

# Photo-crosslinkable polymers as hole-transport materials for organic light-emitting diodes

Ya-Dong Zhang,<sup>a</sup> Richard D. Hreha,<sup>a</sup> Ghassan E. Jabbour,<sup>b</sup> Bernard Kippelen,<sup>b</sup> N. Peyghambarian<sup>b</sup> and Seth R. Marder<sup>\*a,b</sup>

<sup>a</sup>Department of Chemistry, The University of Arizona, Tucson, AZ 85721, USA

<sup>b</sup>Optical Sciences Center, The University of Arizona, Tucson, AZ 85721, USA

Received 5th November 2001, Accepted 11th April 2002

First published as an Advance Article on the web 3rd May 2002

A bis(diarylamino)biphenyl-functionalised methacrylate has been synthesised and polymerised to give a hole-transport polymer; copolymerisation with a chalcone- or cinnamate-functionalised methacrylate affords photo-crosslinkable hole-transport polymers that become insoluble upon exposure to ultra-violet irradiation. Organic light-emitting diodes (OLEDs) were fabricated based on both crosslinked and non-crosslinked hole-transport polymers, and the performances of the devices were evaluated.

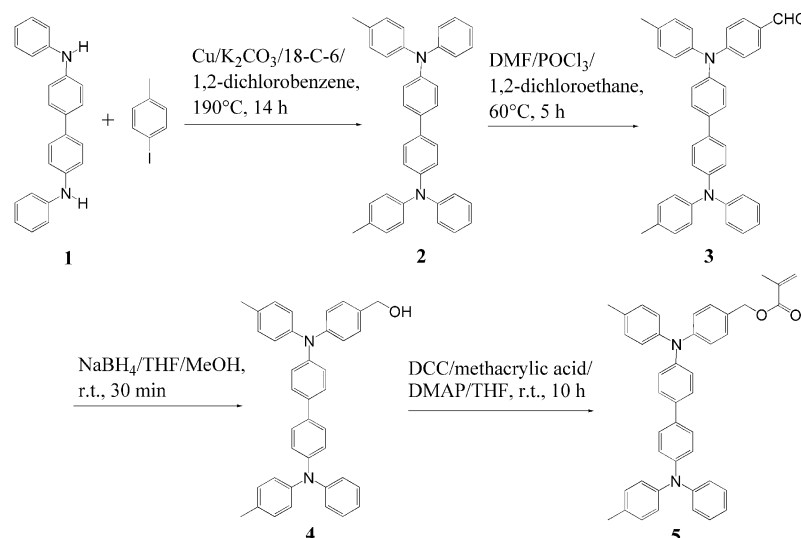
## Introduction

Light-emitting diodes (LEDs) based on organic small molecules<sup>1,2</sup> and polymeric materials<sup>3,4</sup> have recently attracted much attention because of their potential for use in flat panel displays. The most efficient devices to date are multilayer structures composed of hole-transport, emitting, and electron-transport layers sandwiched between two electrodes.<sup>5,6</sup> OLEDs based upon small molecules are generally fabricated by vapor deposition. Polymer-based OLEDs are often fabricated by wet methods such as spin-coating. A requirement for fabricating multilayer devices by such techniques is that application of a subsequent layer does not result in the dissolution of layers that have been applied in previous steps. One approach to circumventing this problem is to decrease the solubility of the layer subsequent to its deposition. The precursor-polymer route which has been used extensively for fabrication of LEDs with the poly(*p*-phenylenevinylene) (PPV) system is an excellent example of such an approach.<sup>7</sup> A soluble PPV precursor is coated onto indium tin oxide (ITO) substrate and thermally converted into an insoluble PPV film. Alternatively, soluble polymers can be converted into insoluble polymers by either

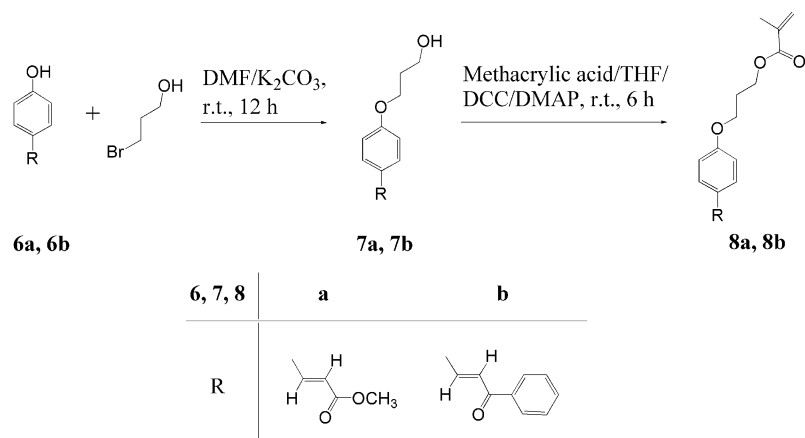
photo-crosslinking or thermal crosslinking reactions.<sup>8</sup> The photo-crosslinking technique is widely used in the casting industry and in photo-resist technology and can allow for the photo patterning of pixels. Recently, photo-crosslinkable side-chain polymers<sup>9,10</sup> and low molecular weight glass compounds<sup>11,12</sup> have been reported for OLEDs. Thermally crosslinkable oligomers and polymers have also been reported.<sup>13</sup> Here we report on the synthesis, characterisation and device performance in two-layer LEDs of a set of photo-crosslinkable side-chain acrylate polymers containing a bis(diarylamino)-biphenyl group as hole-transport agent, and cinnamate<sup>14</sup> and chalcone<sup>15</sup> groups as photo-crosslinking groups.

