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Original article

Photoresponding ionic complex containing azobenzene chromophore for use in birefringent film



Jun Wu^a, Xue-Min Lu^{a,*}, Feng Shan^a, Jun-Fang Guan^a, Qing-Hua Lu^{a,b,*}

^a School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China
^b The State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, China

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ABSTRACT

A novel photoresponding ionic complex (PANDAZO) was prepared by the ionic self-assembly (ISA) of sodium polyacrylate (PANa) and azobenzene chromophores (NDAZO). The ionic complex forms an interdigitated lamellar structure with full overlap of the side chains. The optical anisotropy was investigated by using a polarization pulse laser (355 nm). Furthermore, a high photoinduced birefringence ($\Delta n = 0.365$) was measured by using a continuous 488 nm laser as the pump light. © 2013 Xue-Min Lu and Qing-Hua Lu. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

1. Introduction

Materials with high birefringence have attracted great interest for their versatile application in technologies such as organic lightemitting diodes (OLEDs) [1], photostorage devices [2], optical fibers [3] and telecommunication devices [4]. Different materials are designed and synthesized to gain high birefringence including tolane [5,6], dipheny-diacetylene [7], and azobenzene [8].

Among these materials, azobenzene and its derivatives are actively investigated [9]. Photoinduced anisotropy (PIA) and birefringence (PIB) were attributed to the repeated *trans-cis-trans* photoisomerization cycles of azobenzene chromophores, which endowed the materials containing azobenezene chromophores with various applications in optical information storage [10], polarization holographic gratings [11,12], photomechanics [13], and so forth.

lonic self-assembly (ISA) has emerged as an effective strategy for the design of novel functional materials [14–16]. This approach does not need rigorous and complicated synthetic processes compared to all-covalent polymers. In previous reports, ionic complexes containing azobenzene were prepared and showed photosensitivity under light irradiation. However, the birefringence was low and far from the requirement for practical application [17–19]. Therefore, design and synthesis of materials with high photoinduced orientation and inherent high birefringence by this facile method is still necessary.

Herein, we prepared a novel material (PANDAZO) with high birefringence by ISA of sodium polyacrylate (PANa) and azobenzene chromophores (NDAZO). The ionic complex shows lamellar structure. Under linear pulsed laser irradiation, the complex film exhibits high optical anisotropy. A high photoinduced birefringence up to 0.365 is achieved by using a continuous 488 nm linearly polarized laser as the pump light.

2. Experimental

Sodium polyacrylate (PANa) with a molar mass (Mw) of 5100 was purchased from Aldrich. Sodium nitrite, phenol, *N*,*N*-dimethylaniline, *N*-methylimidazole, potassium carbonate, and the organic solvents utilized in this work were purchased from Sinopharm Chemical Reagent Co. and used without purification. 4-Hydroxy-4'-dimethylaminoazobenzene (**1**) was prepared according to the reported method [20]. FT-IR spectra were recorded on a Perkin-Elmer Paragon 1000 FTIR spectrometer. Normal and polarized absorption spectra of the complex films were recorded on a Perkin-Elmer lambda 750 UV/vis spectrometer. ¹H NMR spectra were acquired on a Varian Mercury Plus 400 MHz spectrometer in DMSO-*d*₆ or CDCl₃ and the chemical shifts were referenced in ppm *versus* tetramethylsilane. Small-angle X-ray diffractogram (SXRD) patterns of the casting films were recorded on a Rigaku X-ray diffractometer D/MAX-2200/PC at a rate of 1°/min

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^{*} Corresponding authors at: School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China.

E-mail addresses: xueminlu@sjtu.edu.cn (X.-M. Lu), qhlu@sjtu.edu.cn (Q.-H. Lu).

over the 2θ range $1-10^{\circ}$. Na⁺ and Br⁻ analysis was performed using an FEI NanoSEM 230 scanning electron microscope equipped with an X-Max 80 energy-dispersive spectrometer (EDS).

