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Synthesis and Optical Properties of Thermally and Photochemically Cross-Linkable Diacetylene-Containing Polymers

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ABSTRACT: A series of diacetylene-containing polymers were prepared by oxidative coupling polymerization of 9,9-bis(4-propargyloxyphenyl)fluorene and dipropargyl 4,4′-(hexafluoroisopropylidene)diphthalimide. The polymers had molecular weights of 42 000−235 300 and polydispersity indices of 1.1−1.8 as determined by gel permeation chromatography using polystyrene standards. All the polymers showed typically amorphous diffraction patterns, good solubility in organic solvents, and good film-forming capability. The polymers were readily cross-linkable upon exposure to UV light at ambient temperature and could also be thermally cured. The diacetylene groups were involved in both thermal and photocuring processes, as determined by ^{13}C CP/MAS NMR and FTIR means. The in-plane and out-of-plane refractive indices of these polymers varied from 1.5454 to 1.6313 and from 1.5329 to 1.6283 at 1550 nm, respectively, according to the monomer ratios in the feed. The birefringence at 1550 nm was significantly reduced from 1.25% for polymer **3e** to 0.3% for polymer **3a** by incorporating the fluorenyl and ether linkages into the polymer backbone. All the polymer thin films on substrates could be directly photopatterned by irradiation at 250−450 nm through a photomask.

Introduction

Polymers have recently emerged as promising optical materials for use in optical waveguide devices, owing to their unique optical property, processability, and low cost for device integration.[1] To be compatible with the semiconductor's fabrication process, optical polymers should possess good thermal stability and be ideally photo- and/or thermally cross-linkable. Precise control of refractive index, birefringence, and optical loss at the telecommunication wavelengths (e.g., 1310 and 1550 nm) is also important for making polymer-based optical waveguide devices and optical interconnects. Although extensive research has been carried out on polymers for waveguide applications for approximately 15 years, polymer waveguide materials suitable for telecommunication applications are not fully commercialized.

Among thermally stable polymers, aromatic polyimides are widely used in the microelectronic industry and have recently been investigated as waveguide materials.[2] The processing of polyimide films often requires the use of a soluble polyamic acid precursor and curing at high temperatures, which tends to lead to the formation of microcavities, voids, and pinholes and thus causes an increase in optical loss. Another difficulty encountered with aromatic polyimides in making polymer waveguides is the large birefringence which arises from orientation of the aromatic imide segments during film formation.[3] In comparison, poly(aryl ether)s have lower birefringence than polyimides due to the presence of flexible ether linkages.[4] Both of these polymers can be patterned by dry or wet etching and pattern transfer techniques.[5] However, to be directly photopatternable, they should contain a photosensitive or photo-cross-linkable group, such as acrylate,[6] carbamate,[7] and chalcone groups.[8] Among many photosensitive groups, the diacetylene group is also known for its ability to cross-link under irradiation or with heat and not evolve volatile byproducts.[9] Upon UV irradiation with a low-[3e,f] or medium-pressure[3b,d] mercury lamp, the diacetylene moieties within the crystalline domains of the polymers undergo intermolecular 1,4-addition reaction to yield highly cross-linked networks.

In connection with our research on polymer-based optical variable attenuators and electrooptic modulators,[10] we have been engaged in the development of optical polymers that are photo- and/or thermally cross-linkable and have a refractive index by design and low birefringence at the telecommunication wavelength of 1550 nm. We report here the synthesis and properties of a series of poly(ether imide)s containing the diacetylene functionality. By varying the ratios of imide and ether components, we could control the refractive index and birefringence. The presence of photosensitive diacetylene moieties in the polymer main chain allowed for direct photopatterning of the polymer films.

Experimental Section

Materials. All the reagents and solvents were obtained from Sigma-Aldrich Canada and were used as received unless otherwise specified. 4,4′-(Hexafluoroisopropylidene)diphthalic anhydride was purchased from Chriskev Co. Inc. Cuprous chloride (BDH Chemicals Ltd.) was purified by dissolution in concentrated HCl followed by precipitation in water, filtration, washing with ethanol and diethyl ether, and drying under vacuum (5 mmHg) at 100 °C. Polymer films were prepared by spin-coating the polymer solution in 1,1,2,2-tetrachloroethane (TCE) (3.5−5.0 wt %) onto a silicon wafer in a two-step process, first at 500 rpm and then at 1800 rpm, followed by drying under vacuum (5 mmHg) at 80 °C for 6−8 h. The film thickness was controlled between 0.7 and 1.0 μm for refractive index measurements and 2.0−2.5 μm for photopatterning.

Measurements. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-400 MHz and Bruker-100 MHz instrument using tetramethylsilane as an internal reference. Infrared (IR) spectra were obtained with a Bomem Michelson 120

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FTIR spectrometer. Melting points were obtained from a Fisher-Johns melting apparatus and were uncorrected. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) relative to polystyrene standards, using *N*,*N*-dimethylformamide (DMF) at 50 °C at a flow rate of 1.0 mL/min. Differential scanning calorimetry (DSC) was performed with a Seiko SSC/ 5200 DSC instrument at a heating rate of 10 °C/min in nitrogen. Thermal stability, as measured by 5% weight loss of the polymer samples, was determined using a Seiko TG/DTA 220 analyzer at a heating rate of 10 °C/min, in nitrogen. Refractive index and birefringence measurements were done using a WASE 32 ellipsometer (J.A. Woolam Co., Inc.) at 1550 nm. UV curing of polymer films was done using an Ultracure 100SS Plus/Novacure system as a source with a 250−450 nm filter at a light intensity of 3500 mW/cm^2. Thermal curing of polymer films was carried out in a vacuum oven at 210 °C for 3 h. Photopatterns imaged by scanning electron microscopy were prepared from polymer films (approximately 2 μm thickness) on silicon wafers. After exposure to UV light through a photomask for 40 min at room temperature, the pattern was developed by immersing the sample consecutively in a TCE bath for 30 s and a chloroform bath for 1 min. The films were further dried in a vacuum oven at 70 °C overnight. SEM images were taken using a JEOL-JSM-6400 scanning microscope.