## Results and discussion

The synthesis and molecular structures of methacrylate monomers with hole-transport moieties and crosslinking moieties are shown in Schemes 1 and 2. The monomers **5**, **8a** and **8b** were synthesised from hydroxy-functionalised compounds by reaction with methacrylic acid, using 1,3-dicyclohexylcarbodiimide (DCC) as a dehydrating agent and 4-dimethylaminopyridine (DMAP) as a catalyst. Pure monomer **5** was obtained by



Scheme 1 Synthesis of bis(diarylamino)biphenyl-functionalised methacrylate monomer, **5**.



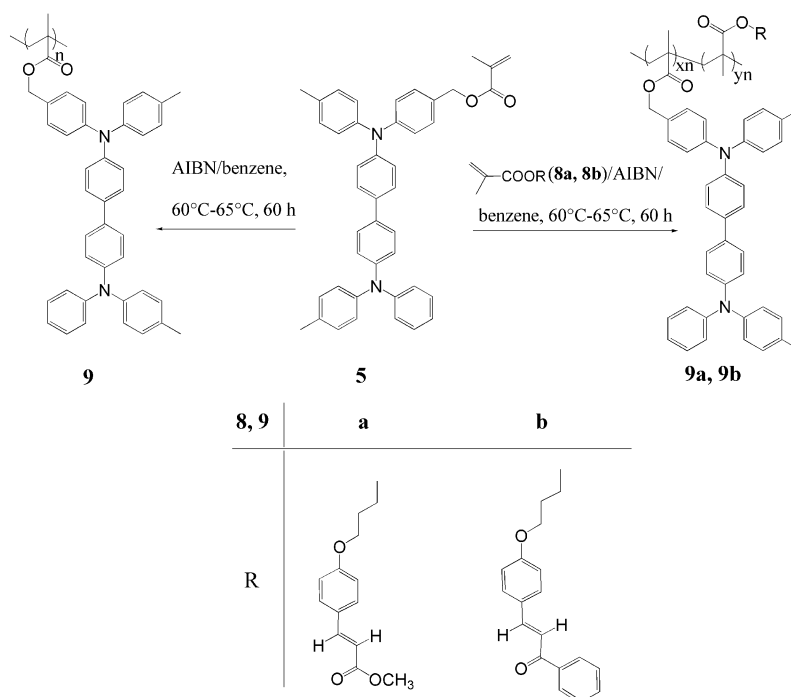
**Scheme 2** Synthesis of monomers **8a** and **8b** with crosslinkable units.

recrystallisation of the crude product from a tetrahydrofuran (THF)–methanol solution (purification on silica gel should be avoided as the compounds decompose on the silica gel support). Compound **4** was obtained by reduction of **3** with sodium borohydride. 4,4'-Bis{*N*-phenyl-*N*-(4-methylphenyl)amino}biphenyl, **2**, was synthesised employing an Ullmann condensation reaction starting from *N,N'*-diphenylbenzidine, **1**, and 4-iodotoluene. A formyl group was introduced into **2** to yield compound **3** via a Vilsmeier reaction employing *N,N*-dimethylformamide (DMF) and phosphorus oxychloride. Alcohols with crosslinkable units, **7a** and **7b**, were synthesised utilising nucleophilic substitution of the corresponding phenols, **6a** and **6b**, on 3-bromopropanol. The monomer **5** was homopolymerised or copolymerised with 30% (mole ratio) of crosslinkable monomers, **8a** and **8b**, using 2,2'-azobis(isobutyronitrile) (AIBN) as an initiator under nitrogen at 60 °C for 60 h (as shown in Scheme 3). All of the polymers were purified by precipitation three times into methanol, once from benzene and twice from THF. The polymers **9** and **9a** were obtained as white powders, and the polymer **9b** was obtained as a pale yellow powder. The structures of the compounds and polymers were confirmed by NMR and elemental analysis (as shown in the Experimental section).

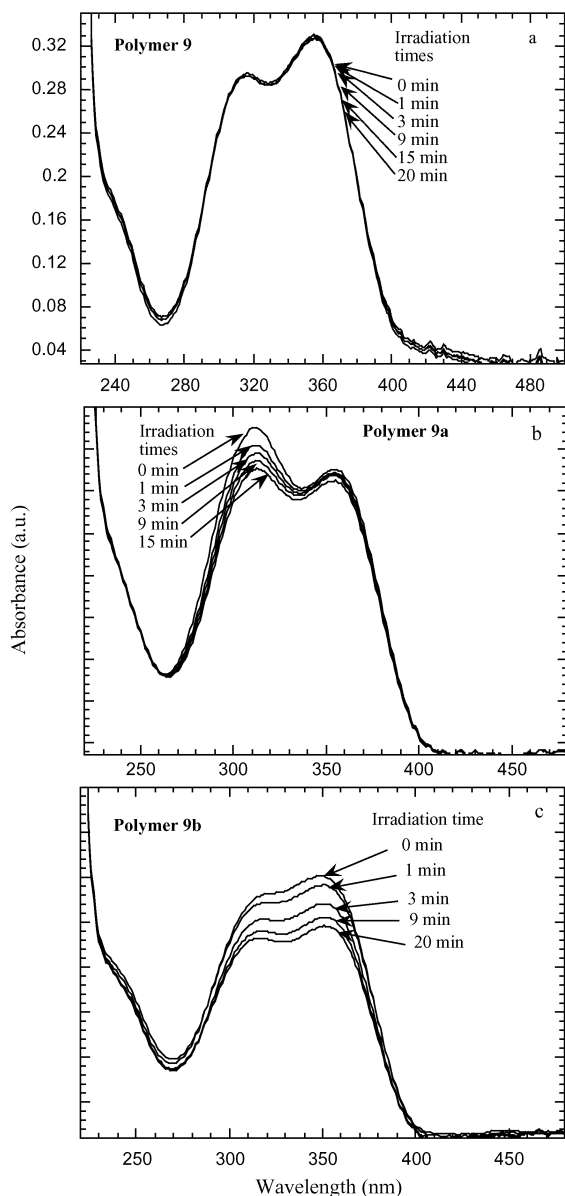
The molecular weights of the polymers were measured by gel permeation chromatography (GPC) with THF as eluant. The weight-average molecular weights ( $M_w$ ) and number-average molecular weights ( $M_n$ ) of these polymers versus linear polystyrene standards are reported in Table 1. All the polymers with high molecular weights show good solubilities in a variety of common organic solvents such as benzene, THF, toluene, chloroform, and dichloromethane. The glass-transition temperatures ( $T_g$ ) of the polymers were determined by differential scanning calorimetry (DSC). Of these polymers, homopolymer **9** exhibits the highest  $T_g$ . It is evident that the incorporation of crosslinking moieties serves to reduce the  $T_g$ . No evidence of other thermal processes such as the melting of a side chain