2.1. Synthesis of 4-(6-bromohexyloxy)-4'-(N,N-dimethylamino) azobenzene (2)

4-Hydroxy-4'-dimethylaminoazobenzene **1** (2.41 g, 10 mmol) was dissolved in acetone, and then 2 equivalent 1,6-dibromohexane (4.83 g, 20 mmol) and 1.5 equivalent potassium carbonate (2.1 g, 15 mmol) were added to the solution. The mixture was refluxed for 24 h with stirring. The residue was filtered off and washed with ethyl acetate. The organic solvent was removed from the combined filtrate and washings under reduced pressure, and petroleum ether (60–90 °C) was added to the concentrate. The resulting precipitate was collected and dried. The crude product was purified by recrystallization from ethanol. Yield: 3.1 g, 77%. ¹H-NMR (400 MHz, CDCl₃): δ 7.84 (4H, ArH), 6.97 (2H, ArH), 6.76 (2H, ArH), 4.02 (2H, OCH₂), 3.43 (2H, BrCH₂), 3.07 (6H, N(CH₃)₂), 1.91 (2H, CH₂), 1.83 (2H, CH₂), 1.52 (4H, CH₂CH₂).

2.2. Synthesis of 1-(6-(4-methoxyazobenzene-4'-oxy)hexyl)-3-methyl-1H-imidazol-3-ium bromide (NDAZO)

Compound **2** (1.0 g, 2.48 mmol) was dissolved in 30 mL tetrahydrofuran. Then 1-methylimidazole (1.63 g, 19.84 mmol) was added to the solution. The mixture was heated to reflux for 72 h. The resulting precipitate was obtained by filtration and washed with tetrahydrofuran and diethyl ether, respectively. The filter cake was dried under vacuum to give NDAZO. Yield: 0.78 g, 65%. ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.13 (1H, N=CH–N), 7.72 (6H, ArH, N–CH=CH–N), 7.03 (2H, ArH), 6.80 (2H, ArH), 4.17 (2H, OCH₂), 4.02 (2H, NCH₂), 3.84 (3H, NCH₃), 3.02 (6H, N(CH₃)₂), 1.76 (4H, CH₂CH₂), 1.45 (2H, CH₂), 1.30 (2H, CH₂).

2.3. Preparation of ionic complex PANDAZO and film

Aqueous PANa solution (5 mg/mL) was added dropwise to aqueous NDAZO solution (1 mg/mL) with a 1:1 molar charge ratio of cations to anions. The resulting precipitate was collected by filtration and washed thoroughly with deionized water to remove residual salts and noncomplexed precursors, and then dried in vacuum at 60 °C for 24 h. PANDAZO films were prepared by spincoating a chloroform/ethanol (9/1, v/v) solution (concentration: 20 mg/mL) onto quartz plates and glass slides (speed: 2000 rpm; time: 20 s) after being filtered through a 0.45 μ m Millipore filter. The thickness of the resultant film was about 200–300 nm, as measured by means of Ellipsometer.

3. Results and discussion

NDAZO unit was prepared according to Scheme 1. NDAZO unit showed good solubility in water. Ionic complex PANDAZO was obtained as a precipitate by adding PANa to the NDAZO solutions in a 1:1 charge ratio. PANDAZO showed excellent solubility in



Fig. 1. FT-IR spectra of (a) NDAZO, (b) PANDAZO and (c) PANa.

chloroform/ethanol (9/1, v/v), DMSO, and *N*-methyl-2-pyrrolidone (NMP). Fig. 1 shows the FT-IR spectra of NDAZO, PANDAZO, and PANa. The stretching vibration bands of the azo moieties in the complex were found at *ca*. 1600, 1366, and 1151 cm⁻¹. The symmetric carboxylate stretch of the complex was found at 1400 cm⁻¹. This result indicated that the NDAZO unit was successfully attached to the PANa main chain.

Fig. 2 shows the ¹H NMR spectra of NDAZO and PANDAZO, with unambiguous assignments to various protons. It can be seen that the phenyl signals of PANDAZO were slightly upfield shifted compared to those of the small molecule NDAZO, while the imidazolium signals were shifted downfield. In particular, a significant downfield shift of the active proton signal "a" of the imidazolium moiety was observed, which resulted from the influence of the opposite negatively charged carboxyl on the main chain. Furthermore, all of the proton signals of NDAZO became broad after attachment to PANa. These results confirmed the formation of ionic complex PANDAZO. In addition, because the proton signals of PANa were overlapped with those of NDAZO, it was difficult to estimate the assembly ratio of the two components by ¹H NMR. Energy-dispersive analysis of the complex indicated the absence of Na⁺ and Br⁻ ions. Therefore, we could assume a 1:1 ratio of carboxylic and imidazolium moieties in the complexes.

