2704 *Macromolecules* **2010**, *43*, 2704–2712
DOI: 10.1021/ma902671m

Macromolecules
ARTICLE

Soluble Main-Chain Azobenzene Polymers via Thermal 1,3-Dipolar Cycloaddition: Preparation and Photoresponsive Behavior

Xiaoqiang Xue, Jian Zhu, Zhengbiao Zhang, Nianchen Zhou, Yingfeng Tu, and Xiulin Zhu*

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science of Soochow University, Suzhou 215123, China

Received December 2, 2009; Revised Manuscript Received February 9, 2010

ABSTRACT: Two soluble polymers containing azobenzene chromophore in main chain were successfully synthesized from α-azide, ω-alkyne A−B type azobenzene monomers, 3′-ethynylphenyl[4-hexoxyl(2-azido-2-methylpropionate)phenyl]azobenzene (EHPA) and 3′-ethynylphenyl[4-(4-azidobutoxy)phenyl]azobenzene (EAPA), via thermal 1,3-dipolar cycloaddition in bulk. Compared to the polymers obtained from Cu(I)-catalyzed 1,3-dipolar cycloaddition ("click" chemistry), the polymers obtained from thermal 1,3-dipolar cycloaddition showed good solubility in common solvents like $CHCl_3$ and THF and good film-forming ability. The polymers were thermally stable up to 330 °C. The structures of the main-chain azobenzene polymers were characterized by gel permeation chromatography (GPC), ^{1}H NMR, UV−vis, and FT-IR spectra. The photoinduced *trans*−*cis* isomerization of the polymers in chloroform ($CHCl_3$) solution was examined. With illumination of linearly polarized Kr^+ laser beam at 413.1 nm, surface relief gratings formed on PEHPA2 spin-coating films were investigated.

Introduction

Over the past two decades, polymers containing azobenzene moieties (azobenzene polymers) have been the subject of intensive research due to their potential applications in photoresponsive and optoelectronic fields,[1−4] such as optical data storage, liquid crystal displays, optical switching, and holographic surface relief gratings (SRGs). The key attractive features are unique reversible *trans*−*cis*−*trans* isomerization cycles of the azobenzene chromophore upon exposure to UV or visible light, which allows orientational distribution perpendicular to the direction of the polarization. When azobenzene polymers in thin film are irradiated with linear polarized light, the photoisomerization possibly induced large-scale shape and dipole movement of the rigid azobenzene chromophore to produce surface relief gratings (SRGs).[5] This property had attracted much attention since it was first reported by Natansohn and Tripathy in 1995.[6] For decades, many kinds of such azobenzene polymers have been developed, including azobenzene chromophore in the side chain[6,7] or in the polymer main chain.[8] Compared to the side-chain polymers, main-chain azobenzene polymers showed good thermal stability, which plays an important role in photoinduced dichroism, birefringence, nonlinear optical properties, and surface profile gratings.[9] However, synthesis of the main-chain azobenzene polymers is not easy,[8−10] as it is normally synthesized by condensation polymerization, and the resulting polymer is hard to be dissolved. The synthesis of main-chain azobenzene polymers is a challenge to polymer chemists, and that calls for the introduction of a new method.

In the 1980s, 1,3-dipolar cycloaddition was systematically studied by Huisgen.[11] Since then, the copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition of azide and terminal alkyne (typical model of "click" chemistry)[12] has drawn widespread attention due to its high efficiency, quantitative yields, and selectivity under mild reaction conditions. For these reasons, "click" chemistry is shown as a powerful tool in material synthesis.[13] Recently, there have been a few papers of azobenzene polymers prepared by step-growth polymerization using "click" chemistry.[14,15] Xiaoqin Shen et al.[14] synthesized 1,2,3-triazole-linked azobenzene dendrons of four generations by click reaction and investigated *trans*−*cis* isomerization of the polymers. Li and co-workers[15] reported new azobenzene-containing hyperbranched and dendronized polymers through "click" chemistry reactions with copper(I) catalysis and demonstrated good second-order nonlinear optical properties. However, those main-chain polymers synthesized via "click" chemistry were found to have solubility problem, unless long alkyl chains were attached to the benzene rings.[16,17] Furthermore, these materials showed poor film-forming abilities and mechanical properties, which made it hard to prepare clarity film device.[18] Thus, it was hard to further investigate these polymer properties for photoresponsive applications.

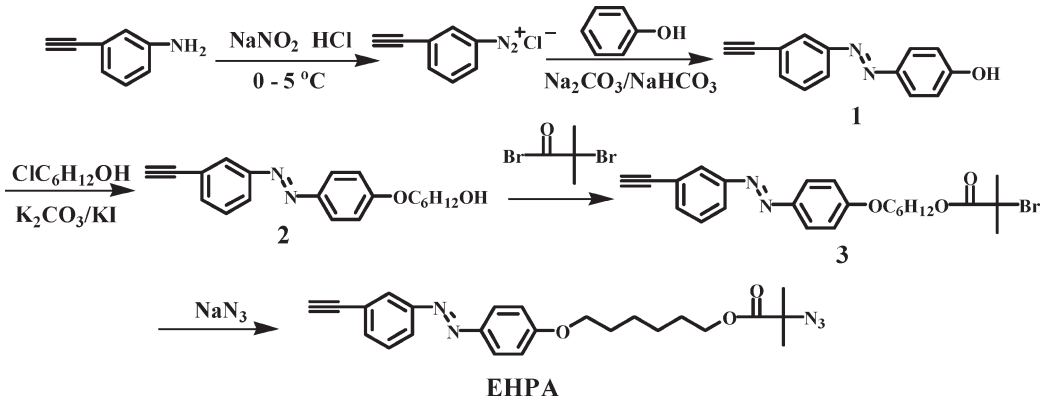
The poor solubility of polymers may be caused by the regular structure of polymer backbone as well as the formation of polymer complexes due to the coordination of the copper ion with the nitrogen-rich heteroatom rings.[16,18,19] Fortunately, in the absence of copper catalysis and organic solvents, the thermal 1,3-dipolar cycloaddition reaction of monomers with azide and alkyne groups yield polymers containing irregular structures of 1,4- and 1,5-substituted 1,2,3-triazole mixtures with high conversion.[20] The obtained main-chain polymers showed excellent solubility and film-forming ability.[18,20]

Following this route, in this paper we selected the A−B type monomer 3′-ethynylphenyl-[4-(4-azidobutoxy)phenyl]azobenzene (EAPA), which formed polymers insoluble in common organic solvents polymerized via $CuSO_4 \cdot 5H_2O$/sodium ascorbate/H_2O "click" way,[21] to polymerize via the alternate way, e.g., through the thermal 1,3-dipolar cycloaddition reaction. The following property investigations of the polymers showed that the obtained polymers were soluble in tetrahydrofuran (THF) and *N*,*N*-dimethylformamide (DMF). However, the attempt to prepare a uniform film for further photoresponsive characterization was

*Corresponding author: e-mail xlzhu@suda.edu.cn, Tel +86-512-65111278, Fax +86-512-65112796.

 Published on Web 02/17/2010

Scheme 1. Synthetic Route of 3′-Ethynylphenyl[4-hexoxyl(2-azido-2-methylpropionate)phenyl]azobenzene (EHPA)



unsuccessful due to its poor film-forming ability. To further improve solubility and film-forming ability of the obtained main-chain azobenzene polymer, an EAPA analogue A−B type azobenzene monomer, 3′-ethynylphenyl[4-hexoxyl(2-azido-2-methylpropionate)phenyl]azobenzene (EHPA), which contained long hexyl chain and ester, was synthesized. The corresponding polymer PEHPA via the thermal 1,3-dipolar cycloaddition reaction in bulk showed good thermal stability and *trans*−*cis*−*trans* isomerization ability. Meanwhile, SRGs formed on the polymer PEHPA's spin-coating films were investigated for the first time with illumination of linearly polarized Kr^+ laser beam at 413.1 nm.

