Macromolecules **1996,** *29,* 1569−1573

Synthesis and Characterization of Polymers Containing in the Chain Backbone Carbazoles Substituted with Two Acceptor Groups as Nonlinear Optical Chromophores

Yadong Zhang, Liming Wang, Tatsuo Wada,* and Hiroyuki Sasabe

Laboratory for Nano-Photonics Materials, Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), Hirosawa 2-1, Wako, Saitama, 351-01 Japan

Received May 2, 1995; Revised Manuscript Received November 29, 1995⊗

ABSTRACT: Polymers containing in the chain backbone carbazoles substituted with two acceptor groups as nonlinear optical chromophores have been synthesized from 3,6-diformyl-9-heptylcarbazole and bis-(cyanoacetate) by the Knoevenagel polycondensation. A one-stage polycondensation was carried out in tetrahydrofuran (THF) solution to yield a carbazole main-chain polymer with low molecular weight in low yield. A two-stage polycondensation first carried out in THF and followed by a solid-state polycondensation yielded a carbazole main-chain polymer with high molecular weight in high yield. Thin films of polymers with good optical quality could be obtained from their chloroform solutions by spin-coating. After electric poling, the films exhibited reasonable second-order nonlinear optical responses and the large off-diagonal tensor components.

Introduction

Second-order nonlinear optical (NLO) polymeric materials have interested many researchers in recent years due to their potential applications in electrooptic devices.[1,2] To date, three types of organic polymeric materials have been developed for this application purpose: guest−host polymers,[3] side-chain polymers,[4−6] and main-chain polymers.[7−10] Second-order NLO effects of such polymeric materials have been demonstrated after the alignment of chromophores by electric poling above the polymeric glass transition temperature. In particular, main-chain NLO polymeric materials have been of interest since NLO chromophores with flexible arrangements (as shown in Figure 1), such as head-to-tail, head-to-head, tail-to-tail, accordion, and random, can be covalently attached to the polymeric main-chain backbone resulting in large second-order optical nonlinearities. Most of the main-chain polymers reported are head-to-tail so that all the chromophore dipole moments point in the same direction along the polymeric main chain.[7,10] New main-chain polymers in which the chromophores are arranged as head-to-tail and accordion have been reported by Lindsay and coworkers.[11,12] Recently, Wright and his co-workers[13−15] have developed some new types of main-chain polymers containing NLO chromophores which were prepared by the Knoevenagel polycondensation technique. In order to stabilize second-order NLO properties, Dalton and his co-workers[16] have synthesized cross-linkable random main-chain polymers.

In our laboratory, we selected carbazole derivatives as basic building blocks for molecular design and synthesis for second-order NLO materials, especially for photorefractive materials which are multifunctional materials and have both second-order nonlinear optical and photoconductive properties.[17−19] Carbazole compounds with multifunctional properties, such as second-order NLO and photoconductive properties,[20,21] have already played an important role in photorefractive materials. Our work on NLO properties of carbazole model compounds show that the 3,6-di-acceptor-substituted carbazole chromophores have some unique second-order NLO properties,[21,22] such as a large off-diagonal tensor component. Recently, we have developed a series of new head-to-tail polymers[22] with mono-acceptor-substituted carbazole chromophores along the polymeric main chain for nonlinear optics. However, we found that it was difficult to obtain good alignment of chromophores from this type of head-to-tail polymer by electric poling. Previously, we presented the synthesis of mono-acceptor-substituted carbazole main-chain polymers with a hydrogen bonding network for stabilizing the dipole alignment after electric poling. Thin films of these polymers show good second-order NLO response.[23,24]

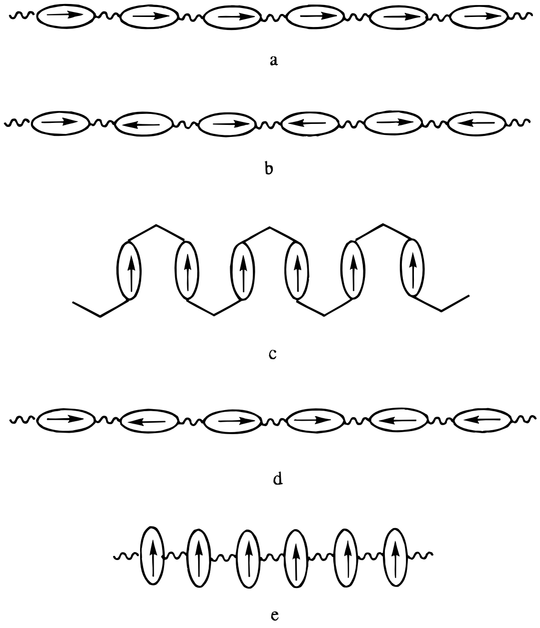


Figure 1. Chromophore arrangements in main-chain polymers: (a) head-to-tail; (b) head-to-head and tail-to-tail; (c) accordion; (d) random; (e) shoulder-to-shoulder.