**Table 1** The glass transition temperatures ( $T_g$ ) and molecular weights, referenced to polystyrene standards, for the polymers **9**, **9a** and **9b**

Polymer	$T_g/^\circ\text{C}$	$M_w$	$M_n$	$M_w/M_n$
<b>9</b>	155	720 000	170 000	4.2
<b>9a</b>	137	810 000	180 000	4.5
<b>9b</b>	133	750 000	180 000	4.2



**Scheme 3** Synthesis of the polymers.



**Fig. 1** UV-vis. spectra of thin films of (a) **9**, (b) **9a**, and (c) **9b** after irradiation with UV light for various time periods.

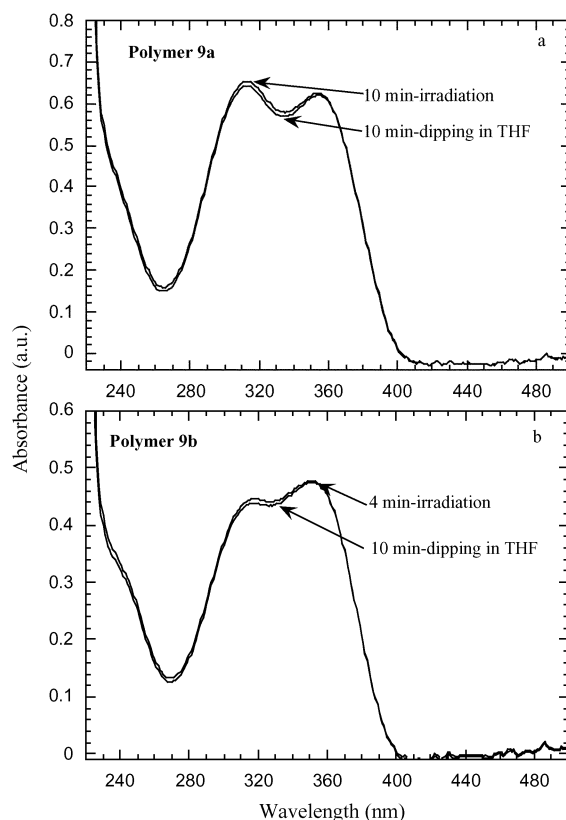
was observed in the temperature range investigated (from 20 to 260 °C) suggesting that the polymers as prepared are amorphous.

Thin films of polymers **9**, **9a** and **9b** on a quartz substrate were obtained by spin-coating at 3000 rpm from THF solution (20.0 mg in 1 cm<sup>3</sup> of THF). The polymer films were irradiated with an unfiltered handle UV source (365 nm, 7 W, UVGL-25) for visualising thin-layer-chromatography plates. The films were kept at a distance of 2 cm from the UV lamp. The crosslinking of the polymers upon UV-irradiation was followed by UV spectroscopy. The decrease of the absorbances at 310 nm (**9a**) and 343 nm (**9b**), attributed to the UV-induced 2 + 2 cycloaddition reactions of cinnamate and chalcone groups respectively, was used to monitor the progress of crosslinking. Because the absorptions of cinnamate and chalcone groups overlap with the absorption of the substituted-diaminobiphenyl moieties, the decrease of the absorbance could be attributed to the contributions of 2 + 2 cycloaddition reactions of crosslinking units and/or photo-decomposition of bis(diaryl-amino)biphenyl moieties. In order to identify the extent of decomposition of bis(diaryl-amino)biphenyl moieties, homopolymer **9**, without crosslinkable units, was synthesised for comparison with **9a** and **9b**. A film of polymer **9** was subjected to the conditions described above. Polymer **9**, which has no

crosslinking units, showed almost no absorbance change at the absorption maxima after UV-irradiation for 25 min (as shown in Fig. 1a), suggesting that the bis(diaryl-amino)biphenyl moiety is relatively photochemically stable under these cross-linking conditions. Thus, we attributed the decrease of the absorption of the polymers **9a** (as shown in Fig. 1b) and **9b** (as shown Fig. 1c) predominantly to the photo-induced 2 + 2 cycloaddition reaction of the crosslinkable groups.

Irradiated polymer **9a** and **9b** films on quartz substrates were used to demonstrate the insolubility of the polymers after UV irradiation. The UV absorption spectra were acquired after dipping the films in THF for different times. Even after soaking the irradiated polymer films for 20 minutes, almost no measurable decrease in absorption (as shown in Fig. 2) was observed, suggesting that the polymers were crosslinked. In contrast, for the uncrosslinked films of the polymers **9a** and **9b** on quartz, it was found that the absorption intensities were dramatically decreased to almost zero after dipping films in THF for 1 minute. These observations demonstrate that the crosslinked copolymers are insoluble in THF. Similarly, crosslinked **9a** and **9b** films on quartz substrates were dipped into other solvents, such as chloroform and dichloromethane, for 1 minute to 3 hours, and also showed almost no absorption changes in UV spectra.