Monomer Synthesis. Monomer 1. In a three-neck, round-bottomed flask equipped with a condenser, sodium hydroxide solution (500 mL, 20 wt %), 9,9-bis(4-hydroxyphenyl)fluorene (10.00 g, 28.5 mmol), and tetra-*n*-butylammonium bromide (1.37 g, 4.20 mmol) were mixed for 1 h at room temperature. Propargyl bromide (10.15 g, 85.2 mmol) was then added, and the reaction mixture was heated to 50−55 °C. After 5 h the reaction was stopped, and the product was extracted with ethyl acetate (3 × 200 mL). The organic layer was washed three times with water and then with a saturated NaCl solution. After drying over anhydrous sodium sulfate and removal of the solvent, the crude product was recrystallized twice from MeOH/EtOAc (3.5/1, v/v) to give light yellow crystals: 7.75 g (63.7% yield); mp 155−156 °C. IR (KBr, cm^{-1}): 3289 ($\equiv$C−H), 2119 (−C$\equiv$C−). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.73 (2 H, d, J = 5.44 Hz), 7.30 (6 H, m), 7.11 (2 H, d, J = 8.97 Hz), 7.11 (4 H, dd, J = 9.9 Hz), 6.8 (4 H, d, J = 9.9 Hz), 4.6 (4 H, d, J = 2.3 Hz), 2.47 (2 H, t, J = 2.4 Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 156.35, 151.57, 139.95, 138.95, 129.19, 127.69, 127.39, 126.03, 120.18, 114.43, 78.64, 75.44, 64.15, 55.75.

Dipropargyl 4,4′-(Hexafluoroisopropylidene)diphthalimide (2). It was prepared according to a known procedure, and its physical and spectral data (mp, ^{1}H NMR, ^{13}C NMR) are in accord with the literature data;[11] mp 150 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 8.08 (1 H, d, J = 8.4 Hz), 8.02 (1 H, d, J = 8.4 Hz), 7.81 (1 H, s), 4.47 (2 H, d, J = 2.5 Hz), 2.80 (1 H, t, J = 2.5 Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 166.58, 166.50, 139.18, 137.07, 134.11, 133.71, 125.23, 124.77, 78.34, 72.89, 66.50, 29.89, 27.68.

Polymer Synthesis. Polymer 3a. To a dried three-neck, round-bottomed flask were added CuCl (0.0115 g, 0.11 mmol), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (0.014 g, 0.12 mmol), pyridine (0.185 g, 2.35 mmol), and 6.6 mL of anhydrous 1,2-dichlorobenzene. To the flask was attached a water condenser and an inlet and outlet for oxygen. The reaction mixture was warmed to 75 °C while oxygen was bubbled through. After 1 h, monomer **1** (1.000 g, 2.34 mmol) in 10 mL of 1,2-dichlorobenzene was added to the catalyst mixture. After 3 h, 5 mL of 1,4-dioxane was added to the viscous solution, and the polymer was then precipitated in 400 mL of methanol containing 2% HCl. The white fibrous polymer was filtered, reverse precipitated from DMF, and dried under vacuum at 60 °C (69% yield). M_n = 235 300; M_w/M_n = 1.2; η_{inh} = 0.565 dL/g (DMF, 30 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.7 (1 H, d, J = 7.42 Hz), 7.34−7.17 (3 H, m), 7.08 (2 H, d, J = 8.7 Hz), 6.72 (2 H, d, J = 8.7 Hz), 4.58 (2 H, s). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 156.18, 151.47, 139.91, 139.12, 129.23, 127.75, 127.44, 126.02, 120.18, 114.40, 74.69, 70.98, 64.13, 56.13, 29.71

Polymer 3b. The above procedure was followed using CuCl (0.013 g, 0.13 mmol), TMEDA (0.014 g, 0.12 mmol), pyridine (0.185 g, 2.350 mmol), monomer **1** (639.5 mg, 1.50 mmol), monomer **2** (259.2 mg, 0.50 mmol), and 16 mL of nitrobenzene. The polymerization was carried out at 70 °C. The white fibrous polymer **3b** was filtered, reverse precipitated from DMF, and dried overnight under vacuum at 60 °C (67% yield). M_w = 69 800; M_w/M_n = 1.8. IR (NaCl, cm^{-1}): 1718.6, 1729.0 (C=O). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.92−7.71 (7 H, m), 7.35−7.21 (12 H, m), 7.09 (6 H, d, J = 8.52 Hz), 6.74 (6 H, d, J = 7.92 Hz), 4.60 (8 H, s), 4.49 (2 H, s). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 165.53, 165.35, 156.18, 151.47, 139.91, 139.13, 138.97, 135.86, 132.77, 132.47, 129.23, 127.73, 127.43, 126.02, 125.16, 124.04, 120.16, 114.40, 74.67, 73.71, 72.72, 71.81, 70.97, 70.91, 67.64, 64.12, 56.14, 56.05, 27.91.