In this paper, we would like to present the synthesis and characterization of new main-chain polymers with di-acceptor-substituted carbazole as NLO chromophores for the enhancement of the off-diagonal tensor components. In these polymers, the NLO chromophores lie

---

⊗ Abstract published in *Advance ACS Abstracts,* February 1, 1996.

0024-9297/96/2229-1569$12.00/0

parallel to each other, “shoulder-to-shoulder” (as shown in Figure 1e). This should-to-shoulder arrangement of NLO chromophores provided a new approach to the design of main-chain polymers with the large off-diagonal tensor components. In shoulder-to-shoulder arrangement the dipole alignment should be easier to achieve by applying an electric field than in structures where their dipole moments are pointing along the polymer main chain.

Experimental Section

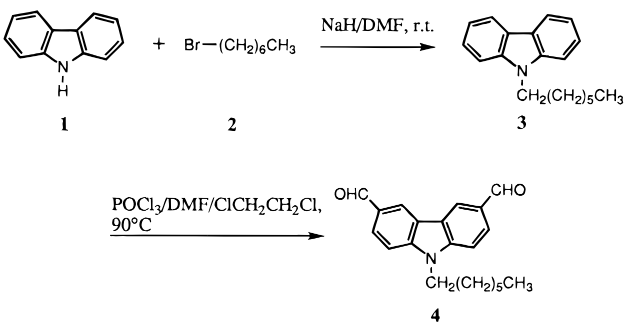
Materials. The carbazole was obtained from Tokyo Kasei Organic Chemicals. *N,N*-dimethylformamide (DMF) and 1,2-dichloroethane and THF from Kanto Chemical Co., Inc. were dried over molecular sieves. The comonomer, bis(cyanoacetate) **(5)**, was synthesized according to the method reported by Wright.[14] All other solvents and chemical reagents were used as received without further purification.

9-Heptylcarbazole, 3. To a solution of carbazole **(1)** (100 g, 0.60 mol) in DMF (300 mL) under stirring was gradually added NaH (60% in oil, 28 g, 0.70 mol) during 1.5 h. The reaction temperature was kept below 30 °C. After hydrogen evolution closed, 1-heptyl bromide **(2)** (110 g, 0.61 mol) was added dropwise at room temperature. After 2 h, the reaction mixture was added to water (1000 mL), and the solution was extracted with ether. The ether was removed, the crude product was purified on a silica column using hexane/ethyl acetate (9.5:0.5) as eluent. White product **3** (149 g) was obtained after removal of solvent in 94% yield. ^{1}H-NMR ($CDCl_3$/TMS): δ 8.09 (d, 2 H, carbazole protons), 7.35−7.47 (m, 4 H, carbazole protons), 7.18−7.24 (m, 2H, carbazole protons), 4.25 (t, 2 H, $-NCH_2-$), 1.84 (m, 2H, $-NCH_2CH_2-$), 1.29 (m, 8 H, $-NCH_2CH_2(CH_2)_4CH_3$), 0.84 (3 H, t, $-CH_3$) ppm.