To investigate the EL properties, OLEDs based on uncross-linked polymers (**9**, **9a**, and **9b**) and crosslinked polymers (derived by irradiation of **9a** and **9b**) as the hole-transporting materials and tris(8-hydroxyquinolate)aluminium (Alq<sub>3</sub>) as the electron-transporting and emitting material were fabricated. The films (~50 nm thickness) were prepared from **9**, **9a**, and **9b** by spin-coating chloroform solutions onto ITO with sheet resistance of 30 Ω/□ (Donnelly Corporation). The photo-crosslinked films of **9a** and **9b** were obtained by 10 minute UV-irradiation (365 nm, 7 W) followed by rinsing with chloroform. The Alq<sub>3</sub> films (~60 nm thickness) were then deposited on the top of both the uncrosslinked hole-transporting polymer films



**Fig. 2** UV-vis spectra of irradiated thin films of (a) **9a** and (b) **9b** before and after dipping in THF.

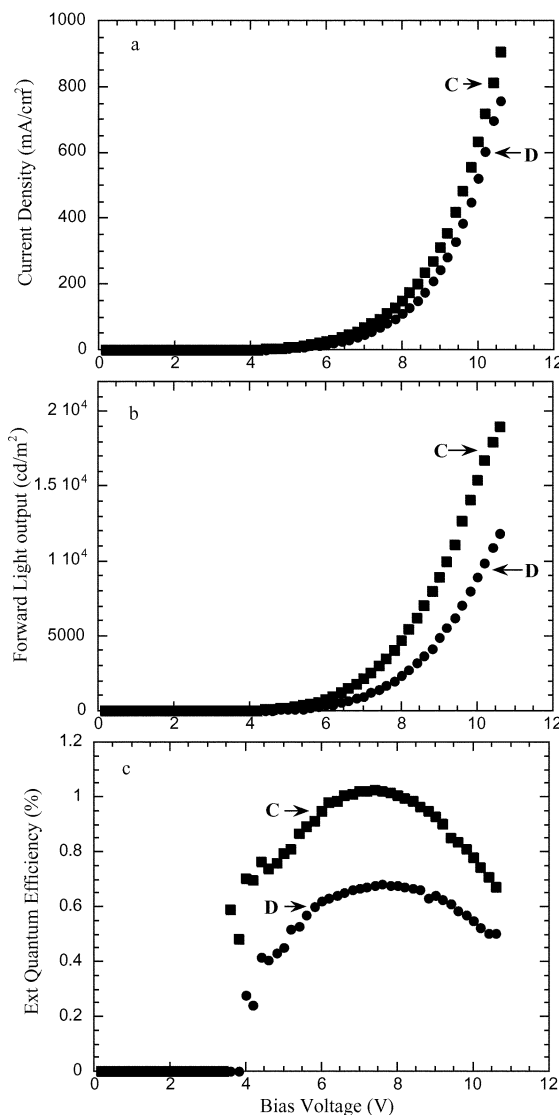
and crosslinked hole-transporting polymer films under a high vacuum (about  $10^{-6}$  Torr). Mg was then deposited as a cathode on the top of  $\text{Alq}_3$  films. Six devices with bilayer structures were constructed according to procedures above with the various hole transporting polymers as shown in Table 2.

The emission of all the devices corresponded to the typical  $\text{Alq}_3$  emission spectrum,<sup>1</sup> resulting in green OLEDs. The current–voltage (I–V), luminescence–voltage (L–V) and the quantum efficiency–voltage characteristics for the devices **C** and **D** are shown in Fig. 3 (similar results have been obtained for **E** and **F**, but the data are not shown). The operating voltages for these devices, defined here as the voltage at which the light is first detected ( $5 \text{ cd m}^{-2}$ ), are roughly 4 V. The brightness and current densities of these bilayer devices increases with the applied voltage. It should be noted that the brightness and the quantum efficiency of the devices, **D** and **F**, fabricated with crosslinked hole-transport films, were lower than the devices, **C** and **E**, fabricated with uncrosslinked polymer hole-transport films. Such a decrease of the performance has also been observed for other crosslinkable polymers.<sup>10</sup> It was found that device **B**, based on UV-irradiated **9** as the hole-transporting layer, also shows lower performance than device **A** based on non-irradiated **9**. However, the degree of the performance decrease from device **A** to device **B** was smaller than the decreases in going from **C** to **D** or from **E** to **F** (Table 2). These results may suggest that the decreases in performance of devices are due to the slight UV-decomposition of the hole-transporting moieties and film morphology changes during photo-crosslinking. It is well known that the performance of OLEDs is very sensitive to the impurities in the materials used and layer morphology changes. Compared with other OLEDs based on photo-crosslinked hole transport films, our devices exhibit much higher brightness and quantum efficiencies.<sup>10,12</sup> Table 2 summarises the device data. Detailed research work on photo-decomposition and morphology changes is in progress. Several approaches can be tried to improve the decrease in the LED performance: using photo-stable hole-transport units, optimizing the ratio of photo-crosslinkable units, using a sensitizer for photocrosslinking at a long wavelength range and using a more active crosslinkable unit to reduce the irradiation time.

In conclusion, hole-transport polymers with cinnamate and chalcone groups as photo-crosslinking moieties have been synthesised and characterised. In this type of polymer, the molar ratio of different crosslinkable moieties can be varied. Insoluble crosslinked films have been obtained by UV-irradiation and demonstrated by UV-vis spectroscopy. The LEDs based on these crosslinked hole-transport layers show reasonable performance under an applied electric field. We are currently working on optimizing both the photo-crosslinkable units and hole-transport units for improving device performances for the photo-crosslinked materials. Epoxy and oxetane groups will be used for minimising the morphology changes. The crosslinkable materials allow us to fabricate and study multilayer devices with spin-coating. In future work, crosslinkable polymers for light emission and electron transport will be synthesised for the fabrication of spin-coated multilayer devices.

