**, 1563 (1992).
- 13 H. Sapper, D. G. Cameron, H. H. Mantsch, *Can. J. Chem.*, **59**, 2543 (1981).