PREPARATION OF LANGMUIR-BLODGETT FILMS OF METHACRYLATE COPOLYMER BEARING AZO-DYE CHROMOPHORES AND THEIR NONLINEAR OPTICAL PROPERTIES

MASAO KATO¹, TAKAYUKI OHONO¹, CHIKARA ISHII¹,
HIRO MATSUDA² and HACHIRO NAKANISHI³

¹*Faculty of Industrial Science and Technology, Science University of Tokyo,
2641 Yamazaki, Noda, Chiba 278, JAPAN,*

²*National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba 305, JAPAN,*

³*Institute for Chemical Reaction Science, Tohoku University, Sendai 980-77, JAPAN*

A methacrylate copolymer, poly(MO), was prepared from radical copolymerization of octadecyl methacrylate and methacrylamide bearing DR-1 type azo-dye chromophore as NLO active group, which was synthesized through 7 reaction steps. Poly(MO) gave LB film on quartz substrate by the vertical dipping method. Transfer of the monolayer at the water-air interface was easier in upstroke than in down stroke. By SHG measurement for the multilayers it was found that only in the first monolayer exists an effective noncentrosymmetric structure of NLO chromophores, showing SHG. Unexpectedly, when a heat treatment was performed SH intensity of the monolayer decreased, whereas that of the multilayers increased significantly. More detailed investigations about this heat response behavior were carried out.

1. Introduction

Langmuir Blodgett Film(LB) technique is considered one of the most promising method to fabricate noncentrosymmetric organic thin films, showing second harmonic generation(SHG). LB films of amphiphilic azo-dye have been investigated as the object of several nonlinear optical(NLO) studies[1-3]. Generally, structure of monomeric LB film does not exhibit higher mechanical and thermal stabilities, thereby degrading NLO properties. Meanwhile, this defect is expected to be improved if the noncentrosymmetric film is prepared by using an amphiphilic NLO polymer functionalized with azo-dye chromophores [4-7].

In this work, copolymer of octadecyl methacrylate(ODMA) and methacrylamide bearing DR-1

type azo-dye chromophore(MAHNA) was synthesized as NLO polymer, and preparations and NLO properties of its LB films were investigated.

2. Experimental

Synthesis

4-[N-methyl-N-(6-methacrylaminohexyl)amino]-4'-nitroazobenzene(MAHNA), as NLO active monomer was synthesized as follows. 6-Iodo-1-hexanol (**1**) was synthesized by halogen exchange reaction between sodium iodide and 6-chloro-1-hexanol in acetone at 60°C. 6-(N-methylanilino)hexanol (**2**) was synthesized by the reaction of N-methylaniline with **1** in dimethyl formamide at room temperature in the presence of sodium bicarbonate. [N-Methyl-N-(6-phthalimido)hexyl]aniline (**3**) was synthesized by tosylation of **2** with tosylchloride, followed by imination of the product with potassium phthalimide, according to the method described in the literature [8]. [(N-Methyl-N-(6-amino)hexyl)]aniline (**4**) was synthesized by the reaction of **3** with hydrazine hydrate [9]. [(N-Methyl-N-(6-methacrylamino)hexyl)]aniline (**5**) was synthesized by the reaction of **4** with methacrylic unhydride in dichloromethane-pyridine mixture at room temperature. MAHNA was synthesized by the reaction of **5** with diazotized p-nitroaniline (pH 3-4) at 0-5°C. Recrystallization from methanol gave dark-red crystals, m.p. 141-142°C.