**Table 2** Device structures and performance

Device	Hole-transport polymer	Current density at 9.0 V ( $\text{mA cm}^{-2}$ )	Max. ext. quant eff. (% photons/e)	Light output at 10 V ( $\text{cd m}^{-2}$ )
<b>A</b>	<b>9</b>	289	1.0 (at 7.4 V)	12000
<b>B</b>	UV-irradiated <b>9</b>	219	0.8 (at 7.6V)	10000
<b>C</b>	<b>9a</b>	310	1.0 (at 7.4 V)	15000
<b>D</b>	UV-irradiated <b>9a</b>	244	0.7 (at 7.6 V)	8900
<b>E</b>	<b>9b</b>	231	0.6 (at 7.8 V)	6500
<b>F</b>	UV-irradiated <b>9b</b>	157	0.4 (at 8.4 V)	3800



**Fig. 3** Device characteristics for the devices **C** and **D** based on non-irradiated and UV-irradiated **9a** respectively.

## Experimental

Chemicals received from commercial sources were used without further purification. NMR spectra were recorded with a Varian Unity Plus at 500 MHz ( $^1\text{H}$ ) and 126 MHz ( $^{13}\text{C}\{^1\text{H}\}$ ) in  $\text{CDCl}_3$ . UV-vis spectra were recorded on thin films on quartz substrates with a Hewlett Packard 8453 spectrometer. Glass-transition temperatures were determined by thermal analysis using a Shimadzu DSC-50 differential scanning calorimeter at a scan rate of  $10^\circ \text{ min}^{-1}$ . The molecular weights of the polymers and polydispersities were determined *via* GPC analyses using JORDI-Gel DVD 500A gel column, calibrated with polystyrene standards with molecular weight range of  $10^4$ – $10^8$ .

#### 4,4'-Bis{*N*-phenyl-*N*-(4-methylphenyl)amino}biphenyl, 2

To a solution of *N,N'*-diphenylbenzidine **1** (7.0 g, 20.8 mmol) and *p*-iodotoluene (13.0 g, 60.0 mmol) in *o*-dichlorobenzene (100 cm<sup>3</sup>) under nitrogen atmosphere was added copper (14.0 g, 218.8 mmol), K<sub>2</sub>CO<sub>3</sub> (30.0 g, 217.1 mmol) and 18-crown-6 (200 mg) at room temperature, and the resultant mixture was stirred at 190 °C for 14 h. Then, the inorganic solids were removed by filtration. These solids were washed with THF four times. After removal of solvent, the crude product was purified by column chromatography on silica gel using toluene–hexane (7 : 3) as solvent. The pure product was obtained in 86% (9.2 g) yield.

<sup>1</sup>H-NMR δ 7.41 (d, 4 H<sub>arom</sub>, *J* = 8.0 Hz), 7.23 (d, 4 H<sub>arom</sub>, *J* = 8.0 Hz), 7.08 (m, 18 H<sub>arom</sub>), 2.32 (s, 6 H, CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR δ: 147.84, 146.79, 145.07, 134.34, 132.82, 129.94, 129.12, 127.15, 124.98, 123.70, 123.51, 122.31, 20.84 ppm.

#### 4-[*N*-(4-Formylphenyl)-*N*-(4-methylphenyl)amino]-4'-[*N*-phenyl-*N*-(4-methylphenyl)amino]biphenyl, 3

To DMF (1.4 g, 19.4 mmol) was added POCl<sub>3</sub> (3.0 g, 19.6 mmol) at 0 °C under nitrogen. After addition of POCl<sub>3</sub>, 4,4'-bis{*N*-phenyl-*N*-(4-methylphenyl)amino}biphenyl, **2** (10.0 g, 19.4 mmol) in 1,2-dichloroethane (60 cm<sup>3</sup>) was added and the reaction mixture was heated at 60 °C for 5 h. After cooling, the reaction mixture was added to water (180 cm<sup>3</sup>). The product was extracted with ethyl acetate (100 cm<sup>3</sup>), and the organic layer was washed with Na<sub>2</sub>CO<sub>3</sub> solution. After removal of ethyl acetate, the crude product was purified on a silica gel column using toluene–ethyl acetate (9 : 1) as the eluant. 57.8% (6.1 g) of product was obtained.

<sup>1</sup>H NMR δ: 9.80 (s, 1 H, -CHO), 7.66 (d, 2 H<sub>arom</sub>, *J* = 8.5 Hz), 7.49 (d, 2 H<sub>arom</sub>, *J* = 8.5 Hz), 7.42 (d, 2 H<sub>arom</sub>, *J* = 8.5 Hz), 7.11 (m, 19 H<sub>arom</sub>) 2.36 (s, 3 H, -CH<sub>3</sub>), 2.35 (s, 3 H, -CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR δ: 190.35, 153.31, 147.68, 147.29, 144.93, 144.76, 143.35, 137.10, 135.21, 133.55, 133.02, 131.28, 130.41, 129.96, 129.16, 128.74, 127.60, 127.33, 126.54, 126.05, 125.10, 123.89, 123.17, 122.54, 118.93, 20.97, 20.83 ppm. Elemental analysis: Calcd. for C<sub>39</sub>H<sub>32</sub>N<sub>2</sub>O: C, 86.00; H, 5.92; N, 5.14. Found: C, 85.85; H, 5.92; N, 5.25%.