Experimental Section

Materials. 3-Ethynylaniline (≥98%; Aldrich), phenol (analytical reagent; Shanghai Chemical Reagent Co. Ltd., Shanghai, China), 6-chlorohexanol (98%; Aldrich), 2-bromoisobutyryl bromide (98%; Aldrich), 1,4-dibromobutane (analytical reagent; Shanghai Chemical Reagent Co. Ltd., Shanghai, China), and sodium azide (≥99.5%; Aldrich) were used as received. *N,N*-Dimethylformamide (Analytical reagent; Shanghai Chemical Reagent Co. Ltd., Shanghai, China) was purified by vacuum distillation over anhydrous calcium hydride (CaH_2) before use. Other reagents were purified using standard procedure before use. EAPA (^{1}H NMR and ^{13}C NMR spectrum of EAPA is shown in the Supporting Information, Figures S6 and S7) was synthesized according to the method described in the literature.[21]

Synthesis of 3′-Ethynylphenyl[4-hexoxyl(2-azido-2-methylpropionate)phenyl]azobenzene (EHPA). The synthetic route of EHPA is shown in Scheme 1, and detailed synthetic procedures and characterization data follow.

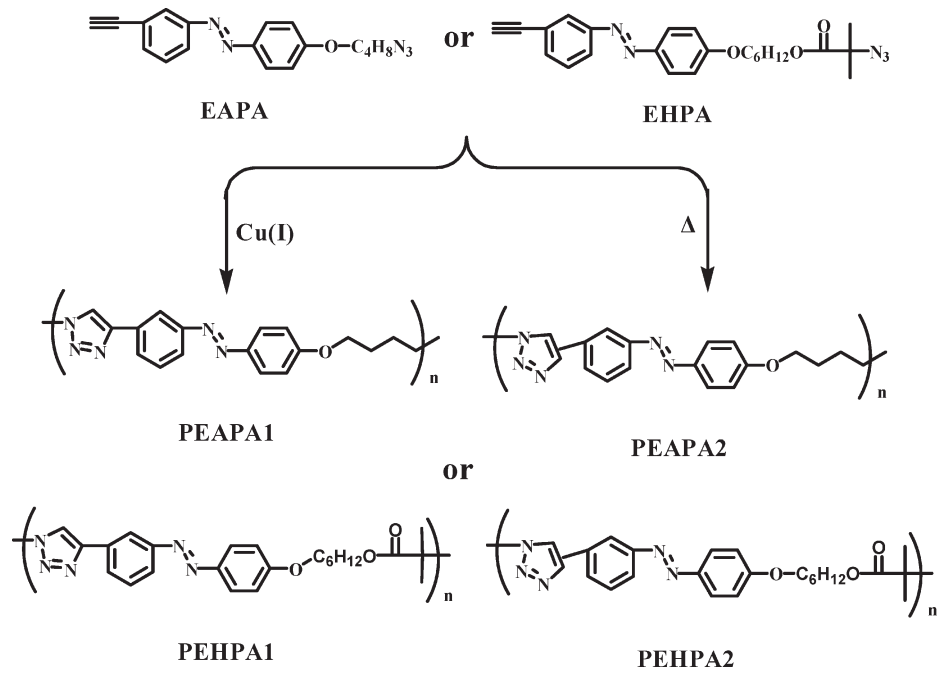
3′-Ethynylphenyl(4-hydroxy)azobenzene (1). 3-Ethynylaniline (5.85 g, 50.0 mmol) was added dropwise to a solution of concentrated HCl (37.0%, 15 mL) in deionized water (30 mL). The mixture was stirred in an ice bath to keep the reaction temperature at 0−5 °C. Then a water solution (10 mL) of sodium nitrite (3.50 g, 50.7 mmol) was added slowly within 10 min. A yellow transparent diazonium salt solution was obtained, after reacted for 60 min at 0−5 °C. Meanwhile, a coupling solution was prepared as follows: phenol (8.00 g, 85.0 mmol), NaOH (4.00 g, 100 mmol), and $NaHCO_3$ (4.20 g, 50.0 mmol) were dissolved in 250 mL of water under vigorous stirring at 0−5 °C. Then the diazonium salt solution was added dropwise to the coupling solution within 20 min at 0−5 °C. The final mixture was reacted at 5 °C for 3 h. The precipitate was collected by filtration, washed with deionized water three times, and dried under vacuum. The crude product was purified by recrystallization from ethanol. Compound **1** was then obtained as red-orange crystal (10.0 g, yield 90.0%). ^{1}H NMR ($CDCl_3$), δ (TMS, ppm): 8.04−7.97 (s, 1H, ArH), 7.94−7.83 (m, 3H, ArH), 7.62−7.52 (d, 1H, ArH), 7.50−7.42 (m, 1H, ArH), 7.00−6.91 (d, 2H, ArH), 5.36−5.27 (s, 1H, ArOH), 3.17−3.10 (s, 1H, ArC≡CH) (spectrum was provided in the Supporting Information, Figure S1). Elemental analysis: Calculated (%): C 75.66, H 4.54, N 12.60. Found (%): C 75.31, H 4.34, N 13.11.

3′-Ethynylphenyl[4-(6-hydroxyhexoxy)phenyl]azobenzene (2). A solution of compound **1** (8.88 g, 40.0 mmol), 6-chlorohexanol (5.44 g, 40.0 mmol), potassium carbonate (5.52 g, 40.0 mmol), a catalytic amount of potassium iodide, and 150 mL of *N,N*-dimethylformamide (DMF) was prepared in a 250 mL round-bottom flask under vigorous stirring. The solution was stirred under reflux at 110 °C for 5 h. After cooling to room temperature, the mixture was poured into 500 mL of water under vigorous stirring. The precipitate was collected by filtration, washed with deionized water three times, and dried under vacuum. The final crude product was purified by recrystallization from ethanol to yield compound **2** as yellow solid (11.9 g, 92.1%). ^{1}H NMR ($CDCl_3$), δ (TMS, ppm): 7.99 (s, 1H, ArH), 7.95−7.87 (d, 2H, ArH), 7.87−7.82 (d, 1H, ArH), 7.56−7.51 (d, 1H, ArH), 7.48−7.41 (m, 1H, ArH), 7.05−6.96 (d, 2H, ArH), 4.10−4.00 (m, 2H, $ArOCH_2$), 3.73−3.62 (m, 2H, $-CH_2OH$), 3.12 (s, 1H, ArC≡CH), 1.89−1.78 (m, 2H, $-CH_2-$), 1.67−1.35 (m, 4H, $-CH_2-$) (spectrum was provided in Supporting Information, Figure S2). Elemental analysis: Calculated (%): C 74.51, H 6.88, N 8.69. Found (%): C 74.71, H 6.62, N 8.32.

6-[4-(3-Ethynylphenylazo)phenoxy]hexyl-2-bromo-2-methylpropanoate (3). Compound **2** (9.66 g, 30.0 mmol), freshly distilled THF (100 mL), and dry triethylamine (4.04 g, 40.0 mmol) were added to a 250 mL three-necked flask. The solution was stirred in an ice bath. A solution of 2-bromoisobutyryl bromide (8.05 g, 35.0 mmol) in dry THF (30 mL) was added dropwise to the mixture at 0−5 °C. The reaction mixture was vigorously stirred for another 5 h at 0−5 °C and then at room temperature overnight. After filtration, the filtrate was dried under vacuum. The remaining yellow mixture was dissolved in dichloromethane and washed with 5% Na_2CO_3 aqueous solution and deionized water for three times. After being dried with anhydrous $MgSO_4$ overnight, dichloromethane was evaporated under reduced pressure. The final crude product was purified by column chromatography (silica gel, ethyl acetate/petroleum ether = 1:5) to yield compound **3** as saffron solid (10.6 g, 75.1%). ^{1}H NMR ($CDCl_3$), δ (TMS, ppm): 8.00 (s, 1H, ArH), 7.95−7.89 (d, 2H, ArH), 7.89−7.84 (d, 1H, ArH), 7.58−7.53 (d, 1H, ArH), 7.49−7.43 (m, 1H, ArH), 7.03−6.98 (d, 2H, ArH), 4.24−4.17 (m, 2H, $ArOCH_2$), 4.09−4.02 (m, 2H, $-CH_2O-$), 3.13 (s, 1H, ArC≡CH), 1.94 (s, 6H, $-CH_3$), 1.90−1.80 (m, 2H, $-CH_2-$), 1.80−1.70 (m, 2H, $-CH_2-$), 1.62−1.42 (m, 4H, $-CH_2-$) (spectrum was provided in Supporting Information, Figure S3); Elemental analysis: Calculated (%): C 61.15, H 5.77, N 5.94. Found (%): C 60.92, H 5.53, N 5.83.