^1H NMR(CDCl_3): δ =8.31(triplet (s), $J=4.6$, 2H, $-\text{N}=\text{N}-\text{C}(\text{CH}_3)_2\text{C}-\text{NO}_2$), 7.91 (multiplet(m), 4H, $>\text{N}-\text{C}(\text{CH}_3)_2\text{C}-\text{N}=\text{N}-\text{C}(\text{CH}_3)_2\text{C}-\text{NO}_2$), 6.73 (doublet (d), $J=9.6$, 2H, $>\text{N}-\text{C}(\text{CH}_3)_2\text{C}-$), 5.80 (s, 1H, $-\text{CONH}-$), 5.67, 5.32 (s, s, 2H, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}-$), 3.45 (t, $J=7.6$, 2H, $-\text{CONH}-\text{CH}_2-$), 3.32 (quartet, $J=6.8$, 2H, $-\text{CH}_2-\text{N-phenyl}$), 3.09 (s, 3H, $\text{CH}_3-\text{N-phenyl}$), 1.96 (s, 3H, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}-$), 1.39-1.65 (m, 8H, $\text{CH}_2(\text{CH}_2)_4\text{CH}_2$).

Octadecyl methacrylate (ODMA) was purchased from Tokyo Kasei and was purified by vacuum distillation just before use.

Copolymerization of MAHNA and ODMA (the mole ratio was 3:7) in tetrahydrofuran with the use of azobisisobutyronitrile as radical initiator was carried out in a vacuum sealed glass tube at 60°C. The copolymer (poly(MO)) thus obtained was purified by reprecipitation from methanol (Yield 10.7%). Copolymer composition calculated from the result of ^1H NMR measurement is

shown in Fig. 1. Molecular weight of poly (MO) was $\bar{M}_n=7100$ ($\bar{M}_w/\bar{M}_n=1.61$).

Method and Measurements

LB Film Preparation: A 0.5 wt % chloroform solution of poly(MO) was spread on water to form a thin layer. The layer was deposited onto quartz substrate by means of the LB vertical lifting method using a film balance controller (Science Keisoku FSD-20).

Characterization of Monomer and Copolymer:

SHG of LB films was measured by the Maker-fringe method using a Q-switched Nd : YAG Laser (Spectra Physics DCR-2; 1064 nm, 8ns/pulses, 10 mJ/pulse). The second order coefficient, d_{33} , was evaluated by use of single-crystal quartz plate of 0.5 mm thickness ($d_{11}=8 \times$

10^{-10} esu). Refractive index was measured with a

Shimadzu AEP-100 ellipsometer. ^1H NMR spectra were recorded on a JEOL EX-400 spectrometer. UV-VIS spectra were obtained on a Shimadzu 3100-S UV-VIS spectrometer. Measurement of molecular weight was obtained using a Tosoh HLC-8020 gel-permeation chromatograph with tetrahydrofuran as eluent. Thermal analysis was performed using a Mettler DSC30 system with a heating rate of 20°C/min.

3. Results and Discussion

DSC chart of poly(MO) is shown in Fig. 2. A very weak endothermic peak at -56°C due to T_g is observed. A sharp endothermic peak appears at 30°C, which might be attributed to fusion of the long alkyl side chains.

The π -A curves of poly(MO) at different temperatures ranging from 10 to 25°C are illustrated in Fig. 3. Poly(MO) monolayer spread on water at the temperature range

could be deposited on substrate by the vertical dipping method maintaining the surface pressure at 20mN/m. The most preferable π -A curve among them is considered to be one observed at 15°C.

Fig.1 Structure of poly(MO)

Fig. 2 DSC chart of poly(MO).

From the curve the limiting area was calculated to be $32\text{\AA}^2/\text{unit}$.

Transfer of poly(MO) at water-air interface onto substrate was easier in upstroke than in downstroke. Namely, up-lift deposition ratio (= deposition during up-lift process / deposition during up-lift and down process) [10] of the film was 0.71. As shown in Fig. 4, a linear relationship between the absorbance at 480 nm due to NLO chromophore and the number of monolayers was observed, indicating that the monolayers were piled up regularly. However, dependence of SH intensity on the number of deposited monolayers did not show a quadratic relationship, far from that SH intensity observed in the first monolayer did not increased, regardless of increase in the number of deposited layers (Fig. 5). The result might indicate that only the first monolayer has an effective noncentrosymmetric structure. Assuming that thickness of poly(MO) monolayer is $30\text{\AA}$ [11], d_{33} of the first monolayer is calculated to be $85 \times 10^{-9}\text{esu}$. Unexpectedly, when heat treatment was performed at 60°C for 5 min, followed by cooling at 22°C SH intensity of the monolayer decreased, whereas that of the multilayers increased significantly, as shown in Fig. 5.