3,6-Diformyl-9-heptylcarbazole, 4. To DMF (27.7 g, 0.38 mol) at 0 °C, phosphorus oxychloride (58 g, 0.38 mol) was added dropwise. The solution was allowed to warm to room temperature, and 9-heptylcarbazole **(3)** (10 g, 0.038 mol) in 1,2-dichloroethane (50 mL) was added. The reaction mixture was heated to 90 °C and kept at this temperature for 24 h. It was poured into water and extracted with chloroform. The chloroform extract was washed with water, and the solvent was removed to yield a deeply colored product which was purified on a silica gel column using hexane/ethyl acetate (7:3) as eluent, yielding 3 g (25%) of 3,6-diformyl-9-heptylcarbazole **(4)** with mp 128 °C. ^{1}H-NMR ($CDCl_3$/TMS): δ 10.13 (s, 2 H, CHO), 8.66 (s, 2 H, carbazole protons), 8.09 (d, $J = 8.6$ Hz, 2 H, carbazole protons), 7.55 (d, $J = 8.6$ Hz, 2 H, carbazole protons), 4.38 (t, 2 H, $-NCH_2-$), 1.92 (m, 2 H, $-NCH_2CH_2-$), 1.27 (m, 8 H, $-NCH_2CH_2(CH_2)_4CH_3$), 0.86 (t, 3 H, $-CH_3$) ppm. IR (KBr): 3022, 2955, 2858, 2725, 1687, 1628, 1593, 1570, 1489, 1385, 1348, 1288, 1234, 1207, 1143 cm^{-1}. Anal. Calcd for $C_{21}H_{23}NO_2$: C, 78.50; H, 7.17; N, 4.36. Found: C, 78.27; H, 7.32; N, 4.23.

Polycondensation in One Stage. Carbazole Main-Chain Polymer 6a. To 3,6-diformyl-9-heptylcarbazole **(4)** (0.500 g, 1.56 mmol) and bis(cyanoacetate) $NCCH_2COO(CH_2)_6OOCCH_2CN$ **(5)** (0.393 g, 1.56 mmol) in THF (10 mL) was added 4-(dimethylamino)pyridine (0.57 g, 4.68 mmol), and the mixture was left at 40 °C for 12 h. The reaction was stopped, and the resulting polymer solution was cooled and poured into a mixture of hexane and ethyl acetate (6:4) to precipitate the polymer. The precipitated polymer was filtered, redissolved and reprecipitated, and dried under reduced pressure to yield a yellow polymer **6a**. ^{1}H-NMR ($CDCl_3$/TMS): δ 8.56 (br s, 2 H, carbazole protons), 8.35 (br s, 2 H, vinyl protons), 8.31 (br d, $J = 8.9$ Hz, 2 H, carbazole protons), 7.46 (br d, $J = 8.9$ Hz, 2 H, protons), 4.37 (br m, 6 H, $-NCH_2-$ and $-OCH_2-$), 1.85 (br m, 6 H, $-NCH_2CH_2-$ and $-OCH_2CH_2-$), 1.57 (br s, 4 H, $-OCH_2CH_2CH_2-$), 1.28 (br m, 8 H, $-NCH_2CH_2(CH_2)_4CH_3$), 0.85 (br t, 3 H, $-CH_3$) ppm. IR (KBr): 3020, 2930, 2220, 1720, 1581, 1479, 1390, 1257, 1236, 1199, 1161, 1093 cm^{-1}. Anal. Calcd for $C_{33}H_{35}N_3O_4$: C, 73.72; H, 6.56; N, 7.82. Found: C, 73.21; H, 6.62; N, 7.64.

Scheme 1



Polycondensation. Carbazole Main-Chain Polymer 6b. To a solution of 3,6-diformyl-9-heptylcarbazole **(4)** (1 g, 3.12 mmol) and bis(cyanoacetate) **(5)** (0.786, 3.12 mmol) in THF (50 mL) was added DMAP (1.14 g, 9.36 mmol). After stirring at 40 °C for 1 h, the solvent THF was removed by nitrogen purge. Polycondensation was carried out at 40 °C for 4 h under nitrogen. The yellow viscous solid was cooled to room temperature and dissolved in chloroform. The polymer product was purified by reprecipitation into a mixture solution of hexane and ethyl acetate (6:4) to give yellow polymer **6b**. ^{1}H-NMR ($CDCl_3$/TMS): δ 8.55 (br s, 2 H, carbazole protons), 8.34 (br s, 2 H, vinyl protons), 8.28 (br d, $J = 8.9$ Hz, 2 H, carbazole protons), 7.43 (br d, $J = 8.9$ Hz, 2 H, carbazole protons), 4.35 (br m, 6 H, $-NCH_2-$ and $-OCH_2-$), 1.85 (br m, 6 H, $-NCH_2CH_2-$ and $-OCH_2CH_2-$), 1.58 (br s, 4 H, $-OCH_2CH_2CH_2-$), 1.28 (br m, 8 H, $N-CH_2CH_2(CH_2)_4CH_3$), 0.84 (br t, 3 H, $-CH_3$). IR (KBr): 3020, 2984, 2219, 1719, 1581, 1479, 1390, 1255, 1234, 1191, 1161, 1091 cm^{-1}. Anal. Calcd for $C_{33}H_{35}N_3O_4$: C, 73.72; H, 6.56; N, 7.82. Found: C, 72.97; H, 6.55; N, 7.68.