3′-Ethynylphenyl[4-hexoxyl(2-azido-2-methylpropionate)phenyl]-azobenzene (EHPA). Compound **3** (9.40 g, 20.0 mmol), DMF (200 mL), sodium azide (1.92 g, 30.0 mmol), and deionized water (10 mL) were added to a 500 mL round-bottomed flask

Scheme 2. Synthetic Route of Polymers PEAPA1 and PEHPA1 by Cu(I)-Catalyzed 1,3-Dipolar Cycloaddition ("Click" Chemistry) of 3′-Ethynylphenyl[4-(4-azidobutoxy)phenyl]azobenzene (EAPA) and 3′-Ethynylphenyl[4-hexoxyl(2-azido-2-methylpropionate)phenyl]azobenzene (EHPA), Respectively, Using 5% $CuSO_4 \cdot 5H_2O$ and 10% Sodium Ascorbate as Catalyst in DMF at Room Temperature, and Polymers PEAPA2 and PEHPA2 by Thermal 1,3-Dipolar Cycloaddition



equipped with a stir bar and a condenser. The mixture was vigorously stirred under reflux at 80 °C for 24 h and then cooled to room temperature. Then water (300 mL) was added. The mixture was extracted with ethyl acetate (3 × 100 mL). The organic layer obtained was dried with anhydrous $MgSO_4$ overnight, filtered, and evaporated in a reduced pressure. The final crude product was purified by column chromatography (silica gel, ethyl acetate/petroleum ether = 1:8) to yield EHPA as yellow solid (7.10 g, 82.0%). ^{1}H NMR ($CDCl_3$), δ (TMS, ppm): 8.02 (s, 1H, ArH), 7.99−7.80 (m, 3H, ArH), 7.66−7.52 (d, 1H, ArH), 7.52−7.41 (m, 1H, ArH), 7.07−6.91 (d, 2H, ArH), 4.29−4.12 (m, 2H, $ArOCH_2$), 4.12−3.95 (m, 2H, $-CH_2N_3$), 3.15 (s, 1H, ArC≡CH), 1.92−1.62 (m, 4H, $-CH_2CH_2-$), 1.62−1.40 (m, 10H, $-CH_2CH_2-$ and $-CH_3$) (spectrum was provided in Supporting Information, Figure S4). ^{13}C NMR ($CDCl_3$), δ (TMS, ppm): 173.1, 162.1, 152.7, 146.9, 133.8, 129.3, 126.2, 125.2, 123.5, 123.2, 114.9, 83.3, 78.0, 68.3, 66.1, 63.4, 29.3, 28.7, 25.89, 24.7 (spectrum was provided in Supporting Information, Figure S5). Elemental analysis: Calculated (%): C 66.49, H 6.28, N 16.16. Found (%): C 66.12, H 6.35, N 16.50. FTIR (KBr, Figure 4 (EHPA)): γ_{max}/cm^{-1} 3260, 2950, 2100, 1720, 1600, 1500, 1470, 1260, 1150, 1000, and 900.

Preparation of PEHPA1 and PEAPA1 by Cu(I)-Catalyzed 1,3-Dipolar Cycloaddition ("Click" Chemistry). The main-chain azobenzene polymer PEAPA1 (Scheme 2) was synthesized as described in a previous report.[21] According to the last work, the obtained polymers PEAPA1 was insoluble in common solvents such as chloroform, THF, and DMF. The monomer EHPA contained long hexyl chains and ester group should improve the solubility of corresponding azobenzene polymer PEHPA1. The typical experiment process of PEHPA1 was followed. EHPA (0.433 g, 10.0 mmol) and $CuSO_4 \cdot 5H_2O$ (0.002 50 g, 0.500 mmol) were dissolved in 10 mL of DMF in a single-necked flask of 50 mL, and then a solution of sodium ascorbate (0.196 g, 1.00 mmol) in deionized water (0.5 mL) was added dropwise to the mixture under vigorous stir at room temperature. The reaction mixture was vigorously stirred in sealed system for 24 h. After that, the content was poured into 250 mL of methanol. The polymer was obtained by filtration and dried at room temperature in vacuum to a constant weight. The conversion of polymerization was determined gravimetrically (0.396 g yield: 91.4%). The obtained polymer PEHPA1 was soluble in chloroform, THF, and DMF. ^{1}H NMR and ^{13}C NMR spectra of polymer PEHPA1 were obtained with $CDCl_3$ as solvent. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) values were determined by GPC calibrated with PS standards ($M_{n,GPC}$ = 18 000 g mol^{-1}, M_w/M_n = 2.00).

Preparation of PEHPA2 and PEAPA2 by Thermal 1,3-Dipolar Cycloaddition. The synthetic route is shown in Scheme 2. A dry 10 mL ampule tube was filled with EAPA (0.638 g, 20.0 mmol) and then placed in an oil bath at 80 °C. A transparent and viscous liquid was obtained. The reaction mixture polymerized continuously at 80 °C for 12 h. Thereafter, the polymerization was transferred into another oil bath at 120 °C for 6 h. The sample was postcured at 150 °C for 6 h, and the polymerization was terminated. The contents were diluted with 20 mL of tetrahydrofuran (THF) and precipitated into 250 mL of methanol. The precipitate (PEAPA2) was filtrated and dried to a constant weight at room temperature in vacuum. The conversion of polymerization was determined gravimetrically (0.520 g, yield: 81.5%). The ^{1}H NMR spectrum of polymer PEAPA2 was obtained with $CDCl_3$ as solvent. The M_n and M_w/M_n values were determined by GPC ($M_{n,GPC}$ = 29 400 g mol^{-1}, M_w/M_n = 2.44).

Polymer PEHPA2 was prepared using similar procedures (0.749 g, yield 86.5%). ^{1}H NMR and ^{13}C NMR spectra of polymer PEHPA2 were obtained with $CDCl_3$ as solvent. The M_n and M_w/M_n values were determined by GPC ($M_{n,GPC}$ = 31 900 g mol^{-1}, M_w/M_n = 1.91).

Preparation of the Polymer Film and Optical Characterization. Thin films of the polymer PEHPA2 were obtained by the following procedure. A $CHCl_3$ solution of the polymer PEAPA2 (0.05 g/mL) was filtered through 0.22 μm pore size filter. Thin films were obtained via spin-coating the solution onto clean glass slide at 3000 rpm. The thicknesses of homogeneous thin films were measured to be about 225 and 456 nm by Ambios Technology XP-2 Stylus Profiler and subsequently dried under vacuum for 24 h at room temperature. The films were allowed to store in a desiccator for further study.

The procedure for SRGs fabrication can be found in a related reference (illustrated in Figure 1).[22] The SRGs measurement

was performed at room temperature with linearly polarized Kr^+ laser beam (413.1 nm, 200 mW/cm^2) as the light source and optically inscribed on the film with p-polarized interfering laser beam. The surface images of the SRGs were detected using atomic force microscopy (AFM, NT-MDT SOLVER P47-PRO). The dynamic diffraction efficiency of the positive first order was measured using an unpolarized low-power diode laser beam (650 nm) in transmission mode.

Analysis and Characterizations. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymers were determined from a Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive index detector, using HR1 (pore size: 100 Å, 100−5000 Da), HR2 (pore size: 500 Å, 500−20 000 Da), and HR4 (pore size 10 000 Å, 50−100 000 Da) columns (7.8 × 300 mm, 5 μm beads size) with a molecular weight range of 100−500 000 Da, calibrated with PS standard samples. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL min^{-1} operated at 30 °C. GPC samples were injected using a Waters 717 plus autosampler. ^{1}H NMR and ^{13}C NMR spectra were recorded on an INOVA 400 MHz nuclear magnetic resonance (NMR) instrument, using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Differential scanning calorimetry (DSC) was performed using a TA Instruments DSC2010 with a heating/cooling rate of 10 °C min^{-1} from 25 to 600 °C under a continuous nitrogen flow. The DSC2010 instrument was calibrated by pure indium for temperature and enthalpy changes. Samples (3−5 mg) were crimped in standard aluminum pans. First-order transitions were taken at the maximum point of endothermic or exothermic peaks and the glass transition temperature (T_g) at the midpoint of the heat capacity jump. Thermogravimetric analysis (TGA) was performed at a heating rate of 10 °C/min from room temperature to 600 °C under a continuous nitrogen flow of 50 mL min^{-1} with a TA Instruments SDT-2960TG/DTA. The temperature of thermal degradation (T_d) was measured at the point of 5% weight loss relative to the weight at room temperature. FT-IR spectra were recorded on a Nicolette-6700 FT-IR spectrometer. Elemental analysis of C, H, and N was conducted with an EA1110 CHNO-S instrument. The UV−vis spectra were determined on a Hitachi U-3900 spectrophotometer at room temperature.