Fig. 3 shows the small-angle X-ray diffractogram of the PANDAZO casting film. A set of reflection peaks with a 1:2:3 ratio of positions was seen, indicating the formation of long-range ordered lamellar structures. The Bragg spacing *d* was 2.89 nm which was in excellent agreement with the calculated length l_0 (2.90 nm) of the fully extended side-chain units. This result indicated the full overlap of the side chains in an interdigitated packing structure, as shown in the insets of Fig. 3 [21]. In addition, the first-order reflection peak is very weak and the second-order reflection peak is the most intense. This might be related to interference effects of an additional plane of symmetry in their lamellar electron density profile [22–24].

The photoinduced orientation behavior of the complex film was investigated. An *s*-polarized pulsed laser (355 nm) was used as the



Scheme 1. The synthetic routes to the NDAZO and PANDAZO.



Fig. 2. ¹H NMR spectra of PANDAZO (up) and NDAZO (down) in DMSO-d₆.



Fig. 3. SXRD profile of the complex PANDAZO at room temperature. The inset is schematic representation of the layered architectures of the PANDAZO complex.

light source. The spin-coated films were fixed on an *X*–*Y* moving platform with speeds of 0.1 mm/s and 5 mm/s in the *X* and *Y* directions, respectively. The incident angle θ was fixed at 15° with respect to the normal of the PANDAZO films. Fig. 4 shows the angular-dependent UV/vis spectra of PANDAZO at its maximum absorption wavelength (395 nm). A periodic change in the absorbance with polarization angle over a period of 180° can be seen. The absorbance in the direction perpendicular to the laser polarization direction ($\theta = 90^\circ$, A_\perp) was the highest, while that in the direction parallel to laser polarization direction ($\theta = 180^\circ$, $A_{//}$) was the lowest, which indicated that the preferred direction of the azo chromophores was perpendicular to the laser polarization. The in-plane orientation order parameter *S* was calculated by



Fig. 4. Angular-dependent polarized UV/vis spectra of PANDAZO at 395 nm after irradiation with 25 mW/cm^2 by pulse polarization laser (355 nm).



Fig. 5. Photoinduced birefringence recorded in a thin film of PANDAZO with a 488 nm linearly polarized beam (165 mW/cm²) at room temperature. The points at which the pumping light was switched on and off are marked with arrows.

 $(A_{//} - A_{\perp})/(A_{\text{large}} + 2A_{\text{small}})$, where $A_{//}$ and A_{\perp} are the UV/vis absorbance parallel and perpendicular to the laser polarization direction, respectively. A_{large} and A_{small} is the larger and smaller absorbance of $A_{//}$ and A_{\perp} , respectively. The orientation order parameter *S* of PANDAZO film at 395 nm was -0.59, the negative sign of which means that the oriented direction of azobenzene was perpendicular to the laser polarization [25].

To investigate photoinduced birefringence, a continuous linearly polarized 488 nm laser with energy of 165 mW/cm² was used as the pump light. A weak He-Ne laser at 650 nm was used as the probe light. The birefringence (Δn) was calculated by $I = I_0 \sin^2(\pi \Delta n d/\lambda)$, where I is the intensity of the transmittance, I_0 is the intensity of the probe beam, λ is the wavelength, *d* is the thickness of the film. The relationship between photoinduced birefringence and irradiation time is shown in Fig. 5. The birefringence value (Δn) increased with the irradiation time increasing, and reached a high saturation value (0.354) after 40 min. The low absorbance of the PANDAZO film at 488 nm resulted in a long response time. Irradiation at shorter wavelengths might improve the dynamics of the recording process. Finally, it is noted that the photoinduced birefringence showed a slight increase and reached a higher value of about 0.365 after turning off the pump light. The ultimate high orientation may be attributed to the rigid molecular structure and the fact that the orientation was fixed in the aggregated phase. These results showed PANDAZO to be an ideal photoresponding material.

4. Conclusion

We prepared a photoresponding complex by ionic selfassembly. The ionic complex PANDAZO formed interdigitated lamellar microstructures with full overlap of the side chains. Effective photoinduced anisotropy (S = -0.59) was observed under irradiation by a pulsed laser. Polarized UV spectra revealed that the preferred direction of the azobenzene chromophores was perpendicular to the laser polarization direction. A high birefringence ($\Delta n = 0.365$) was induced by using a 488 nm linearly polarized laser as the pump light.

Acknowledgments

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