Characterization. Nuclear magnetic resonance (NMR) spectra were recorded by a JEOL JNM-EX270 FINMR SYSTEM spectrometer operating at 270 MHz. Infrared (IR) spectra were measured on a Shimadzu FTIR-4100 infrared spectrophotometer. Ultraviolet (UV) spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Elemental analyses were performed at the Microanalytical Laboratory of RIKEN. The number and weight average molecular weights of main-chain polymers were estimated by gel permeation chromatography (GPC) (columns Waters Ultrastyragel 500, 10^4, and 10^5 Å; detector JASCO 857-UV detector; eluent chloroform). Melting points were determined by a Perkin-Elmer DSC-7 with a heating rate of 1 °C/min. Glass transition temperatures (T_g) were also obtained on a Perkin-Elmer DSC-7 with a heating rate of 10 °C/min.

To prepare films for second harmonic measurements, a polymer solution in chromoform was filtered through a 0.45 μm filter and then spin-coating onto indium−tin oxide (ITO) coated glass slides. The films were dried in an oven at room temperature under a vacuum for 24 h.

Results and Discussion

Synthesis of Monomers and Polymers. The syntheses of all monomers and polymers were performed as described in the reaction schemes. 3,6-Diformyl-9-heptylcarbazole **(4)** was prepared in two steps starting from carbazole **(1)** by nucleophilic substitution and formylation (Scheme 1). The bis(cyanoacetate) comonomer $NCCH_2COO-(CH_2)_6-OOCH_2CN$ **(5)** was prepared in high yield[15] from diols and ethyl cyanoacetate in the presence of tetra-*n*-butyl orthotitanate. Knoevenagel polycondensation of 3,6-diformyl-9-heptylcarbazole **(4)** and bis(cyanoacetate) **(5)** afforded a novel type of polymer **6** which contains 3,6-di-acceptor-substituted carbazole as a NLO chromophore. It was found that the molecular weights and yields of these carbazole main-chain polymers were very dependent on the condition of polycondensation. A one-stage polycondensation

Scheme 2

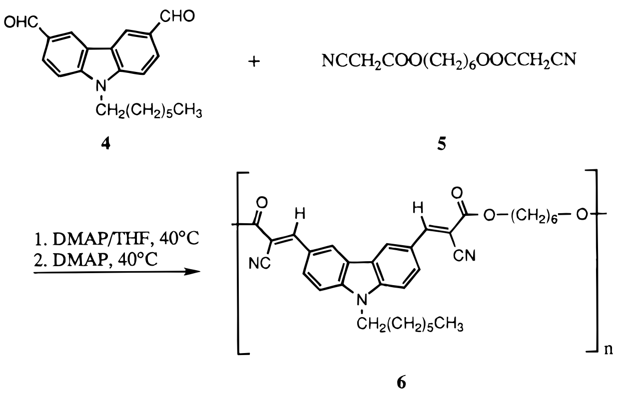


Table 1. Synthesis of Polymers 6 from 3,6-Diformyl-9-heptylcarbazole (4) and Bis(cyanoacetate) (5)

	reacn time (h)			solubility[b]	
polymer	in THF	in solid state	yield[a] (%)	$CHCl_3$	THF
6a	24	0	33	+	+
6b	1	4	92	+	+

[a] Isolated yield. [b] (+) soluble at room temperature.

Table 2. Molecular Weight and Glass Transition Temperature of Polymer 6

polymer	M_w[a]	M_n[a]	polydispersity	T_g (°C)
6a[b]	14 000	8 900	1.6	82.7
6b[c]	83 000	16 000	5.1	87.3

[a] Determined by GPC relative to polystyrene standards. [b] Obtained by one-stage Knoevenagel polycondensation. [c] Obtained by two-stage Knoevenagel polycondensation.

carried out in THF solution yielded a carbazole main-chain polymer with low molecular weight in low yield. However, a polycondensation first carried out in THF solution and followed by solid-state polycondensation yielded a carbazole main-chain polymer with higher molecular weight in higher yield. It was found that the rate of solid-state polycondensation was much more rapid than polycondensation in solution. The polycondensation conditions are shown in Table 1. The mechanism of the two-stage polycondensation is now under further study.