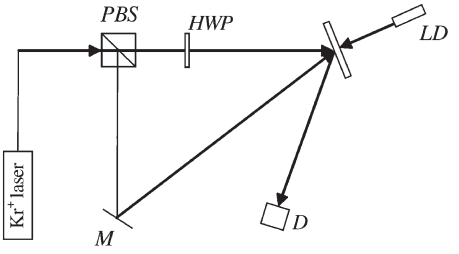


Figure 1. Experimental setup for recording and detecting surface relief gratings (SRGs): PBS, a polarization beam splitter; M, a mirror; HWP, a half-wave plate; LD, a laser diode that emits 650 nm beam; D, a first-order diffracted beam intensity detector.

Results and Discussion

Synthesis of Polymers via 1,3-Dipolar Cycloaddition. The step-growth click chemistry of EAPA as monomer was carried out efficiently using 5% $CuSO_4 \cdot 5H_2O$ and 10% sodium ascorbate as the catalyst in DMF. As our previously report,[21] the formed polymer, PEAPA1, was insoluble in common organic solvents. The reason may be caused by regioregular 1,2,3-triazole and azobenzene group in the main chain[21] and the formation of complexes of copper ion with polymer triazole rings in final product.[19] In order to improve the solubility of this kind main-chain azobenzene polymer, monomer EHPA (analogue of EAPA) containing long alkyl chain and ester structures was synthesized following Scheme 1. This monomer was polymerized under the same condition of EAPA, e.g., using 5% $CuSO_4 \cdot 5H_2O$ and 10% sodium ascorbate as the catalyst. The obtained polymer, PEHPA1, was soluble in common organic solvents, such as $CHCl_3$, THF, and DMF. The number-average molecular weight (M_n) of PEHPA1 was 18 000 g/mol by gel permeation chromatography (GPC) using THF as the eluent and polystyrene as the calibration standard (shown in Table 1). This result indicates that the introducing of long alkyl chain and ester structures successfully improved the solubility of main-chain azobenzene polymers.

However, attempts on film photoproperty investigations of PEHPA1 were unsuccessful due to its poor film-forming ability via spin-coating. Thus, an alternative procedure was used to improve the film-forming ability of polymer. As mentioned in the Introduction, thermal 1,3-dipolar cycloaddition of alkynes and azides produced polymer with regio-random structure in good yields, and the introduction of copper ion into polymer system was also hindered. Therefore, monomer EAPA and EHPA were attempted to polymerize via thermal 1,3-dipolar cycloaddition to obtain corresponding polymer PEAPA2 and PEHPA2, respectively. The reactions were carried out in bulk with a temperature procedure of 80 °C/12 h, 120 °C/6 h, and 150 °C/6 h. Figure 2 shows the appearance of reaction mixture (monomer EHPA) before and after successive step-growth polymerization. The obtained polymer (PEHPA2) showed as a clear solid. The number-average molecular weights of the obtained polymers PEAPA2 and PEHPA2 were estimated by GPC as 29 400 and 31 900 g/mol. The number-average molecular weight of PEHPA2 (M_n = 31 900) was higher than that of PEHPA1 (M_n = 18 000 g/mol). As predicted, this thermal 1,3-dipolar cycloaddition polymerization of monomer EAPA afforded polymer PEAPA2 with good solubility in common solvents, such as THF and DMF.

Table 1. Characteristics Data of Polymers PEAPA1, PEAPA2, PEHPA1, and PEHPA2

sample	catalyst	conversion[a] (%)	M_n[b] (g/mol)	M_w[b] (g/mol)	M_w/M_n[b]	T_g[c] (°C)	T_d[d] (°C)	solubility
PEAPA1[e]	$CuSO_4$/SA	89.3				134	357	
PEAPA2[f]	thermal	81.5	29 400	71 900	2.44	78	352	THF,[g] DMF[g]
PEHPA1[e]	$CuSO_4$/SA	91.4	18 000	36 000	2.00	88	337	$CHCl_3$,[g] THF, DMF
PEHPA2[f]	thermal	86.5	31 900	61 000	1.91	83	340	$CHCl_3$, THF, DMF

[a] Conversion determined by gravimetry. [b] Determined by gel permeation chromatography (GPC) using tetrahydrofuran (THF) as the eluent. M_n: the number-average molecular weight. M_w: the weight-average molecular weight. M_w/M_n: molecular weight distribution. [c] The glass transition temperature (T_g) was measured using a TA Instruments DSC2010 with a heating/cooling rate of 10 °C min^{-1} under a continuous nitrogen flow. [d] The temperature of thermal degradation (T_d) was measured at the point of 5% weight loss relative to the weight at room temperature with a TA Instruments SDT-2960TG/DTA. [e] Polymers PEAPA1 and PEHPA1 were obtained by Cu(I)-catalyzed 1,3-dipolar cycloaddition of 3′-ethynylphenyl[4-(4-azidobutoxy)-phenyl]azobenzene (EAPA) and 3′-ethynylphenyl[4-hexoxyl(2-azido-2-methylpropionate)phenyl]azobenzene (EHPA), respectively, using 5% $CuSO_4 \cdot 5H_2O$ and 10% sodium ascorbate as catalyst in *N*,*N*-dimethylformamide (DMF) at room temperature. [f] Polymers PEAPA2 and PEHPA2 were obtained by thermal 1,3-dipolar cycloaddition in bulk of EAPA and EHPA, respectively, with a temperature procedure of 80 °C/12 h, 120 °C/6 h, and 150 °C/6 h. [g] Soluble in THF, DMF, $CHCl_3$ (chloroform).

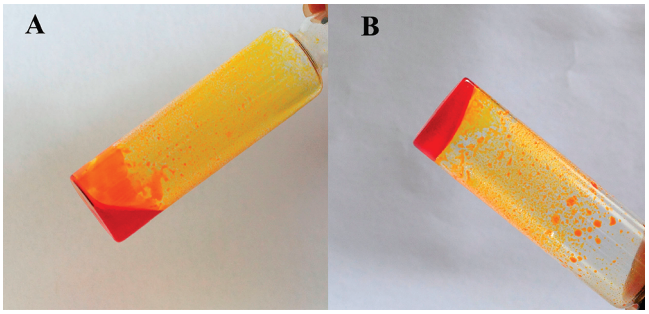


Figure 2. Images of monomer 3′-ethynylphenyl[4-hexoxyl(2-azido-2-methylpropionate)phenyl]azobenzene (EHPA) in a dry 10 mL ampule tube via thermal 1,3-dipolar cycloaddition: before polymerization (A) at 80 °C and after polymerization (B) at 150 °C. The polymerization reactions were carried out in bulk with a temperature procedure of 80 °C/12 h, 120 °C/6 h, and 150 °C/6 h.

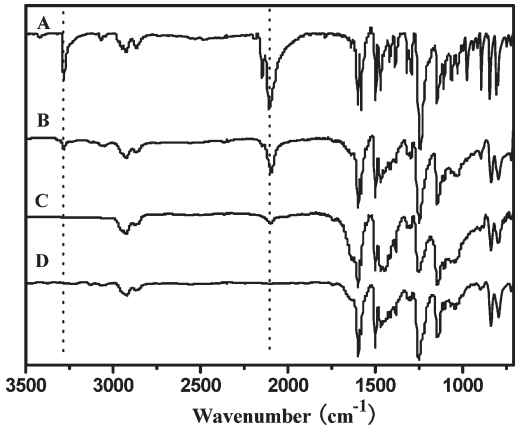


Figure 3. FT-IR spectra of monomer 3′-ethynylphenyl[4-(4-azidobutoxy)phenyl]azobenzene (EAPA) (A); PEAPA2 after thermal 1,3-dipolar cycloaddition polymerization of the monomer EAPA in bulk at 80 °C/12 h (B); 80 °C/12 h + 120 °C/6 h + 150 °C/6 h (C); and PEAPA1 catalyzed 1,3-dipolar cycloaddition ("click" chemistry) of the monomer EAPA using 5% $CuSO_4 \cdot 5H_2O$ and 10% sodium ascorbate as catalyst in DMF at room temperature (D).

Most importantly, the obtained PEHPA2 showed good film-forming property, which would be significantly favored in the application of optics device, such as SRG.