Polymer 3c. The same procedure as for polymer **3b** was used, employing CuCl (0.019 g, 0.19 mmol), TMEDA (0.023 g, 0.19 mmol), pyridine (0.278 g, 3.52 mmol), monomer **1** (0.639 g, 1.49 mmol), monomer **2** (0.777 g, 1.49 mmol), and 24 mL of nitrobenzene. The white fibrous polymer was filtered, reverse precipitated from DMF, and dried overnight under vacuum at 60 °C (55% yield). M_w = 50 200; M_w/M_n = 1.1. IR (NaCl, cm^{-1}): 1718.6, 1729.0 (C=O). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.92−7.71 (4 H, m), 7.35−7.21 (4 H, m), 7.09 (2 H, d, J = 8.00 Hz), 6.74 (2 H, d, J = 7.92 Hz), 4.62 (2 H, s), 4.48 (2 H, s). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 165.55, 165.37, 156.17, 151.45, 139.91, 139.13, 138.99, 135.88, 132.77, 132.46, 135.88, 132.77, 132.46, 129.23, 127.73, 127.43, 126.02, 125.15, 124.71, 124.05, 121.85, 120.16, 114.38, 74.65, 73.69, 72.72, 71.80, 70.96, 70.90, 67.62, 64.11, 56.15, 56.05, 27.01, 27.86.

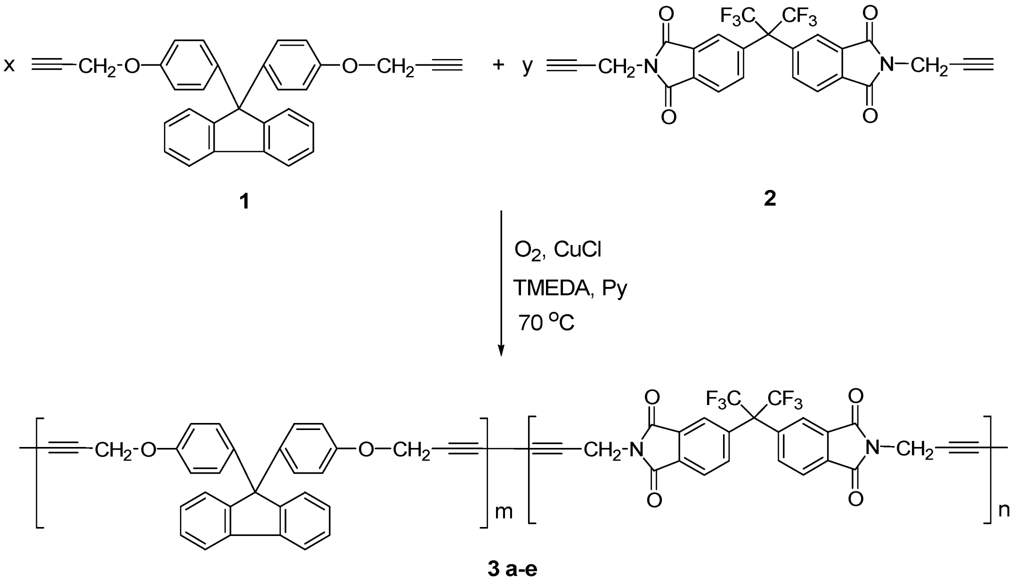
Polymer 3d. The above procedure was followed using CuCl (0.013 g, 0.13 mmol), TMEDA (0.015 g, 0.13 mmol), pyridine (0.180 g, 2.35 mmol), monomer **1** (0.213 g, 0.5 mmol), monomer **2** (0.777 g, 1.5 mmol), and 16 mL of nitrobenzene. The white fibrous polymer was filtered, reverse precipitated from DMF, and dried overnight under vacuum at 60 °C (51% yield). M_n = 25 300; M_w/M_n = 1.1. IR (NaCl, cm^{-1}): 1718.6, 1729.0 (C=O). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.94−7.72 (10 H, m), 7.38−7.24 (4 H, m), 7.09 (2 H, d, J = 8.6 Hz), 6.74 (2 H, d, J = 8.4 Hz), 4.63 (2 H, s), 4.49 (6 H, s). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 165.52, 165.35, 156.20, 151.48, 139.93, 139.19, 139.01, 135.89, 132.80, 132.49, 129.24, 127.73, 127.43, 126.44, 126.03, 125.16, 124.03, 120.16, 114.40, 74.69, 73.72, 72.74, 71.83, 70.96, 70.91, 67.62, 64.14, 56.20, 56.10, 27.93.

Results and Discussion

Monomer Synthesis. Monomer **1** was prepared in high yield from propargyl bromide and 9,9-bis(4-hydroxyphenyl)fluorene in an aqueous solution of sodium hydroxide in the presence of a small amount of tetra-*n*-butylammonium bromide as a phase transfer catalyst.[11] The IR spectrum showed the characteristic absorption of the acetylene at 3289 cm^{-1} for $\equiv$C−H and at 2119 cm^{-1}for −C$\equiv$C−. Additional structural proof was obtained from ^{13}C NMR and ^{1}H NMR spectra. Two characteristic peaks for acetylenic carbons were found in the ^{13}C NMR spectrum at 75.44 and 78.64 ppm. The ^{1}H NMR spectrum showed the ethynyl proton as a triplet at 2.47 ppm.

Polymer Synthesis. The syntheses of polyether **3a**, copoly(ether imide)s **3b**, **3c**, and **3d,** and polyimide **3e** were carried out using the oxidative coupling method developed by Hay (Scheme 1).[12] Copoly(ether imide)s **3b**, **3c**, and **3d** were obtained using three different ratios of monomers **1** and **2**. The ether/imide molar ratios in the final copolymers were determined by NMR from the methylenic protons at 4.6 ppm (OCH$_2$−C$\equiv$C−) and 4.4 ppm (NCH$_2$−C$\equiv$C−). The relative ratios of monomer **1** to monomer **2** in the final polymers were found to be very close to the feed ratios and thus could be easily adjusted and controlled.