Fig. 6 shows that SHG of poly(MO) multilayers (10 layers) reveals an interesting

Fig.3 Surface pressure-area isotherms of poly(MO) at 10,15,20,25 and 30°C .

Fig.4 Relationship between absorbance at 480nm and the number of layers.

Fig.5 Heat response of SH intensity related to the number of layers.
□ : Before heat treatment
■ : After heat treatment at 60°C for 5min

heat response behavior toward the repeated heating-cooling treatment. The SH intensity increased up to 3 times in contrast with original one when the heat treatment was performed at 50°C for 5 min, followed by cooling at 22°C. The phenomenon seems to occur by the fact that the orientation of NLO chromophores in the first monolayer is disordered by heating, however, after cooling it becomes much higher than before the heating as the result of the reorientation-crystallization of NLO chromophores. Probably, the upper layers exert a covering

effect to restrain thermal motion of the orientated NLO chromophores in the first monolayer at 22°C to give stable SHG. The heat treatment more than 50°C SH intensity decreased with increasing temperature.

Average tilt angle of the orientated NLO chromophores can be given by the following calculation.

Relationship between d_{33} and average tilt angle, θ , of NLO chromophores is expressed by eq. (1) [12].

$$d_{33} = N \cdot f^{(2\omega)} \cdot f^{(\omega)} \cdot f^{(\omega)} \cdot \beta_{xxx} \cdot \cos^3\theta \quad (1)$$

where f is the local field factor, β_{xxx} is the second-order hyperpolarizability and N is the NLO chromophore density. Since refractive index, n , of the monolayer was measured to be 1.62 (633 nm), if $n_{\omega} = n_{2\omega} = n$ is assumed Lorentz correction factor defined as $f^{(\omega)} = (n_{\omega}^2 + 2)/3$ will be expressed by $f^{(\omega)} = f^{(2\omega)} = f = 1.57$. Thus, eq.(1) is convertible to eq.(2).

$$\cos^3\theta = d_{33}/N \cdot f^3 \cdot \beta_{xxx} \quad (2)$$

Here, β_{xxx} can be used that of DR-1 azo-dye (1.2×10^{-28} esu [6]). N is 2.95×10^{-20} mol $\cdot$ cm $^{-3}$.

By using eq. (2) average tilt angles of NLO chromophores depending on the number of poly(MO) monolayers before and after heat treatment at 60°C for 5 min were calculated and the result is demonstrated in Fig. 7. A reasonable correlation was obtained between Fig. 5 and Fig. 7.

4. Conclusion

The heat response behavior in SHG for poly(MO) multilayers is considered to occur by the fact

Fig.6 Changes in SH intensities of copolymer LB film(10 layers) by heat treatment. Heat treatment : Heating for 5min, and cooling 22°C.

the orientation of NLO chromophores in the first monolayers is disordered by heating, however, after cooling it becomes much higher than before the heating due to the reorientation-crystallization of NLO chromophores. Perhaps, the upper layers exert a covering effect to restrain thermal motion of the orientated NLO chromophores in the first monolayer at low temperature to give stable SHG.

Fig.7 Changes in average tilt angles of NLO chromophores in poly(MO) LB film by heat treatment at 60°C for 5min.

- : Monolayer , before heat treatment.
 $d_{33} = 92 \times 10^{-9}\text{esu}$
- : Monolayer , after heat treatment.
 $d_{33} = 85 \times 10^{-9}\text{esu}$
- : Multilayers , before heat treatment.
- : Multilayers , after heat treatment.

5. References

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