Structural and Thermal Characterization of the Polymers. The course of polymerization reaction was first followed by Fourier transform infrared (FT-IR) spectra. The FT-IR spectra of PEAPA2 and PEHPA2 at different polymerization stages are shown in Figure 3, respectively. The signals at 3280 cm^{-1} (≡C−H), 2148 cm^{-1} (C≡C) and 2109 cm^{-1} (−N_3) (Figure 3A) were the characteristic absorption peaks of the alkyne and azide groups in EAPA. As shown in Figure 3B,C, the characteristic absorption peaks at 3280, 2148, and 2109 cm^{-1} decrease as the reaction proceeds, which indicated the gradual consumption of the reactive groups during the thermal reaction. In addition, the FT-IR spectra of PEAPA2 were similar to that of PEAPA1 in Figure 3D. Similar changes in FT-IR during the polymerization of EHPA are shown in Figure 4. The characteristic absorption peaks of the alkyne at 3270 cm^{-1} and azide groups at 2100 cm^{-1} of EHPA (Figure 4A) rapidly decreased under thermal (Figure 4B,C) or Cu(I)-mediated (Figure 4D) 1,3-dipolar cycloaddition reactions. On the other hand, the absorption peak at 1050 cm^{-1}, corresponding to triazole group, emerged and increased after thermal treatments, indicating the formation of triazole group during polymerization process. These results indicated that the alkyne and azide groups in these two monomers were

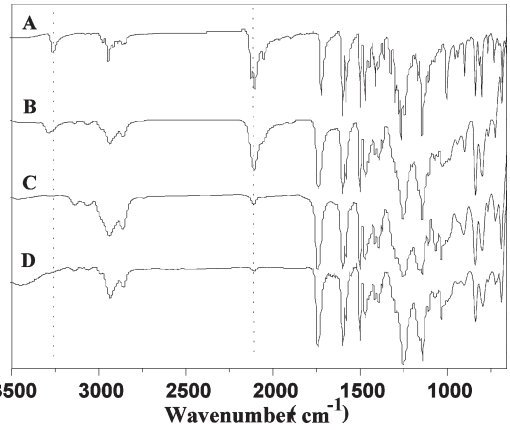


Figure 4. FT-IR spectra of 3′-ethynylphenyl[4-hexoxyl-(2-azido-2-methylpropionate)phenyl]azobenzene (EHPA): (A); PEHPA2 after polymerization thermal 1,3-dipolar cycloaddition polymerization of the monomer EHPA in bulk at 80 °C/12 h ($M_{n,GPC}$ = 4300 g/mol) (B); 80 °C/12 h + 120 °C/6 h + 150 °C/6 h ($M_{n,GPC}$ = 31 900 g/mol) (C); and PEHPA1 ($M_{n,GPC}$ = 18 000 g/mol) catalyzed 1,3-dipolar cycloaddition ("click" chemistry) of the monomer EHPA using 5% $CuSO_4 \cdot 5H_2O$ and 10% sodium ascorbate as catalyst in DMF at room temperature (D).

reacted to form triazole ring after thermal activated step-growth polymerization. However, all of these final polymers showed a weak absorption at about 2100 cm^{-1}, which were caused by the remaining of terminal unreacted azide group.

The polymerization course of PEHPA2 was also followed by GPC. When the reaction mixture of monomer EHPA was polymerized continuously at 80 °C for 12 h, the number-average molecular weight of PEHPA was 4300 g/mol. After the polymerization was further carried out at 120 °C for 6 h, the number-average molecular weight of PEHPA increased to 18 600 g/mol. The final polymer showed the number-average molecular weight of 31 900 g/mol after further reaction at 150 °C for 6 h. It can be seen that the number-average molecular weights measured by GPC increased with the reaction time and temperature.

To further confirm the polymerization reaction, ^{1}H NMR spectra of PEHPA1 and PEHPA2 were investigated and are shown in Figure 5. Compared to the ^{1}H NMR spectrum of EHPA (monomer, Figure 1), the chemical shift of the alkyne group at around 3.15 ppm in EHPA (h in Figure 1) rapidly decreased in the spectra of PEHPA1 and PEHPA2, which indicated the consuming of alkyne group during the step-growth polymerization. A weak chemical shift at 3.15 ppm showed in the ^{1}H NMR of polymers should be assigned to the remaining alkyne group at the terminal of polymer main chain. After polymerization, the signals of methyl groups at 1.31−1.62 ppm (j in Figure 1) adjacent to azide functionality shifted to 2.86−2.10 ppm (g in Figure 5). A new resonance signal at 8.27 ppm (a in Figure 5) appeared and can be assigned to the proton of the 1,2,3-triazole ring (1,4-regioisomer) (PEHPA1 and PEHPA2). Furthermore, the molecular weight can be calculated from the ^{1}H NMR spectrum according to the ratio of the polymer terminal groups to the polymer main chain, using the following equation: $M_{n,NMR} = 433*I_{3.58\text{-}4.31}/4I_{3.15}$, where $M_{n,NMR}$ is the number-averaged molecular weight calculated from ^{1}H NMR, $I_{3.58\text{-}4.31}$ is the integral of the signals (e and f) at 3.58−4.31 ppm, and $I_{3.15}$ is the integral of the signals at 3.15 ppm in Figure 5. It can be estimated that the molecular weights of PEHPA1 and PEHPA2 were 8400 and 14 800 g/mol, respectively. The number-averaged molecular weights obtained by NMR were lower than the GPC values ($M_{n,GPC}$), which could be due to discrepancies in PS standards used for calibrate GPC curves.

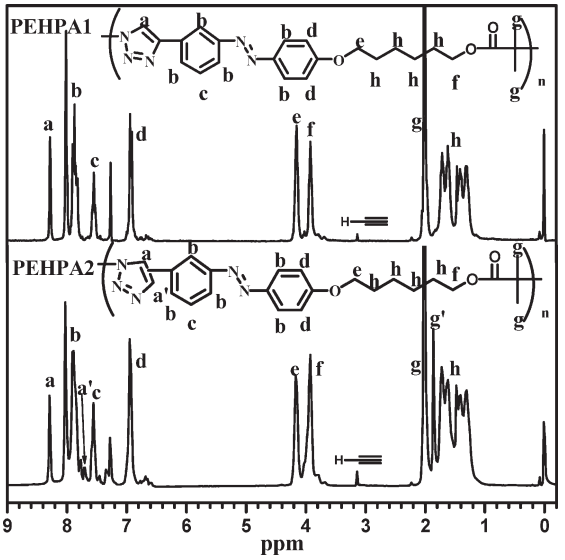


Figure 5. ^{1}H NMR spectra of the polymer PEHPA1 prepared by catalyzed 1,3-dipolar cycloaddition ("click" chemistry) of the monomer, 3′-ethynylphenyl[4-hexoxyl(2-azido-2-methylpropionate)phenyl]azobenzene (EHPA), using 5% $CuSO_4 \cdot 5H_2O$ and 10% sodium ascorbate as catalyst in DMF at room temperature ($M_{n,GPC}$ = 18 000 g mol^{-1}, M_w/M_n = 2.00) and PEHPA2 prepared by thermal 1,3-dipolar cycloaddition of EHPA in bulk with a temperature procedure of 80 °C/12 h, 120 °C/6 h, and 150 °C/6 h ($M_{n,GPC}$ = 31 900 g mol^{-1}, M_w/M_n = 1.91) in $CDCl_3$.

It should be noted that in the ^{1}H NMR spectrum of PEHPA2, besides of the strong resonance peaks at 2.06−2.10 ppm (g) and 8.27 ppm (a) for triazole ring of 1,4-regioisomer, there were two weak resonance peaks at 1.86 ppm (g′) and 7.70 ppm (a′). These two weak resonance peaks can be assigned to the protons in methyl group adjacent to 1,2,3-triazole ring of 1,5-regioisomer in polymer PEHPA2. Thus, the regioisomer ratio in polymer PEHPA2 can be calculated from the ratio of the characteristic signals in Figure 5 (PEHPA2). The 1,4-regioisomeric ratio ($F_{1,4}$) was given by eqs 1 and 2:

$$F_{1,4} = I_g/(I_g + I_g') \quad (1)$$

$$F_{1,4}' = I_a/(I_a + I_a') \quad (2)$$

where I_g is the integral of the signals at 2.06−2.10 ppm (g), I_g' is the integral of the signals at 1.86 ppm (g′), I_a is the integral of the signals at 8.27 ppm (a), and I_a' is the integral of the signals at 7.70 ppm (a′) in Figure 5 (PEHPA2). From the eqs 1 and 2, the 1,4-regioisomeric ratios ($F_{1,4}$, $F_{1,4}'$) of PEHPA2 were calculated to be 78% and 76%, respectively. The small difference should be caused by the error in integral of ^{1}H NMR spectrum. Moreover, the ^{13}C NMR spectrum of polymer PEHPA2 also indicated that polymer PEHPA was successfully obtained by the thermal 1,3-dipolar cycloaddition reaction in bulk (see the Figure 6). The signals at 83.3 and 78.0 ppm (i and h in Figure S5) due to the alkyne group in the monomer (EHPA) disappeared after 1,3-dipolar cycloaddition reaction. Two new resonance signals at 119.5 and 119.1 ppm (h in Figure 6) were assigned to the carbons in the 1,2,3-triazole ring. The signals at 173.1, 63.4, and 24.7 ppm (m, e, and a in Figure S5) due to carbons adjacent to azide group shifted to 171.5, 64.8, and 25.9 ppm (n, e, and a in Figure 6) for the formation of 1,2,3-triazole ring after polymerization. Besides of the strong resonance peaks n, e, and a in Figure 6 for triazole ring of 1,4-regioisomer in polymer PEHPA2, there were also weak resonance peaks at