Scheme 1. Syntheses of Polymers 3a−3e



Polymer 3	x	y	m	n
a	1.0	0.0	1.0	0.0
b	3.0	1.0	3.1	1.0
c	1.0	1.0	1.0	1.0
d	1.0	3.0	1.0	2.8
e	0.0	1.0	0.0	1.0

x, y: molar ratio in the feed; m, n: molar ratio in the polymer

Table 1. Characterization of Diacetylene Polymers 3a−3e

polymer	monomer 1 (mol %)	M_w[a] ($\times 10^{-3}$)	M_n[a] ($\times 10^{-3}$)	M_w/M_n[a]	T_d[b] (°C)	n_{TE}[c]	n_{TM}[d]	Δn[e]
3a	100.0	235.3	201.7	1.2	334	1.6313	1.6283	0.0030
3b	72.2	69.8	38.8	1.8	350	1.6145	1.6097	0.0048
3c	50.2	46.0	41.2	1.1	364	1.5945	1.5878	0.0067
3d	25.3	42.4	38.5	1.1	383	1.5796	1.571	0.0086
3e	0	N/A[f]	N/A	N/A	414	1.5454	1.5329	0.0125

[a] GPC values vs polystyrene standards. [b] Decomposition temperature as calculated at 5% weight loss in N_2, as assessed by TGA at a heating rate of 10 °C/min. [c] In-plane refractive index at 1550 nm at ambient temperatures. [d] Out-of-plane refractive index at 1550 nm at ambient temperatures. [e] Birefringence. [f] Not measured.

Polymers **3a**−**3d** were isolated as white fibrous materials and displayed excellent solubility in chlorinated hydrocarbons, DMF, *N*-methylpyrrolidinone, *N*,*N*-dimethylacetamide, and tetrahydrofuran. Transparent, tough, flexible films could be cast from TCE or DMF. The weight-average molecular weights as determined by gel permeation chromatography relative to polystyrene standards ranged from 42 400 to 235 300 (Table 1).

The ^{1}H NMR, ^{13}C NMR, and IR spectra of the polymers were consistent with their assigned structures. No residual ethynyl protons due to unreacted acetylene groups were observed for the polymers by ^{1}H NMR. The characteristic $\equiv$C−H and −C$\equiv$C− peaks for **1** (3289 and 2119 cm^{-1}) and **2** (3281 and 2138 cm^{-1}) were no longer observable in the IR spectra of the polymers. The ^{13}C NMR spectra also showed that the terminal ethynyl carbons were transformed into diacetylenic carbons after polymerization. For example, two diacetylenic carbons at 74.71 and 70.99 ppm in the spectrum of polymer **3a** (Figure 3a) replaced the two ethynyl carbons at 78.64 and 75.44 ppm which were observed in the spectrum of monomer **1**. For polymers **3b**, **3c**, and **3d** the significant features in the ^{13}C NMR spectra were the appearance of six new peaks at 74.67 and 70.97 ppm attributed to the symmetric diacetylene carbons of the ether fragments and at 73.71, 72.72, 71.81, and 70.91 ppm for the diacetylene carbons due to the different diad units in the copolymers.

All the polymers were characterized by thermogravimetric analysis and differential scanning calorimetry (DSC) under a nitrogen atmosphere. The onset temperatures for 5% weight loss ranged from 334 to 414 °C (Table 1). As expected, higher thermal stability was found for the copolymers with a higher imide/ether molar ratio. DSC analyses showed that they all undergo an exothermic reaction with onset temperatures around 170 °C. The temperature for the maximum exotherm varied from 229 to 262 °C and was higher for the polymers with higher imide content (Figure 1).

Polymer Cross-Linking. Thermal and photochemical cross-linking of diacetylene polymers **3a**−**3e** were studied and compared. Typically, after 40 min of exposure to UV light at 254−450 nm, all the polymer films became insoluble and changed the color from transparent to yellow. Clearly, the changes in color and solubility

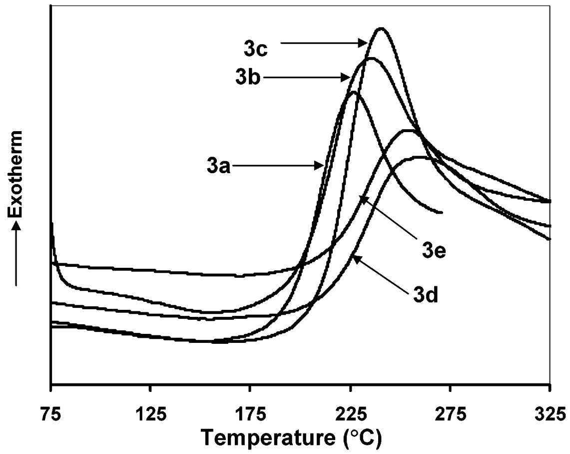


Figure 1. DSC traces of polymers **3a**–**3e**.

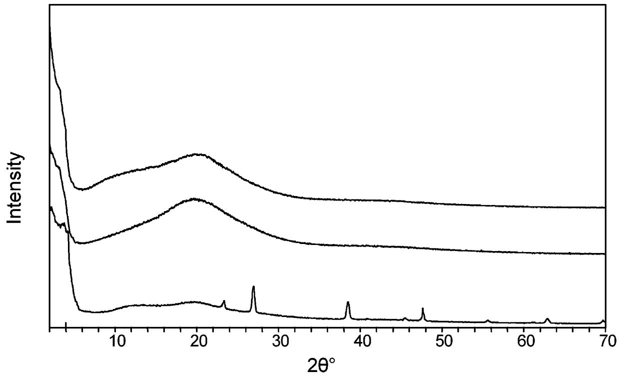


Figure 2. WAXD of polymer **3a**: (a) uncured, (b) UV irradiated, and (c) thermally treated at 210 °C for 3 h.

are attributed to cross-linking of the diacetylene moieties.[3,13] These polymers are amorphous as shown by powder wide-angle X-ray diffraction before and after photoirradiation (Figure 2), suggesting that the cross-linking process would not increase the optical loss caused by scattering due to the formation of the crystalline domains.