#### 4-[*N*-(4-Hydroxymethylphenyl)-*N*-(4-methylphenyl)amino]-4'-[*N*-phenyl-*N*-(4-methylphenyl)amino]biphenyl, 4

To a solution of 4-[*N*-(4-formylphenyl)-*N*-(4-methylphenyl)amino]-4'-[*N*-phenyl-*N*-(4-methylphenyl)amino]biphenyl, **3** (6.0 g, 11.0 mmol) in THF (40 cm<sup>3</sup>) was added NaBH<sub>4</sub> (2.0 g, 52.9 mmol) in water (5 cm<sup>3</sup>) at room temperature. The reaction was stirred at room temperature for 30 min. Water (250 cm<sup>3</sup>) was added. The product was extracted with ethyl acetate (100 cm<sup>3</sup>), and, after removal of ethyl acetate, the crude product was purified on a silica gel column using toluene–ethyl acetate (7 : 3) as the eluant, and 99.7% (6.0 g) of product was obtained.

<sup>1</sup>H NMR δ: 7.42 (d, 4 H<sub>arom</sub>, *J* = 8.5 Hz), 7.25 (d, 4 H<sub>arom</sub>, *J* = 8.5 Hz), 7.08 (m, 17 H<sub>arom</sub>), 4.63 (s, 2 H, -OCH<sub>2</sub>), 2.36 (s, 1 H, -OH), 2.32 (s, 6 H, -CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR δ: 147.82, 147.48, 146.83, 146.64, 145.06, 144.95, 134.58, 134.52, 134.25, 132.97, 132.85, 129.96, 129.94, 129.12, 128.24, 127.18, 127.15, 124.99, 123.71, 123.61, 123.56, 123.59, 122.34, 66.90, 21.10 ppm. Elemental analysis: Calcd. for C<sub>39</sub>H<sub>34</sub>N<sub>2</sub>O: C, 85.68; H, 6.27; N, 5.12. Found: C, 85.42; H, 6.55; N, 5.03%.

#### 4-[*N*-(4-Methacryloyloxymethylphenyl)-*N*-(4-methylphenyl)amino]-4'-[*N*-phenyl-*N*-(4-methylphenyl)amino]biphenyl, 5

To a solution of 4-[*N*-(4-hydroxymethylphenyl)-*N*-(4-methylphenyl)amino]-4'-[*N*-phenyl-*N*-(4-methylphenyl)amino]biphenyl, **4** (6.0 g, 11.0 mmol), methacrylic acid (1.0 g, 11.6 mmol) in THF (30 cm<sup>3</sup>) and DMAP (0.1 g, 0.8 mmol) was added DCC (2.4 g, 11.7 mmol) at room temperature. The reaction mixture

was stirred at that temperature for 10 h. The reaction mixture was added to methanol (250 cm<sup>3</sup>) and the product was precipitated. The solid product was collected and recrystallised from THF–methanol. After collecting and drying under vacuum, 77.2% (5.2 g) of white product was obtained.

<sup>1</sup>H NMR δ: 7.42 (m, 4 H<sub>arom</sub>), 7.24 (m, 4 H<sub>arom</sub>), 7.09 (m, 17 H<sub>arom</sub>) 6.16 (s, 1 H, -C=C-H), 5.83 (s, 1 H, -C=C-H), 5.12 (s, 2 H, -OCH<sub>2</sub>), 2.33 (s, 6 H, -CH<sub>3</sub>), 1.97 (s, 3 H, -CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR δ: 167.34, 147.85, 147.82, 146.88, 146.51, 145.06, 144.83, 136.29, 134.75, 134.21, 133.19, 132.87, 130.01, 129.93, 129.40, 129.30, 129.13, 127.21, 127.16, 125.72, 125.22, 125.00, 123.89, 123.72, 123.46, 122.93, 122.35, 66.24, 20.84, 18.39 ppm. Melting point 72–74 °C. Elemental analysis: Calcd. for C<sub>43</sub>H<sub>38</sub>N<sub>2</sub>O<sub>2</sub>: C, 84.01; H, 6.23; N, 4.56. Found: C, 84.03; H, 6.17; N, 4.68%.

#### Methyl 4-(3-hydroxypropoxy)cinnamate, 7a

To a solution of 4-hydroxycinnamate **6a** (6.0 g, 33.7 mmol) and 3-bromopropanol (5.0 g, 40.7 mmol) in DMF (30 cm<sup>3</sup>) was added K<sub>2</sub>CO<sub>3</sub> (10.0 g, 72.5 mmol). The reaction was stirred at room temperature for 12 h. Water (200 cm<sup>3</sup>) was added to the reaction mixture. The precipitate was collected by filtration. After recrystallisation from an acetone–water mixture, 90.0% (7.2 g) of **7a** was obtained as white crystals.

<sup>1</sup>H NMR δ: 7.64 (d, 1 H, H-C=C, *J* = 16.0 Hz), 7.48 (d, 2 H<sub>arom</sub>, *J* = 9.0 Hz), 6.91 (d, 2 H<sub>arom</sub>, *J* = 9.0 Hz), 6.32 (d, 1 H, H-C=C, *J* = 16.0 Hz), 4.16 (t, 2 H, OCH<sub>2</sub>, *J* = 7.0 Hz), 3.88 (m, 2 H, OCH<sub>2</sub>), 3.79 (s, 3 H, OCH<sub>3</sub>), 2.06 (m, 2 H, CH<sub>2</sub>), 1.71 (t, 1 H, OH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR δ: 167.78, 160.55, 144.47, 129.65, 126.99, 115.07, 114.68, 65.32, 59.73, 51.53, 31.81 ppm. Elemental analysis: Calcd. for C<sub>12</sub>H<sub>16</sub>O<sub>4</sub> (224.25): C, 64.27; H, 7.19. Found: C, 64.43; H, 7.09%.

#### 4-(3-hydroxypropoxy)chalcone, 7b

**7b** was synthesised by the same method as described for **7a** starting from **6b** (5.0 g, 22.3 mmol) and 3-bromopropanol (3.1 g, 22.3 mmol). The crude product was purified by recrystallisation from acetone/water. The pure product was obtained as a pale yellow solid in 91.9% (5.7 g) yield.