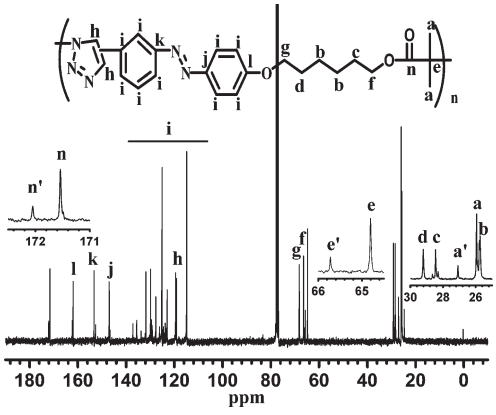


Figure 6. ^{13}C NMR spectrum of the polymer PEHPA2 prepared by thermal 1,3-dipolar cycloaddition of 3′-ethynylphenyl[4-hexoxyl(2-azido-2-methylpropionate)phenyl]azobenzene (EHPA) in bulk with a temperature procedure of 80 °C/12 h, 120 °C/6 h, and 150 °C/6 h ($M_{n,GPC}$ = 31 900 g mol^{-1}, M_w/M_n = 1.91) in $CDCl_3$.

172.0 ppm (n′), 65.7 ppm (e′), and 27.1 ppm (a′) corresponding to the 1,5-regioisomer. Therefore, the 1,4-regioisomeric ratios ($F_{1,4}$) of PEHPA2 can be calculated by the ^{13}C NMR signals as 77% from the similar eqs 1 or 2.

Thus, the NMR results confirmed that the alkyne and azide groups in EAPA and EHPA successfully formed the triazole ring in PEAPA2 (see Supporting Information: Figure S8, PEAPA2, $M_{n,GPC}$ = 4300 g mol^{-1}, M_w/M_n = 1.86) and PEHPA2 via thermal 1,3-dipolar cycloaddition reaction. It also proved that the thermal 1,3-dipolar cycloaddition reactions of terminal alkyne and azide groups proceeded in a usual regiorandom way including 1,4-regioisomer and 1,5-regioisomer.

The obtained main-chain azobenzene polymers were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Figure S9 and S10 in the Supporting Information). The thermal properties of PEAPAs and PEHPAs are summarized in Table 1. The glass transition temperatures (T_gs) of PEAPA1 and PEHPA1 were 134 and 88 °C, which were higher than that of PEAPA2 (78 °C) and PEHPA2 (83 °C), respectively. This should be attributed to the introducing of regioisomer via thermal 1,3-dipolar cycloaddition, which reducing the regular packing of polymer chain. TGA results of polymers showed that all polymers were thermally stable up to 330 °C under a nitrogen atmosphere. The introduction of triazole ring into the polymer backbone plays an additional favorable role in improving the thermal stability.[21,23]

Photoisomerization Behaviors. Under 365 nm ultraviolet irradiation, azobenzene compounds undergo isomerization from *trans*- to *cis*-forms and show photoisomerization behavior. The UV−vis absorption spectra of PEHPA2 in $CHCl_3$ solution were recorded at different time intervals until photostationary state was reached (Figure 7). The absorption peak at around 350 nm was the characteristic intense $\pi-\pi^*$ transition of *trans*-form azobenzene in polymer. After irradiation with 365 nm UV light, the *trans*-form of azobenzene changed to the *cis*-form, which showed the absorption peak at 440 nm in the UV−vis spectrum. Meanwhile, the absorption peak of *trans*-form azobenzene at 350 nm decreased rapidly, while the intensity of the *cis*-form azobenzene (440 nm) slightly increased with the irradiation time. Photoisomerization behavior of monomer EHPA and polymer PEHPA1 was similar to that of PEHPA2.

The rate of *trans*−*cis* photoisomerization of EHPA, PEHPA1, and PEHPA2 in $CHCl_3$ solution was analyzed. The

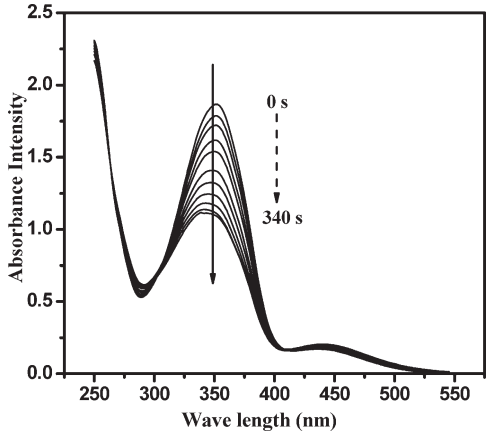


Figure 7. UV−vis absorption changes of polymer PEHPA2 prepared by thermal 1,3-dipolar cycloaddition of the monomer 3′-ethynylphenyl-[4-hexoxyl(2-azido-2-methylpropionate)phenyl]azobenzene (EHPA) in bulk with a temperature procedure of 80 °C/12 h, 120 °C/6 h, and 150 °C/6 h ($M_{n,GPC}$ = 31 900 g mol^{-1}, M_w/M_n = 1.91) under different time interval during the irradiation time with 365 nm UV light in $CHCl_3$ at room temperature. The concentration of solution is 5.0 × 10^{-6} M.

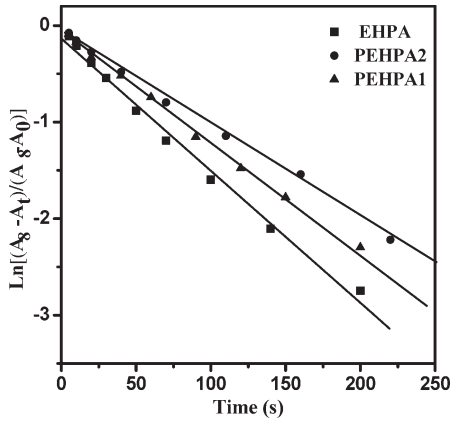


Figure 8. First-order *trans*−*cis* isomerization kinetic of monomer 3′-ethynylphenyl[4-hexoxyl(2-azido-2-methylpropionate)phenyl]azobenzene (EHPA), PEHPA1 (prepared by catalyzed 1,3-dipolar cycloaddition of EHPA using 5% $CuSO_4 \cdot 5H_2O$ and 10% sodium ascorbate as catalyst in DMF at room temperature, $M_{n,GPC}$ = 18 000 g mol^{-1}, M_w/M_n = 2.00), and PEHPA2 (prepared by thermal 1,3-dipolar cycloaddition of the monomer EHPA in bulk with a temperature procedure of 80 °C/12 h, 120 °C/6 h, and 150 °C/6 h, $M_{n,GPC}$ = 31 900 g mol^{-1}, M_w/M_n = 1.91) in chloroform solution under different time interval at room temperature. The concentration of the solution is 5.0 × 10^{-6} M.

photoisomerization kinetics of these compounds are plotted in Figure 8. The results confirmed the first-order kinetic plot for the *trans*−*cis* photoisomerization of EHPA, PEHPA1, and PEHPA2. The first-order rate constant was determined by formula 3

$$\ln\left(\frac{A_\infty - A_t}{A_\infty - A_0}\right) = -k_e t \qquad (3)$$

where A_∞, A_0, and A_t are absorbance at 350 nm at time infinite, time zero, and time t, respectively. Deduced from Figure 8, the photoisomerization rate constant, k_e, of EHPA, PEHPA1, and PEHPA2 was 0.014, 0.011, and 0.010 s^{-1}, respectively. The rate constant of EHPA was the highest among these three compounds due to the low *trans*-to-*cis* transition resistance existed in small molecular. Two polymers, e.g., PEHPA1 and PEHPA2, showed similar rate