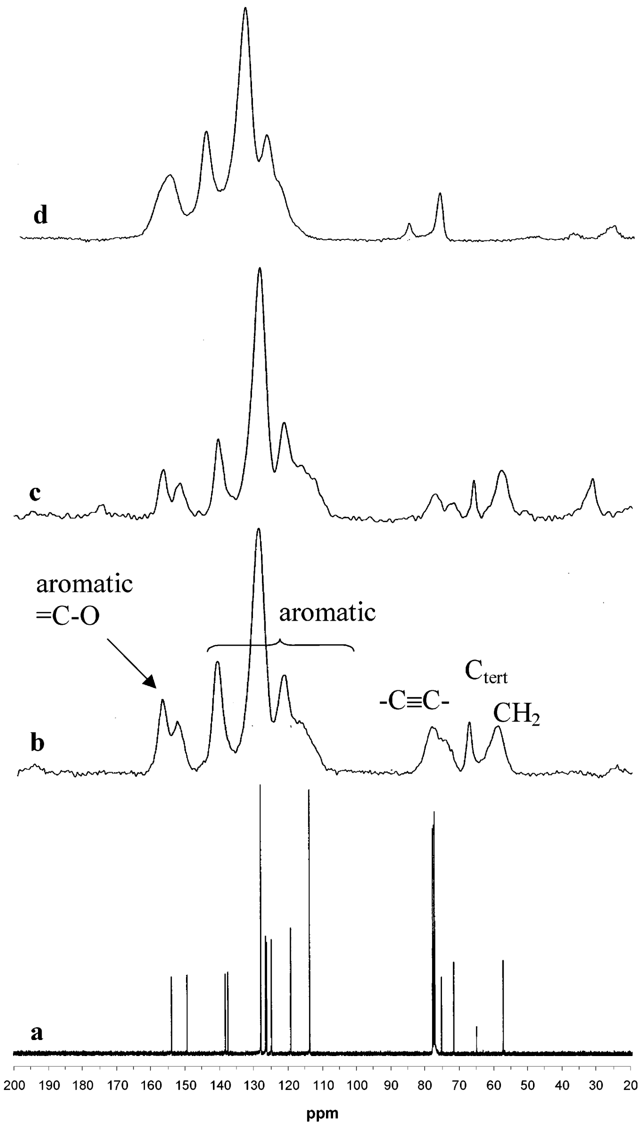


Figure 3. Changes in ^{13}C NMR spectra of polymer **3a**: (a) in $CDCl_3$ before irradiation, (b) ^{13}C CP/MAS NMR spectrum before irradiation, (c) ^{13}C CP/MAS NMR spectrum after UV irradiation for 40 min, and (d) ^{13}C CP/MAS NMR spectrum after thermal treatment at 210 °C for 3 h.

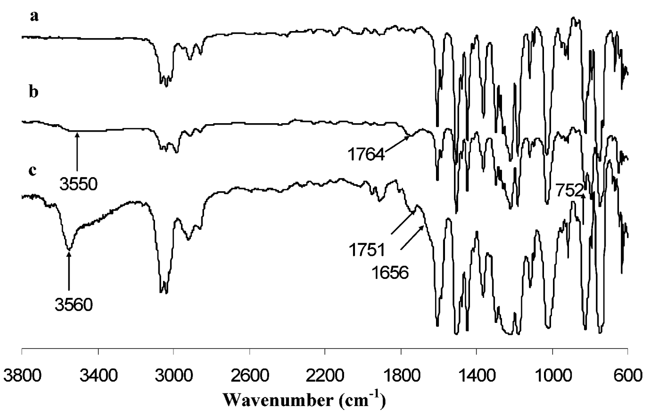


Figure 4. IR spectra of polymer **3a**: (a) before irradiation, (b) after UV irradiation for 20 min, and (c) after thermal treatment at 210 °C for 3 h.

To further study the photoinduced structural changes, ^{13}C CP/MAS NMR experiments were carried out on polymer **3a**. Figure 3 displays the ^{13}C CP/MAS NMR spectra of polymer **3a** cured for 40 min at 254–450 nm and that of a nonirradiated sample. Characteristic peaks in the nonirradiated sample were observed at 55 ppm ($-CH_2-O-$), 60 ppm (tertiary aliphatic carbon), 70–85 ppm (diacetylene carbon atoms), 100–140 ppm (aromatic carbons), and 150–160 ppm (aromatic $=C-O$). For the cured sample, the relative intensity of peaks at 74.7 ppm decreased, and a small shoulder at 110 ppm appeared, corresponding to the $C=C$ carbon that is formed from the 1,4-addition reaction of diacetylene. Two new peaks also appeared after photo-cross-linking for a tertiary aliphatic carbon at 28.7 ppm (from CP/MAS dipolar dephasing experiment) and a carbonyl carbon at 173.5 ppm, suggesting that another type of reaction occurred simultaneously or sequentially during photo-cross-linking. IR studies of thin polymer films on a sodium chloride plate also indicated the structural changes at the acetylenic moiety. The intensity of the $\equiv C-C$ stretching vibration band at 916–948 cm^{-1} decreased (Figure 4b), along with the appearance of two new peaks at 1751 cm^{-1} (carbonyl group) and at 3550 cm^{-1} (hydroxy group). These results suggest that the $-CH_2O-$ linkages were also involved in the photocuring process to a certain extent and are responsible for the formation of the new carbonyl and hydroxy groups in the cross-linking process.