^{1}H-NMR, IR, and elemental analysis data shown in the Experimental Section are in accordance with the chemical structures of the samples. Polymers **6** with an absorption maximum at about 421 nm in chloroform solution are soluble in common organic solvents, such as chloroform and THF. Thin films of carbazole main-chain polymers **6** with excellent optical quality could be obtained by spin-coating from chloroform solution. It could be found that films of the polymers **6** are the most transparent at the second harmonic wavelength (532 nm).

Gel Permeation Chromatography. The molecular weights of polymers **6** were estimated in chloroform by gel permeation chromatography (GPC) using polystyrene as a standard to give the weight and number average molecular weights shown in Table 2. The carbazole main-chain polymer **6a** obtained by a one-stage Knoevenagel polycondensation had a low molecular weight and a narrower distribution compared with polymer **6b** prepared by a two-stage Knoevenagel polycondensation. GPC of products of the one-stage polycondensation were characterized by a single peak in the low molecular weight region. These products were shown to be macrocyclic compounds.[25] The Knoevenagel reaction yielding macrocycles in high yield is now under investigation.

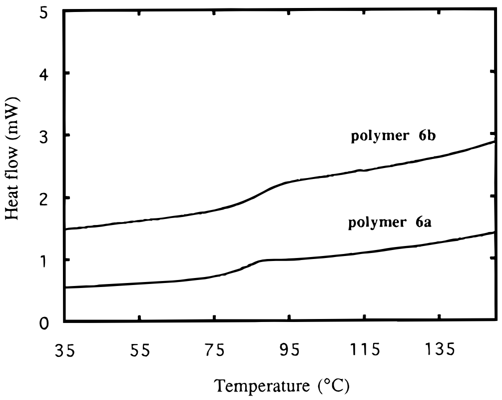


Figure 2. DSC traces of carbazole main-chain polymers **6**.

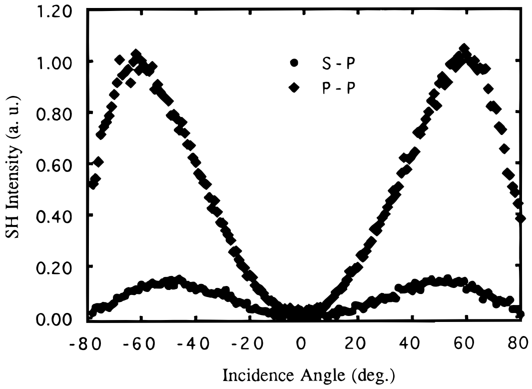


Figure 3. SH intensity versus incidence angle for a poled polymer **6a** film with 0.14 μm thickness.

Thermal Properties. Differential scanning calorimetric (DSC) analysis showed no crystalline transitions for polymers **6** (Figure 2). The glass transition temperatures (T_g) were dependent on the molecular weights of polymers **6**. The results are summarized in Table 2. The T_g of polymer **6b** with a higher molecular weight obtained by the two-stage polycondensation is a little higher than that of polymer **6a**.

Second-Order Nonlinear Optical Properties. The carbazole main-chain polymer **6a** was primarily selected for nonlinear optical study. The refractive indices of polymer **6a** at the fundamental (1064 nm) and second harmonic wavelength (532 nm) were determined with the m-line technique.[26] The refractive indices are 1.6450 and 1.7501 at the wavelengths 1064 and 532 nm, respectively. The orientation of chromophores in the polymeric thin films which could be monitored by second harmonic generation (SHG) were achieved by the corona poling technique at about 100 °C; the electric field applied was about 7.5 kV/cm. The SHG measurements were performed using a polarized Q-switched Nd-YAG laser beam ($l = 1064$ nm). A Y-cut quartz crystal plate ($d_{11} = 0.5$ pm/V) was used as a reference. The second harmonic (SH) intensity of a 0.14 μm film of polymer **6a** was measured using the standard Maker fringe technique.[27] Figure 3 shows the relation between the SH intensity and the incident angle. The SH intensity of polymer **6a** was measured at room temperature at incident angles between −80 and +80°. The second harmonic coefficients (d_{33} and d_{31}) of polymer **6a** were calculated from the angular dependence of the SH intensity using the formulas of Hayden for uniaxial