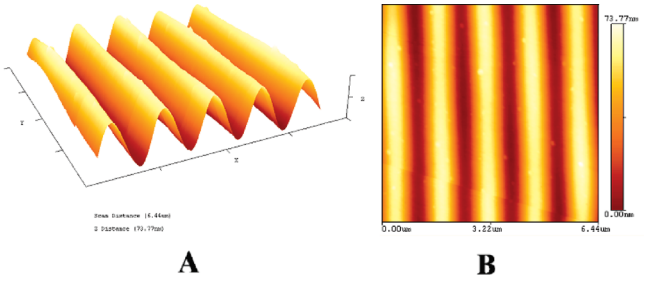


Figure 9. AFM images of the SRGs formed on PEHPA2 (thermal 1,3-dipolar cycloaddition of the monomer 3′-ethynylphenyl[4-hexoxyl-(2-azido-2-methylpropionate)phenyl]azobenzene (EHPA) in bulk with a temperature procedure of 80 °C/12 h, 120 °C/6 h, and 150 °C/6 h; $M_{n,GPC}$ = 18 000 g mol^{-1}; M_w/M_n = 2.00) film via spin-coating on the clean glass with thickness of 456 nm. 3D view of the SRG (A) and plane view of the SRG (B).

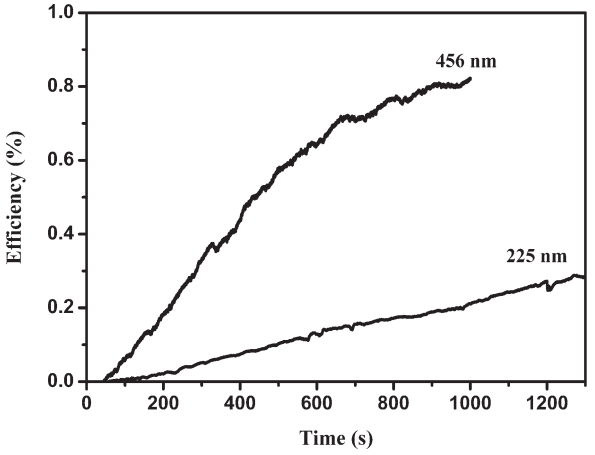


Figure 10. Diffraction efficiency as a function of the laser irradiation time for PEHPA2 (thermal 1,3-dipolar cycloaddition of the monomer 3′-ethynylphenyl[4-hexoxyl(2-azido-2-methylpropionate)phenyl]azobenzene (EHPA) in bulk with a temperature procedure of 80 °C/12 h, 120 °C/6 h, and 150 °C/6 h; $M_{n,GPC}$ = 18 000 g mol^{-1}; M_w/M_n = 2.00) film via spin-coating on the clean glass with thickness of 225 and 456 nm.

constants. The results confirmed there were the accordant rates of *trans*−*cis* photoisomerization for EHPA, PEHPA1, and PEHPA2, which showed first-order photoisomerization behavior of azobenzene units.

Photoinduced Surface Relief Gratings. The obtained polymer PEHPA2 has good film-forming property, which provides the opportunity for the investigation of its surface relief grating (SRG) ability. Thereby, thin films of polymer PEHPA2 were prepared via spin-coating on the clean glass. The homogeneous thin film thicknesses were measured to be 225 and 456 nm. Then, the SRG measurement[5−7] was performed at room temperature with linearly polarized Kr^+ laser beam and characterized by the inscription rates and the saturation levels of SRGs formation. Atomic force microscopy (AFM) observation indicated that surface relief structures with regular spaces were fabricated on the film surfaces of PEHPA2. For the film with thickness of 456 nm, Figure 9 shows AFM three-dimensional (A) and plane (B) images of the alternate surface relief structures with regular spaces fabricated on the polymer film surfaces after Kr^+ laser irradiated for 1000 s at room temperature. From AFM images, the surface modulation depth was about 74 nm, and the grating spacing was about 1400 nm. Moreover, the rates of gratings formation can be probed by measuring the first-order diffraction efficiency of the SRG. Figure 10 shows the increase

of the diffraction efficiency of SRG with the irradiation time. The diffraction efficiency of the polymer film rapidly increased to about 0.82% until saturation level at 1000 s. In the same way, the diffraction efficiency of SRG with a thickness of 225 nm film was up to about 0.28% with saturation level at 1300 s, which was much lower than that of sample with a thickness of 456 nm.[24]

Conclusion

Four polymer samples labeled as PEAPA1, PEAPA2, PEHPA1, and PEHPA2 were prepared from the monomer 3′-ethynylphenyl[4-(4-azidobutoxy)phenyl]azobenzene (EAPA) and 3′-ethynylphenyl[4- hexoxyl(2-azido-2-methylpropionate)phenyl]-azobenzene (EHPA). The polymers PEAPA1 and PEHPA1 were obtained through copper(I) catalysis "click" chemistry technique, while PEAPA2 and PEHPA2 were obtained through thermal 1,3-dipolar cycloaddition technique. All of these polymers showed high thermally resistance (T_d above 330 °C). The polymers PEHPA2 and PEAPA2 showed better solubility than PEHPA1 and PEAPA1 in common organic solvents due to the formation of regiorandom structures as well as no complex of copper ion with polymer triazole rings. Most of all, PEHPA2 showed good film-forming ability, which offered the opportunity to explore these polymers for optical devices for the first time. The film prepared from PEHPA2 showed efficient surface relief gratings (SRGs) formation ability. The diffraction efficiency from SRG with film thickness of 465 nm was measured to be about 0.82%. The reported result provided a convenient alternative route to preparation main-chain azobenzene polymers with good solubility and film formation property. This should be favored in the investigation of optical devices based on azobenzene polymers.

Acknowledgment. The financial support from the National Nature Science Foundation of China (Nos. 20874069, 50803044, 20974071, and 20904036), the Specialized Research Fund for the Doctoral Program of Higher Education contract grant (No. 200802850005), and the Qing Lan Project and the Program of Innovative Research Team of Soochow University is gratefully acknowledged.

Supporting Information Available: ^{1}H NMR spectra of the compounds, monomer EAPA, EHPA, polymer PEAPA2 ($M_{n,GPC}$ = 4300 g mol^{-1}, M_w/M_n = 1.86) in $CDCl_3$; ^{13}C NMR spectra of the monomer EAPA, EHPA, polymer PEHPA2 in $CDCl_3$; DSC and TGA spectra of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Kumar, G.; Neckers, D. C. *Chem. Rev.* **1989**, *89*, 1915–1937. (b) Brown, D.; Natansohn, A.; Rochon, P. *Macromolecules* **1995**, *28*, 6116–6123. (c) Stephan, Z. Z.; Dietrich, H. *Adv. Mater.* **1998**, *10*, 855–859. (d) Natansohn, A.; Rochon, P. *Chem. Rev.* **2002**, *102*, 4139–4175. (e) Delaire, J. A.; Nakatani, K. *Chem. Rev.* **2000**, *100*, 1817–1845. (f) Barrett, C. J.; Mamiya, J.; Yagerc, K. G.; Ikeda, T. *Soft Matter* **2007**, *3*, 1249–1261. (g) Zhao, Y.; He, J. *Soft Matter* **2009**, *5*, 2686–2693.

(2) (a) Gibons, W. M.; Shannon, P. J.; Sun, S. T.; Swetlin, B. J. *Nature* **1991**, *351*, 49–50. (b) Pedersen, T. G.; Johansen, P. M.; Pedersen, H. C. *J. Opt. A: Pure Appl. Opt.* **2000**, *2*, 272–278. (c) Hore, D.; Natansohn, A.; Rochon, P. *J. Phys. Chem. B* **2003**, *107*, 2197–2204. (d) Hafiz, H. R.; Nakanishi, F. *Nanotechnology* **2003**, *14*, 649–654. (e) Rasmussen, P. H.; Ramanujam, P. S.; Hvilsted, S.; Berg, R. H. *J. Am. Chem. Soc.* **1999**, *121*, 4738–4743.

(3) (a) Ishow, E.; Lebon, B.; He, Y. N.; Wang, X. G.; Bouteiller, L.; Galmiche, L.; Nakatani, K. *Chem. Mater.* **2006**, *18*, 1261–1267. (b) Beth, L. L.; Stefan, A. M.; Hanrry, A. A. *Adv. Mater.* **2004**, *16*, 1746–1750. (c) Zeng, Q.; Li, Z. A.; Li, Z.; Ye, C.; Qin, J. G.; Tang, B. Z. *Macromolecules* **2007**, *40*, 5634–5637. (d) Yu, H.; Shishido, A.; Iyoda, Y.; Ikeda, T. *Macromol. Rapid Commun.* **2007**, *28*, 927–931.