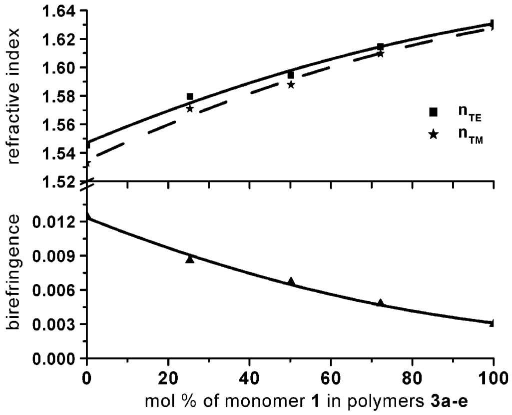


Figure 5. Plot of refractive index and birefringence (at 1550 nm) vs mol % of monomer **1** in polymers **3a**−**3e**.

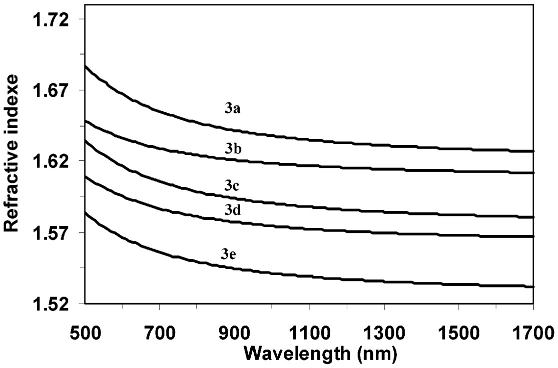


Figure 6. Refractive index dispersion of polymers **3a**−**3e**.

In a comparative experiment, thermal curing of polymer **3a** was carried out at 210 °C and induced a drastic change in color from transparent to a dark red and in the film quality (insoluble and brittle). The ^{13}C CP/MAS NMR spectrum (Figure 3d) confirmed extensive reactions involving the diacetylene and methyleneoxy groups, as the peaks at 70−85 ppm (alkyne carbons) and at 50 ppm ($-CH_2O-$) almost completely disappeared. IR spectra of the thermally cured polymer (Figure 4c) showed also the presence of a peak at 1655 cm^{-1} for the newly formed alkene bonds, a newly formed hydroxy group at 3560 cm^{-1}, and a carbonyl group at 1736 cm^{-1}, suggesting that a Claisen rearrangement reaction had taken place to yield the fragments structurally similar to a phenol and quinone.[14] X-ray diffraction analysis (Figure 6c) indicated the formation of small ordered domains for the thermally cross-linked polymer **3a**. Similar behaviors were observed for polymers **3b**, **3c**, and **3d.** This kind of short-range ordering in polymer waveguide is expected to induce a propagation loss and birefringence due to scattering. Therefore, long-time heating above 210 °C should be avoided when making a waveguide device from polymers **3a**−**3d**.

Optical Property. Optical materials with different refractive indices are required as a core and a cladding part of an optical waveguide. The core material must have a higher refractive index than the cladding material. The larger the difference in the refractive indices between the core and the cladding, the bigger the numeric aperture of the light guide and a better high-density optical guide. Since the in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices and birefringence of an optical polymer are important parameters of waveguide devices, the optical properties of polymers **3a**−**3e** were determined by ellipsometry at 1550 nm at room temperature.

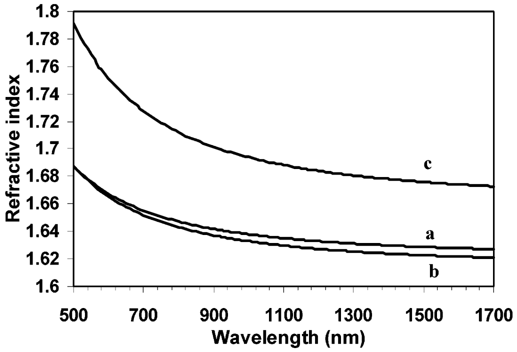


Figure 7. Refractive index dispersion of polymer **3a**: (a) uncured, (b) UV irradiated, and (c) thermally treated sample at 210 °C for 3 h.

It is known that the free volume and polarizability induced by various functional groups in a polymer can affect its refractive index. Usually, a large free volume and small electronic polarizability decreases the refractive index. It was previously shown that polyimides could have different refractive indices at 1300 or 630 nm by changing the ratio of different dianhydrides with diamines.[3,5a,b,d] Han et al.[5c] demonstrated that polyimides having variable refractive indices ($n_{TE} = 1.5176-1.5714$, $\Delta n_{TE} = 0.0519$ and $n_{TM} = 1.5076-1.5590$, $\Delta n_{TE} = 0.0538$) can be obtained by copolymerization of 4,4′-(hexafluoroisopropylidene)diphthalic anhydride with chlorinated and fluorinated diamines. The fluorine atom has relatively low polarizability and larger steric volume than the hydrogen atom, thus being able to lower the refractive index.[3a]

As shown in Figure 5, the refractive indices of our polymers could be controlled by varying the molar ratio of the two monomers and were found to vary between 1.5454 and 1.6313 for the in-plane (TE) polarization ($\Delta n_{TE} = 0.0859$) and from 1.5329 to 1.6283 for the out-of-plane (TM) polarization ($\Delta n_{TM} = 0.0954$). The values of the refractive indices decreased as the amount of the fluorocarbon content in the polymer (mol %, monomer **2**) increased. The n_{TE} and n_{TM} reached maximum values (1.6313 and 1.6283) for polymer **3a** derived solely from monomer **1**. Photo-cross-linking induced only a small decrease in the refractive index, typically about 0.4×10^{-3} to 6.5×10^{-3} for n_{TE} and 0.4×10^{-3} to 6.2×10^{-3} for n_{TM}. In contrast, thermal cross-linking resulted in a slightly larger increase in refractive index of about 0.3×10^{-2} for n_{TE} and 1.8×10^{-2} for n_{TM}.