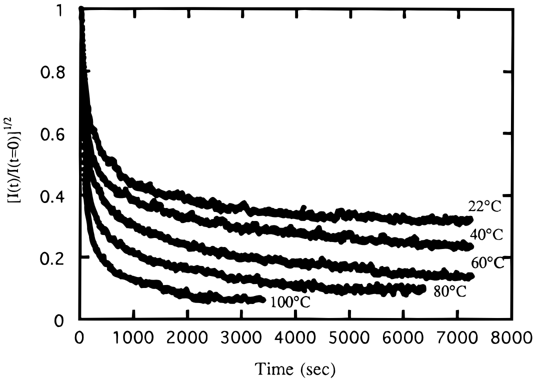


Figure 4. Relaxation behavior of the SHG signal for carbazole main-chain polymer **6a**.

materials.[28] The SH intensity at an incident angle of −60 or +60° was chosen, because these angles gave the maximum value of SH intensity. Values of 10.6 and 7.7 pm/V were obtained for d_{33} and d_{31}, respectively. It should be pointed out that the second-order susceptibilities obtained from this carbazole main-chain polymer are nonresonance values because of the no absorption at the second harmonic wavelength (532 nm). In the case of carbazole substituted with two acceptor groups, one of the interesting features is that the vector direction of the net dipole moment is not parallel to that of the chromophore charge-transfer (CT) axis. As a consequence, the CT contribution to the nonlinear polarizabilities of this chromophore has an intrinsic two-dimensional character. Therefore, this disubstituted carbazole chromophore can be expected to show a different behavior under the electric field-induced alignment of the net dipole moments.[29] Generally, in poled polymers containing one-dimensional CT chromophores, such as *p*-nitroaniline, the diagonal tensor component d_{33} is 3 times larger than the other component, such as d_{31}.[30] Our main-chain polymers with 3,6-di-acceptor-substituted carbazole which is a two-dimensional CT chromophore was found to possess $d_{31} > {}^{1}/_{3}d_{33}$. Thus, these main-chain polymers can be used as candidates for the enhancement of the off-diagonal tensor component.

The stability of the NLO response was monitored as a function of temperature. Figure 4 shows five relaxation curves which were obtained from the same sample at the different temperatures under the same poling conditions. The vertical axis is the square root of normalized SH intensity, which is proportional to the nonlinear optical polarization and the second-harmonic coefficient. In each case, the incident angle of the fundamental light was fixed at 45°, the incident light was p-polarized, and p-polarized harmonic light was detected. After the sample was heated to about 100 °C, an electric field of 7.5 kV/cm was applied for about 10 min. This poling electric field was held until the sample was cooled to the measurement temperature. The temporal behavior of SHG signals was recorded immediately after the poling voltage was switched off. Each relaxation curve shows that the SH intensity first decays fast followed by a slow rate of relaxation. This relaxation behavior shows two modes for relaxation of chromophore orientation.[31] Similar decay results have been reported in other NLO polymer systems, such as guest−host polymers,[32−34] side-chain polymer,[35,36] and main-chain polymer.[37] This two-mode decay in SH intensity was associated with combined effects coming from both NLO chromophore motion in the local free volume and the injected charge decaying. Once the poling electric field was turned off, the NLO chromophores in sufficiently large local free volume had great freedom to rotate out of their poling-imposed alignment. At the same time, the injected charge decaying after the applied voltage was removed would maintain an electric field across the polymer film to assist the stabilization of the aligned chromophore dipoles. This rotation in large local free volume and the injected charge decaying resulted in a fast decay in the SH intensity. It was found that the decay rate of the SH intensity increased with temperature. This was due to the larger local free volume in the glassy matrix at higher temperature allowing the NLO chromophores to rapidly rotate into the disorder distribution.

Conclusion

We have synthesized carbazole main-chain polymers in which NLO chromophores were aligned as a shoulder-to-shoulder style by one- or two-stage Knoevenagel polycondensation techniques. These polymers could be efficiently poled by an electric field and exhibited unique nonlinear optical property (enhancement of nonlinear optical off-diagonal tensor component, $d_{31} > {}^{1}/_{3}d_{33}$). The flexiblity of the design and synthesis of the shoulder-to-shoulder main-chain NLO polymers allows modification of the polymer structure to further improve the NLO properties such as temporal NLO stability. The key monomers, 3,6-diformylcarbazole derivatives are available in our laboratory, many types of new materials based on carbazole can be expected. Photorefractive properties of such low-T_g polymers were demonstrated by a two-beam coupling experiment. Research work on photoconductive and photorefractive properties of these carbazole main-chain polymers is now in progress.