(4) (a) Chen, X. B.; Zhang, Y. H.; Liu, B. J.; Zhang, J. J.; Wang, H.; Zhang, W. Y.; Chen, Q. D.; Pei, S. H.; Jiang, Z. H. *J. Mater. Chem.* **2008**, *18*, 5019–5026. (b) Li, W. H.; Nagano, S.; Seki, T. *New J. Chem.* **2009**, *33*, 1343–1348. (c) Wang, D. R.; Ye, G.; Zhu, Y.; Wang, X. G. *Macromolecules* **2009**, *42*, 2651–2657. (d) Kulikovska, O.; Goldenberg, L. M.; Kulikovsky, L.; Stumpe, J. *Chem. Mater.* **2008**, *20*, 3528–3534.

(5) (a) Li, Y.; He, Y.; Tong, X.; Wang, X. *J. Am. Chem. Soc.* **2005**, *127*, 2402–2403. (b) Ho, M. S.; Barrett, C.; Paterson, J.; Esteghamatian, M.; Natansohn, A.; Rochon, P. *Macromolecules* **1996**, *29*, 4613–4618. (c) Andruzzi, L.; Hvilsted, S.; Ramanujam, P. S. *Macromolecules* **1999**, *32*, 448–454.

(6) (a) Rochon, P.; Batalla, E.; Natansohn, A. *Appl. Phys. Lett.* **1995**, *66*, 136–138. (b) Kim, D. Y.; Tripathy, S. K.; Li, L.; Kumar, J. *Appl. Phys. Lett.* **1995**, *66*, 1166–1168.

(7) (a) Zhang, Y. Y.; Cheng, Z. P.; Chen, X. R.; Zhang, W.; Wu, J. H.; Zhu, J.; Zhu, X. L. *Macromolecules* **2007**, *40*, 4809–4817. (b) Zhao, Y.; Qi, B.; Tong, X.; Zhao, Y. *Macromolecules* **2008**, *41*, 3823–3831. (c) Forcen, P.; Oriol, C.; Sanchez, R.; Alcala, S.; Hvilsted; Jankova, K.; Loos, J. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1899–1910.

(8) (a) Wu, Y, L.; Natansohn, A.; Rochon, P. *Macromolecules* **2004**, *37*, 6090–6095. (b) Che, P. C.; He, Y. N.; Wang, X. G. *Macromolecules* **2005**, *38*, 8657–8663. (c) Lee, T. S.; Kim, D. Y.; Jiang., X. L.; Li., L.; Kunar, J.; Tripathy, S. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 283–289. (d) Yu, X. W.; Luo, Y. H.; Deng, Y.; Yan, Q.; Zou, G.; Zhang, Q. J. *Eur. Polym. J.* **2008**, *44*, 881–888.

(9) (a) Tsutsumi, N.; Yoshizaki, S.; Sakai, W.; Kiyotsukuri, T. *Macromolecules* **1995**, *28*, 6437–6442. (b) Lee, T. S.; Kim, D. Y.; Jiang, X. L.; Li, L.; Kumar, J.; Tripathy, S. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 283–289. (c) Sandhya, K. Y.; Pillai, C. K. S.; Sato, M.; Tsutsumi, N. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 1527–1535. (d) Lee, T. S.; Kim, D. Y.; Jiang, X. L.; Li, L.; Kumar, J.; Tripathy, S. *Macromol. Chem. Phys.* **1997**, *198*, 2279–2289.

(10) (a) Xu, Z. S.; Drnoyan, V.; Natansohn, A.; Rochon, P. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2245–2253. (b) Wu, Y. L.; Natansohn, A.; Rochon, P. *Macromolecules* **2001**, *34*, 7822–7828.

(11) Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; pp 1−176.

(12) (a) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004–2021. (b) Baut, N. L.; Diaz, D. D.; Punna, S.; Finn, M. G.; Brown, H. R. *Polymer* **2007**, *48*, 239–244. (c) Bakbak, S.; Leech, P. J.; Carson, B. E.; Saxena, S.; King, W. P.; Bunz, U. H. F. *Macromolecules* **2006**, *39*, 6793–6795. (d) Barner, L.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C. *Macromol. Rapid Commun.* **2007**, *28*, 539–559.

(13) (a) Yuan, Y. Y.; Wang, Y. C.; Du, J. Z.; Wang, J. *Macromolecules* **2008**, *41*, 8620–8625. (b) Malkoch, M.; Schleicher, K.; Drockenmuller, E.; Hawker, C. J.; Russell, T. P.; Wu, P.; Fokin, V. V. *Macromolecules* **2005**, *38*, 3663–3678. (c) Wang, Q.; Chan, T. R.; Hilgraf, R.; Fokin, V. V.; Sharpless, K. B.; Finn, M. G. *J. Am. Chem. Soc.* **2003**, *125*, 3192–3193. (d) Opsteen, J. A.; Hest, J. C. M. *Chem. Commun.* **2005**, *1*, 57–59.

(14) Shen, X. Q.; Liu, H. W.; Li, Y. S.; Liu, S. Y. *Macromolecules* **2008**, *41*, 2421–2425.

(15) (a) Li, Z. A.; Yu, G.; Hu, P.; Ye, C.; Liu, Y. Q.; Qin, J. G.; Li, Z. *Macromolecules* **2009**, *42*, 1589–1596. (b) Li, Z. A.; Yu, G.; Ye, C.; Qin, J. G.; Li, Z. *Macromolecules* **2009**, *42*, 6463–6472.

(16) Qin, A. J.; Lam, J. W. Y.; Tang, L.; Jim, C. K. W.; Zhao, H.; Sun, J. Z.; Yang, B. Z. *Macromolecules* **2009**, *42*, 1421–1424.

(17) (a) Meudtner, R.; Hecht, S. *Macromol. Rapid Commun.* **2008**, *29*, 347–351. (b) Nagao, Y.; Takasu, A. *Macromol. Rapid Commun.* **2009**, *30*, 199–203. (c) Binauld, S.; Damiron, D.; Hamaide, T.; Pasault, J. P.; Fleury, E.; Drockenmuller, E. *Chem. Commun.* **2008**, *35*, 4138–4140. (d) Chernykh, A.; Agag, T.; Ishida, H. *Polymer* **2009**, *50*, 382–390.

(18) Qin, A. J.; Lam, J. W. Y.; Jim, C. K. W.; Zhang, L.; Yan, J. J.; Haussler, M.; Liu, J. Z.; Dong, Y. Q.; Liang, D. H.; Chen, E. Q.; Jia, G. C.; Tang, B. Z. *Macromolecules* **2008**, *41*, 3808–3822.

(19) (a) Chan, T. R.; Hilgraf, R.; Sharpless, K. B.; Fokin, V. V. *Org. Lett.* **2004**, *6*, 2853–2855. (b) Donnelly, P. S.; Zanatta, S. D.; Zammit, S. C.; White, J. M.; Williams, S. J. *Chem. Commun.* **2008**, *21*, 2459–2461.

(20) (a) Qin, A. J.; Jim, C. K. W.; Lu, W. X.; Lam, J. W. Y.; Haussler, M.; Dong, Y. Q.; Sung, H. H. Y.; Wikkiams, I. D.; Wong, G. K. L.; Tang, B. Z. *Macromolecules* **2007**, *40*, 2308–2317. (b) Tian, J. J.; Wan, L. Q.; Huang, J. Z.; Hu, Y. H.; Huang, F. R.; Du, L. *Polym. Adv. Technol.* **2007**, *18*, 556–561.

(21) Xue, X. Q.; Zhu, J.; Zhang, W.; Zhang, Z. B.; Zhu, X. L. *Polymer* **2009**, *50*, 4512–4519.

(22) Kucharski, S.; Janik, R.; Szkodzinska, J. *Colloids Surf., A* **2002**, *198−200*, 359–365.

(23) Smitha, P.; Asha, S. K.; Pillai, C. K. S. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4455–4468.

(24) Fukuda, T.; Matsuda, H.; Shiraga, T.; Kimura, T.; Kato, M.; Viswanathan, N. K.; Kumar, J.; Tripathy, S. K. *Macromolecules* **2000**, *33*, 4220–4225.