The optical dispersion property of all the polymers was also determined by ellipsometry (Figure 6) as another important parameter for waveguide devices.[15] The dispersion values were calculated as $dn/d\lambda$ in the wavelength range of interest for the three typical telecommunication wavelengths (810, 1310, and 1550 nm). These values were larger at 840 nm, varying from -4×10^{-5} to -6×10^{-5} nm^{-1}, and smaller at 1310 and 1550 nm, ranging from -1×10^{-5} to -2×10^{-5} nm^{-1}. There was no change in dispersion after photo-cross-linking at all the wavelengths of interest. A large change in dispersion was observed at 840 nm after thermal cross-linking, as the values were almost doubled and reached -12×10^{-5} nm^{-1}. At longer wavelengths the dispersion values increased up to only -2×10^{-5} nm^{-1}. Figure 7 displays the optical dispersion of polymer **3a** before and after thermal treatment and photo-cross-linking.

The difference between n_{TE} and n_{TM} defines the birefringence (Δn) of the polymer films. Optical anisotropy expressed by the birefringence value must be low for most waveguide applications, as large anisotropy may cause problems such as near-coupled noise due to crosstalk in the performance of the device.[16] Some polyimides are known to have large birefringence (e.g., 0.18 for Kapton type polyimide), while small birefringence of 4.8×10^{-3} was reported for a polymer derived from 4,4′-(hexafluoroisopropylidene)diphthalic anhydride and 4,4′-[9-(2,7-dibromofluorenylidene)]dianiline.[17] The birefringence of polymers **3a**−**3e** were found to be directly related to the content of monomer **1** in the polymer ranging from 1.25×10^{-2} to 3×10^{-3}. Polymer **3a** has the lowest birefringence, which can be attributed to the fluorenyl group that is oriented perpendicularly to the polymer main chain. This bulky cardo moiety prevents the polymer chains from close packing and hence hinders the in-plane orientation process. The flexible hexafluoroisopropylidene and ether linkages also contribute to lowering the film birefringence by increasing the chain mobility and decreasing the chain packing.

The 1,4-addition reaction of diacetylene moieties involved in the photo-cross-linking process induces the formation of small conjugated domains of double and triple bonds. The degree of conversion of these moieties is however small as estimated from their peak intensities by spectroscopic means (roughly 15%). For the polymers having a higher molar ratio of monomer **1** these cross-links do not affect tremendously the chain packing density (due to the presence of the bulky fluorenyl moieties) as the observed variation in film thickness was small (typically about 1%). However, the increase of molar ratio of monomer **2** in the polymers allowed for better chain packing, as demonstrated by higher variations in film thickness to as much as 16% for polymer **3e**. This can explain the observed lower birefringence of 3.0×10^{-3} for polymer **3a** and the higher value (1.25×10^{-2}) for polymer **3e**.

In comparison with the photo-cross-linking process, the thermal cross-linking process induced drastic structural changes in polymers and resulted in the formation of small crystalline domains, as proved by X-ray diffraction analysis. Furthermore, the film thickness changed more after cross-linking, from 9.6% for polymer **3a** to 18.9% for polymer **3e**, demonstrating a greater packing density upon thermal treatment. Accordingly, the birefringence in the cross-linked polymers was higher (2.87×10^{-2}). The presence of newly formed hydroxy and carbonyl groups also explains an increase in the refractive index values, as these groups are known to have larger polarizabilities than the ether groups.

To demonstrate the photopatterning capability of our polymers, thin polymer films were spin-coated on silicon wafers and exposed to UV irradiation through a photomask for 40 min. Figure 8 shows a typical scanning electron micrograph (SEM) of a patterned film produced by direct irradiation using a 3500 mW/cm^2 light source. The top view shows that the features are very well-defined (Figure 8a). The cross section of one of the ridges of approximately 12 μm width reveals a rough, wrinkled surface, which was likely the result of the nonoptimized etching or washing process. Optimization of film processing, cross-linking, and etching is required in order to achieve a high-quality ridge waveguide.

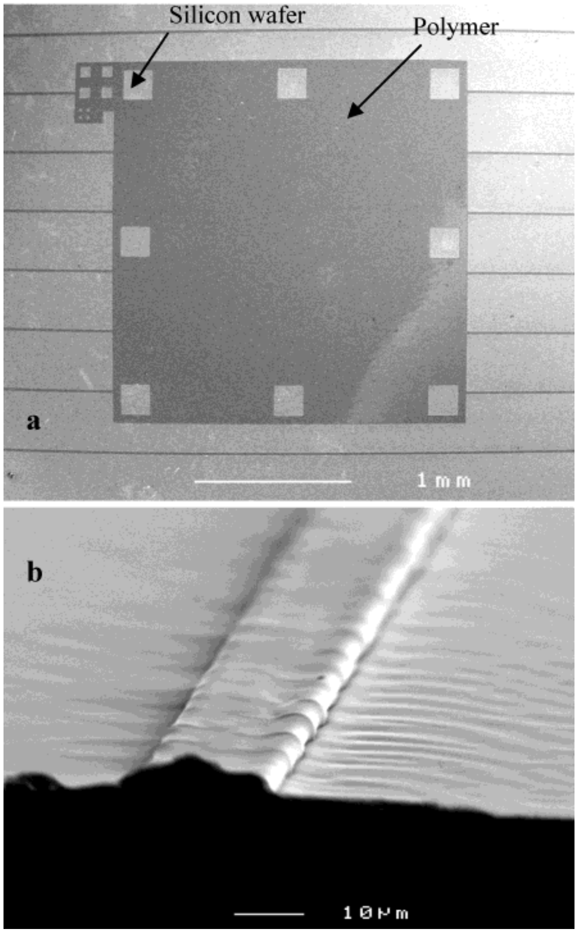


Figure 8. SEM images of photopatterned film of polymer **3a**: (a) top view and (b) cross section.

