



Synthesis and optical properties of azobenzene side chain polymers derived from the bifunctional fumaric acid and itaconic acid



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ABSTRACT

Three type polymers containing the same azobenzene side chain group with different backbone structures, *poly(DMAz6Fm)*, *poly(DMAz6It)* and *poly(MAz6Ac)* derived respectively from fumaric acid, itaconic acid and acrylic acid, were synthesized. The dependence of photo-response properties on the polymeric architecture was investigated for the solutions and films. By irradiation of the linearly polarized light (436 nm), uniaxial orientations of the thin films were induced and anisotropic properties were investigated by measurements of the order parameters and birefringence values.

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1. Introduction

Liquid crystal polymers (LCPs) containing azobenzene groups have been a subject of study in both industrial and academic research due to high photosensitivity combined with strong fatigue resistance [1–18]. Azobenzene derivatives undergo reversible *trans*–*cis* isomerization and they generally oriented perpendicularly to the polarization plane of the incident light via *trans*–*cis*–*trans* isomerization cycle, so that optical anisotropy of the films can be induced [3]. The light induced orientation behavior is applicable to birefringent optical devices, optical memories, and even light-induced macro motion for actuators and manipulation [4–17].

For LCPs, orientation order is generally decided by a competition between the long range orientational order imparted by their mesogenic properties and the tendency to maximize the conformational entropy common to all chain system [27]. For the side-chain LCPs, the flexibility is largely maintained and opens a variety of potential applications [27–35], and their orientation behavior was affected by mesogen types as a side chain, substitution degree of the side chain, the length of the spacer and backbone chain structure [36–46].

Many other research groups extensively have studied the photochemically induced phase transition for LCPs containing azobenzene groups and devoted to the study of the photoorientation process [19–26]. The odd–even effect with various length of the flexible alkyl spacer and cooperation effect with non-photochromic mesogenic units are well known [44–46]. Generally, only one mesogenic side groups in a repeating unit had been usually employed. If one monomer unit carries more than one mesogenic side groups, it may promote the formation of mesophase and improve photo-response.

However, the reports for disubstituted polymers are very scarce mainly due to the difficulty encountered in synthesis. Han and Shigehara et al. have reported the radical polymerization of fumarate monomers containing two mesogenic groups, it was difficult polymerization was reported by Han and Shigehara et al., due to the poor solubility and steric hindrance between two bulky symmetrical mesogens [37–41]. For poly(dialkylfumarate) with mesogenic groups, polymerization capability and LC phases depended on bulkiness of backbone chain according to the report of Shigehara et al. [37]. On the other hand, Samui and Shiraishi et al. reported enhancement of LC phase for copolymers having itaconate moieties with two azobenzene groups in a repeating unit, due to the isolated and closely packed mesogenic groups [42,43].

Herein, with great interest on polymer architecture having paired LC side chain, we synthesized azobenzene side chain polymers, *poly(DMAz6Fm)*, *poly(DMAz6It)* and *poly(MAz6Ac)* derived respectively

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from fumaric acid, itaconic acid and acrylic acid, and investigated the effect of different mesogenic substitution degree and position on their photoinduced orientation behaviors as well as their LC properties.

2. Experimental

2.1. Synthesis

All reagents were purchased from general chemical industries. 4-Methoxy-4'-(6-bromo-hexyloxy)azobenzene (MAz6OH) was prepared by a well-known method and employed as a common side chain mesogenic group for fumarate, itaconate and acrylate polymers. 4, 4'-Methoxyazobenzenehexyloxy acrylate (MAz6Ac), di-(4, 4'-methoxyazobenzenehexyloxy) fumarate (DMAz6Fm) and di-(4, 4'-methoxyazobenzenehexyloxy) itaconate (DMAz6It) were respectively prepared by following previously reported methods [6,37,43].

2.2. Poly((4, 4'-methoxyazobenzenehexyloxy) acrylate) (poly(MAz6Ac))

By general radical polymerization, poly(MAz6Ac) was obtained as 50% yield. Mn = 6400, Mw = 8600 and Mw/Mn = 1.35, determined by GPC.

2.3. Poly(di-(4, 4'-methoxyazobenzenehexyloxy) fumarate) (poly(DMAz6Fm)) [37]

After 0.14 mol/L of DMAz6Fm was dissolved with warm chlorobenzene, polymerization was carried out in a degassed glass tube in the presence of dimethyl 2,2'-azobis(2-methylpropionate) (MAIB; purchased from Wako pure chemical industries Ltd.,) as an initiator at 100 °C for 72 h. After polymerization, reaction solution was cooled to room temperature and the precipitate was assembled and isolated by gel filtration chromatography (Sephadex LH-20 purchased from GE healthcare). Eluent solvent of tetrahydrofuran was evaporated and poly(DMAz6Fm) was obtained. Conversion was determined for 20~30% by time of flight mass spectrometry with the method of matrix assisted laser desorption/ionization (MALDI TOF-MS; Bruker Daltonics, Autoflex-K101 Reflectron). Mn = 3200, Mw = 3300 and Mw/Mn = 1.04, determined by gel permeation chromatography (GPC; JASCO 870UV (254 nm), 880PU, 865CO Shodex DEGAS, KF-804L, THF eluent (HPLC grade), 40 °C, 1 ml/min). Average polymerization degree was 4.5. Mn = 2110, Mw = 2150 and Mw/Mn = 1.02, determined by MALDI TOF-MS. ¹H-NMR spectrum of poly(DMAz6Fm) was shown in Fig. 1(c).