<sup>1</sup>H NMR δ: 8.01 (d, 2 H<sub>arom</sub>, *J* = 8.0 Hz), 7.76 (d, 1 H, C=C-H, *J* = 16.0 Hz), 7.56 (m, 5 H<sub>arom</sub>), 7.42 (d, 1 H, C=C-H, *J* = 16.0 Hz), 6.94 (d, 2 H<sub>arom</sub>, *J* = 8.0 Hz), 4.15 (t, 2 H, OCH<sub>2</sub>, *J* = 6.0 Hz), 3.87 (m, 2 H, OCH<sub>2</sub>), 2.06 (m, 3 H, OH and CH<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR δ: 190.61, 160.90, 144.70, 138.35, 132.56, 130.21, 128.52, 128.34, 127.54, 119.63, 114.81, 65.46, 59.86, 31.83 ppm. Elemental analysis: Calcd. for C<sub>18</sub>H<sub>18</sub>O<sub>3</sub> (282.33): C, 76.57; H, 6.43. Found: C, 76.48; H, 6.57%.

#### Methyl 4-(3-methacryloyloxypropoxy)cinnamate, 8a

Monomer **8a** was prepared by the same method as described for monomer **5** starting from **7a** (5.0 g, 21.0 mmol). The crude product was purified on a silica gel column using hexane/ethyl acetate (8 : 2) as eluant. After removal of solvents, pure white product was obtained in 86.7% (5.2 g) yield by recrystallisation from acetone/water.

<sup>1</sup>H NMR δ: 7.63 (d, 1 H, H-C=C, *J* = 16 Hz), 7.46 (d, 2 H<sub>arom</sub>, *J* = 9 Hz), 6.90 (d, 2 H<sub>arom</sub>, *J* = 9 Hz), 6.33 (d, 1 H, H-C=C, *J* = 16 Hz), 6.11 (s, 1 H, H-C=C), 5.57 (s, 1 H, H-C=C), 4.35 (t, 2 H, OCH<sub>2</sub>, *J* = 6.0 Hz), 4.10 (t, 2 H, OCH<sub>2</sub>, *J* = 6.0 Hz), 3.79 (s, 3 H, OCH<sub>3</sub>), 2.19 (m, 2 H, CH<sub>2</sub>), 1.94 (s, 3 H, CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} δ: 167.65, 167.22, 169.47, 144.38, 136.13, 129.65, 127.10, 125.53, 115.20, 114.68, 64.42, 61.27, 51.50, 28.47, 18.25 ppm. Elemental analysis: Calcd. for C<sub>17</sub>H<sub>20</sub>O<sub>5</sub> (304.34): C, 67.09; H, 6.62. Found: C, 67.00; H, 6.50%.

### 4-(3-Methacryloyloxypropoxy)chalcone, **8b**

Monomer **8b** was prepared by the same method as described for monomer **5** starting from **7b** (5.0 g, 18.7 mmol). The crude product was purified on a silica gel column using toluene–ethyl acetate (9.5 : 0.5) as eluant. After removal of solvents, pure pale yellow product in 95.4% (6.2 g) was obtained by recrystallisation from acetone–water.

$^1\text{H NMR}$   $\delta$ : 8.00 (d, 2  $\text{H}_{\text{arom}}$ ,  $J = 8.5$  Hz), 7.77 (d, 1 H, C=C-H,  $J = 15.5$  Hz), 6.90–7.54 (m, 5  $\text{H}_{\text{arom}}$ ), 7.41 (d, 1 H, H-C=C,  $J = 15.5$  Hz), 6.94 (d, 1  $\text{H}_{\text{arom}}$ ,  $J = 8.5$  Hz), 6.11 (s, 1 H, H-C=C), 5.58 (s, 1 H, H-C=C), 4.36 (t, 2 H,  $\text{OCH}_2$ ,  $J = 6.0$  Hz), 4.11 (t, 2 H,  $\text{OCH}_2$ ,  $J = 6.5$  Hz), 2.19 (m, 2 H,  $\text{CH}_2$ ), 1.94 (s, 3 H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$ : 190.48, 167.27, 160.80, 144.58, 138.39, 136.16, 132.53, 130.19, 128.52, 128.36, 127.63, 125.59, 119.71, 114.81, 112.69, 64.50, 61.30, 28.49, 18.29 ppm. Melting point 69–70 °C Elemental analysis: Calcd. for  $\text{C}_{22}\text{H}_{22}\text{O}_4$  (350.41): C, 75.41; H, 6.33. Found: C, 75.23; H, 6.27%.

### Polymer **9**

Monomer **5** (1.00 g, 1.63 mmol) and AIBN (2.70 mg, 0.016 mmol) were dissolved in dry benzene (4  $\text{cm}^3$ ) under nitrogen. The polymerisation mixture was deoxygenated and was then placed in an oil bath at 60 °C for 60 h. The polymer **9** was precipitated into methanol three times. After drying under vacuum, white **9** was obtained in 96.0% (0.96 g) yield.

$^1\text{H NMR}$   $\delta$ : 7.17 (s, br, 4  $\text{H}_{\text{arom}}$ ), 7.08 (s, br, 4  $\text{H}_{\text{arom}}$ ), 6.90 (m, br, 17  $\text{H}_{\text{arom}}$ ), 4.77 (s, br, 2 H,  $-\text{OCH}_2$ ), 2.20 (s, br, 6 H, 2  $\times$   $\text{CH}_3$ ), 2.11 (s, br, 3 H,  $-\text{CH}_3$ ), 0.77 (m, br, 2 H,  $-\text{CH}_2$ ) ppm. Elemental analysis: Calcd. for  $\text{C}_{43}\text{H}_{38}\text{N}_2\text{O}_2$ : C, 84.01; H, 6.23; N, 4.56. Found: C, 84.09; H, 6.53; N, 4.70%.