Conclusions

The refractive indices and birefringence of a series of diacetylene polymers can be adjusted and controlled through copolymerization of two different monomers. The photo-cross-linking is more suitable than thermal cross-linking for making the waveguide devices from these diacetylene polymers.

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References and Notes

(1) (a) Kurokawa, T.; Takato, N.; Katayama, Y. *Appl. Opt.* **1980**, *19*, 3124. (b) Hartman, D. H.; Lalk, G. R.; Howse, J. W.; Krchnavek, R. R. *Appl. Opt.* **1989**, *28*, 40.

(2) (a) Sullivan, C. T. *SPIE Optoelectronic Materials, Devices Packaging and Interconnects II* **1988**, *994*, 92. (b) Reuter, R.; Franke, H.; Feger, C. *Appl. Opt.* **1988**, *27*, 2565. (c) Matsuuda, T.; Hasuda, Y.; Nishi, S.; Yamada, N. *Macromolecules* **1991**, *24*, 5001. (d) Matsuuda, T.; Ishizawa, M.; Hasuda, Y.; Nishi,

S. *Macromolecules* **1992**, *25*, 3540. (e) Matsuuda, T.; Yamada, N.; Nishi, S.; Hasuda, Y. *Macromolecules* **1993**, *26*, 419.

(3) (a) Ree, M.; Kim, K.; Woo, S. H.; Chang, H *J. Appl. Phys.* **1997**, *8*, 698. (b) Harris, F. W.; Cheng, S. Z. D. U.S. Patent 5,344,916 (Sept 6, 1994). (c) Boesse, D.; Lee, H.; Yoon, D. Y.; Swalen, J. D.; Rabolt, J. F. *J. Polym. Sci., Part B: Polym. Phys.* **1992**, *30*, 1321. (d) Takasaki, T.; Kuwana, Y.; Takahashi, T.; Hayashida, S. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4832.

(4) Lee, H. J.; Oh, M. C.; Ahn, J.; H.; Han, S. G. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2355.

(5) (a) Matsuura, T.; Kobayashi, J.; Ando, S.; Maruno, T.; Saski, S.; Yamamoto, F. *Appl. Opt.* **1999**, *38*, 966. (b) Matsuura, T. *J. Photopolym. Sci. Technol.* **1997**, *10*, 31. (c) Han, K.; Lee, H. J.; Rhee, T. H. *J. Appl. Polym. Sci.* **1999**, *74*, 107. (d) Kobayashi, J.; Matsuura, T.; Hida, Y.; Saski, S.; Maruno, T. *J. Lightwave Technol.* **1998**, *16*, 1024. (e) Rooks, M. J.; Rousell, H. V.; Johnson, L. M. *Appl. Opt.* **1990**, *29*, 3880.

(6) Kim, K.-H.; Jang, S.; Harris, F. W. *Macromolecules* **2001**, *34*, 8925.

(7) Rames-Langlade, G.; Monjol, P.; Sekiguchi, H.; Mercier, R.; Sillion, B. *Polymer* **1997**, *38*, 4964.

(8) Feng, K.; Tsushima, M.; Matsumoto, T.; Kurosaki, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 685.

(9) (a) Wegner, G. *Z. Naturforsch.* **1969**, *24B*, 824. (b) Fomin, S.; Neyra, R.; Ogawa, T. *Polym. J.* **1994**, *26*, 845. (c) Rezac, M. E.; Sorensen, E. T.; Beckham, H. W. *J. Membr. Sci.* **1997**, *136*, 249. (d) Miller, T. M.; Kwock, E. W.; Baird, T.; Hale, A. *Chem. Mater.* **1994**, *6*, 1569. (e) Liang, R. C.; Reiser, A. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 451. (f) Beckham, H. W.; Rubner, M. F. *Macromolecules* **1993**, *26*, 5198. (g) Hay, A. S. U.S. Patent 3,594,175 (July 20, 1971). (h) Ogawa, T.; Fomine, S. *Trends Polym. Sci.* **1994**, *2*, 308.

(10) (a) Weir, C. A. M.; Hadizad, T.; Beaudin, A. M. R.; Wang, Z. Y. *Tetrahedron Lett.* **2003**, *44*, 4697. (b) Qi, Y.; Desjardins, P.; Meng, X. S.; Wang, Z. Y. *Opt. Mater.* **2002**, *21*, 255. (c) Qi, Y.; Desjardins, P.; Wang, Z. Y. *J. Opt. A: Pure Appl. Opt.* **2002**, *4*, S273. (d) Qi, Y.; Wang, Z. Y. *Macromolecules* **2003**, *36*, 3146.

(11) Karangu, N. T.; Rezac, M. E.; Beckham, H. W. *Chem. Mater.* **1998**, *10*, 567.

(12) Hay, A. S.; Bolon, D. A.; Leimer, K. R. *J. Polym. Sci., Part A1* **1970**, *8*, 1022.

(13) Wegner, G. *Makromol. Chem.* **1970**, *134*, 219.

(14) (a) Dirlikov, S. K.; Feng, Y. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (1), 363. (b) Picklesimer, L. G. U.S. Patent 4,226,800 (Oct 7, 1980).

(15) Eldada, L. *IEEE J. Sel. Top. Quantum Electron.* **2000**, *6*, 54.

(16) Goesche, U.; Lee, H.; Yoon, D. Y.; Siemens, R. L.; Smith, B. A.; Volksen, W. *Colloid Polym. Sci.* **1994**, *272*, 1321.

(17) Li, B.; Prexta, L. A.; Shen, Z.; Cheng, S. Z. D.; Harris, F. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2000**, *41* (1), 105.

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