2.4. Poly(di-(4, 4'-methoxyazobenzenehexyloxy) itaconate) (poly(DMAz6It)) [43]

Polymerization of DMAz6It was carried out in a degassed glass tube in the presence of 1,1'-azobis(cyclohexanecarbonitrile) (ABCN;

purchased from Wako pure chemical industries Ltd.) as an initiator in toluene at 100 °C for 72 h. After polymerization, the contents of tube were poured into a large amount of warm methanol to isolate precipitate. The precipitate was dissolved in tetrahydrofuran and then polymer was isolated by gel filtration chromatography. Eluent solvent was evaporated and poly(DMAz6It) was obtained. Conversion was determined for 20~30% by MALDI TOF-MS. Mn = 3200, Mw = 3400 and Mw/Mn = 1.09, determined by GPC. Average polymerization degree was 4.3.

2.5. Film fabrication

Poly(DMAz6It) and poly(MAz6Ac) were respectively dissolved in cyclohexanone as 5 wt% solutions, and the films were fabricated on glass substrates by spin coating method at 1000 rpm for 5 s and 3000 rpm for 30 s in sequence. The thicknesses of the films were estimated to be 190 nm by surface profiler (VeecoDektak 150).

2.6. Characterization

Molecular structures were determined by ¹H-NMR spectroscopy (JEOL JNM-EX400; 400 MHz). Elemental analysis was performed on Yanako CHN Corder MT-6 spectrometer. The phase transition behaviors were estimated by differential scanning calorimetry (DSC; Seiko I&G DSC 5020) and polarized optical microscope (POM; Olympus BH-2). X-ray diffraction (XRD) studies were performed using a RigakuSmartLab (CuKα radiation).

Light irradiation was carried out with an ultra-high pressure mercury lamp (USHIO SX-UI 500H) through a heat absorbing filter (NAF-50s-50H) and a band filter for either UV (Sigma UTVAF-36U, λ = 365 nm, 25 mW/cm²) or visible light (Sigma SCF-50s-42L, λ = 436 nm, 138 mW/cm²) with/without polarizer. Irradiation of linearly polarized visible light was carried out normal to a sample.

Absorption spectra were recorded on a UV-vis absorption spectroscope (Perkin Elmer Lambda 650). Polarized absorption spectra were measured by rotating a polarization plane of the monitor light. The sample was placed normal to the propagation of the monitor light. The values of the order parameter (S) were determined by a spectroscopic method and calculated by following Eq. (1) [6]:

$$S = \frac{A_{\perp} - A_{\parallel}}{A_{\perp} + 2A_{\parallel}} \quad (1)$$

where, A_{\perp} and A_{\parallel} are polarized absorbances perpendicular and parallel respectively to the polarization direction of their radiated linearly polarized light (436 nm).

Birefringence (Δn) was determined by following Eq. (2) [52]:

$$\frac{I_{\perp}}{I_{\parallel}} = \sin^2 \left(\frac{\pi \cdot \Delta n \cdot d}{\lambda} \right) \quad (2)$$

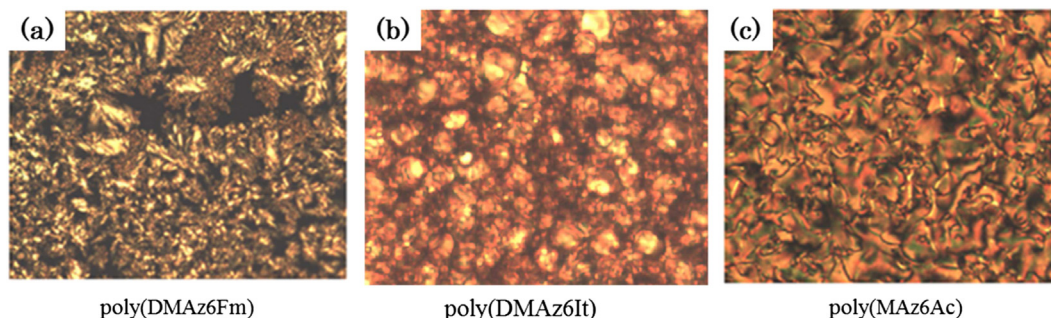


Fig. 1. POM images of poly(DMAz6Fm) (a), poly(DMAz6It) (b) and poly(MAz6Ac) (c) in the range of LC phases.

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