### Polymer **9a**

**9a** was prepared in analogy to **9** in 91.7% yield starting from monomer **5** (0.90 g, 1.47 mmol), cinnamate monomer (0.19 g, 0.63 mmol) and AIBN (2.70 mg, 0.016 mmol).

$^1\text{H NMR}$   $\delta$ : 7.50 (d, br, H-C=C), 7.25 (s, br,  $\text{H}_{\text{arom}}$ ), 7.12 (s, br,  $\text{H}_{\text{arom}}$ ), 6.90 (m, br,  $\text{H}_{\text{arom}}$ ), 6.18 (d, br, H-C=C), 4.79 (s, br,  $-\text{OCH}_2$ ), 4.01 (s, br,  $-\text{OCH}_2$ ), 3.86 (s, br,  $-\text{OCH}_2$ ), 3.64 (s, br,  $-\text{OCH}_3$ ), 2.24 (s, br,  $-\text{CH}_3$ ), 2.16 (s, br,  $-\text{CH}_3$ ), 1.97 (s, br,  $-\text{CH}_2$ ), 0.81 (m, br,  $-\text{CH}_2$ ) ppm. Elemental analysis: Calcd. for  $(\text{C}_{43}\text{H}_{38}\text{N}_2\text{O}_2)_{0.7}(\text{C}_{17}\text{H}_{20}\text{O}_5)_{0.3}$  (521.64): C, 81.05; H, 6.30; N, 3.76. Found: C, 80.72; H, 5.83; N, 3.99%.

### Polymer **9b**

**9b** was prepared in analogy to **9** in 91.2% yield starting from monomer **5** (0.90 g, 1.47 mmol), chalcone monomer (0.22 g, 0.63 mmol) and AIBN (2.70 mg, 0.016 mmol).  $^1\text{H NMR}$   $\delta$ : 7.82 (s, br,  $\text{H}_{\text{arom}}$ ), 7.63 (d, br, H-C=C), 7.15 (m, br,  $\text{H}_{\text{arom}}$ , H-C=C), 4.79 (s, br,  $-\text{OCH}_2$ ), 4.05 (s, br,  $-\text{OCH}_2$ ), 3.87 (s, br,  $-\text{OCH}_2$ ), 2.25 (s, br,  $-\text{CH}_3$ ), 2.12 (s, br,  $-\text{CH}_3$ ), 1.93 (m, br,  $-\text{CH}_2$ ), 0.80 (m, br,  $-\text{CH}_2$ ) ppm. Elemental analysis: Calcd. for  $(\text{C}_{43}\text{H}_{38}\text{N}_2\text{O}_2)_{0.7}(\text{C}_{22}\text{H}_{22}\text{O}_4)_{0.3}$  (535.46): C, 82.32; H, 6.25; N, 3.66. Found: C, 81.57; H, 6.41; N, 3.81%.

This work was supported by the US Office of Naval Research through the MURI Center for Advanced Multifunctional Nonlinear Optical Polymers and Molecular Assemblies (CAMP), by the Ballistic Missiles Defense Organisation through AASERT grant # F49620-96-1-0295, and by the NSF through a CAREER grant (B.K.).

### References

- 1 C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913.
- 2 C. Adachi, K. Nagai and N. Tamoto, *Appl. Phys. Lett.*, 1995, **66**, 2679.
- 3 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burna and A. B. Holmes, *Nature*, 1990, **347**, 539.
- 4 D. Braun and A. J. Heeger, *Appl. Phys. Lett.*, 1991, **58**, 1982.
- 5 V. Bulovic, G. Gu, P. E. Burrows, S. R. Forrest and M. E. Thompson, *Nature*, 1996, **381**, 29.
- 6 R. C. Kwong, S. Sibley, T. Dubovoy, M. Baldo, S. R. Forrest and M. E. Thompson, *Chem. Mater.*, 1999, **11**, 3709.
- 7 E. Buchwald, M. Meier, S. Karg, P. Posch, H. W. Schmidt, P. Stroehriegel, W. Riess and M. Schwoerer, *Adv. Mater.*, 1995, **7**, 839.
- 8 H. R. Allcock, *Chem. Mater.*, 1994, **6**, 1476.
- 9 X. C. Li, T. M. Yong, J. Gruner, A. B. Holmes, S. C. Moratti, F. Cacialli and R. H. Friend, *Synth. Met.*, 1997, **84**, 437.
- 10 E. Bellmann, S. E. Shaheen, S. Thayumanavan, S. Barlow, R. H. Grubbs, S. R. Marder, B. Kippelen and N. Peyghambarian, *Chem. Mater.*, 1998, **10**, 1668.
- 11 M. S. Bayerl, T. Braig, O. Nuyken, D. C. Muller, M. Groß and K. Meerholz, *Macromol. Rapid Commun.*, 1999, **20**, 224.
- 12 A. Bacher, C. H. Erdelen, W. Paulus, H. Ringsdorf, H. W. Schmidt and P. Schuhmacher, *Macromolecules*, 1999, **32**, 4551.
- 13 G. Klarner, J.-I. Lee, V. Y. Lee, E. Chan, J.-P. Chen, A. Nelson, D. Markiewicz, R. Siemens, J. C. Scott and R. D. Miller, *Chem. Mater.*, 1999, **11**, 1800.
- 14 L. M. Minsk, J. G. Smith, W. P. Van Deusen and J. F. Wright, *J. Appl. Polym. Sci.*, 1959, **11**, 302.
- 15 C. C. Unruh, *J. Appl. Polym. Sci.*, 1959, **6**, 358.