References and Notes

(1) *Nonlinea Optical Properties of Organic Molecules and Crystal*; Chemla, D. S., Zyss, J., Eds.; Academic Press: New York, 1987.
(2) *Nonlinear Optical Properties of Organic and Polymeric Materials*; William, D. J., Ed.; ACS Symposium Series 233; American Chemical Society: Washington, DC, 1983.
(3) Singer, K. D.; Sohn, J. E.; Lalama, S. J. *Appl. Phys. Lett.* **1986**, *49*, 248.
(4) Rondou, P.; Beylen, M. V.; Samyn, C.; S'heeren, G.; Persoons, A. *Makromol. Chem.* **1992**, *193*, 3045.
(5) Muller, H.; Nuyken, O.; Strohriegl, P. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 125.
(6) Choi, D. H.; Wijekoon, W. M. K. P.; Kim, H. M.; Prasad, P. N. *Chem. Mater.* **1994**, *6*, 234.
(7) Fuso, F.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules* **1991**, *24*, 1710.
(8) Zentel, R.; Baumann, H.; Scharf, D. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 124.
(9) Xu, C.; Wu, B.; Becker, M. W.; Dalton, L. R.; Ranon, P. M.; Shi, Y.; Steier, W. H. *Chem. Mater.* **1993**, *5*, 1439.
(10) Mitchell, M. A.; Tomida, M.; Padias, A. B.; Hall, H. K., Jr. *Chem. Mater.* **1993**, *5*, 1044.
(11) Stenger-Smith, J. D.; Fischer, J. W.; Henry, R. A.; Hoover, J. M.; Nadler, M. P.; Nissan, R. A.; Lindsay, G. A. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1623.
(12) Stenger-Smith, J. D.; Henry, R. A.; Hoorer, J. M.; Lindsay, G. A.; Nadler, M. P.; Nissan, R. A. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2899.
(13) Wright, M. E.; Mullick, S. *Macromolecules* **1992**, *25*, 6045.
(14) Wright, M. E.; Toplikar, E. G. *Macromolecules* **1992**, *25*, 6050.
(15) Wright, M. E.; Sigman, M. S. *Macromolecules* **1992**, *25*, 6055.
(16) Xu, C.; Wu, B.; Dalton, L. R. *Macromolecules* **1992**, *25*, 6716.
(17) Kippelen, B.; Tamura, K.; Peyghambrian, N.; Padias, A. B.; Hall, H. K., Jr. *Phys. Rev. B* **1993**, *48*, 10710.
(18) Peng, Z.; Bao, Z.; Yu, L. *J. Am. Chem. Soc.* **1994**, *116*, 6003.
(19) Zhang, Y.; Ghosal, S.; Casstevens, M. K.; Burzynski, R. *Appl. Phys. Lett.* **1994**, *66*, 256.

(20) Tamura, K.; Padias, A. B.; Hall, H. K., Jr.; Peyghambarian, N. *Appl. Phys. Lett.* **1992**, *60*, 1803.
(21) Wada, T.; Zhang, Y. D.; Choi, Y. S.; Sasabe, H. *J. Phys. D: Appl. Phys.* **1993**, *26*, B221.
(22) Wada, T.; Zhang, Y. D.; Yamakado, M.; Sasabe, H. *Mol. Cryst. Liq. Cryst.* **1993**, *277*, 85.
(23) Zhang, Y. D.; Yamakado, M.; Wada, T.; Sasabe, H. *J. Photopolym. Sci. Technol.* **1993**, *6*, 201.
(24) Wang, L. M.; Zhang, Y. D.; Wada, T.; Sasabe, H. To be published.
(25) Zhang, Y. D.; Wada, T.; Sasabe, H. To be published.
(26) Tien, P. K.; Ulrich, R.; Martin, R. J. *Appl. Phys. Lett.* **1969**, *14*, 291.
(27) Jerphagnon, J.; Kurtz, S. K. *J. Appl. Phys.* **1970**, *41*, 1667.
(28) Hayden, L. M.; Sauter, G. F.; Ore, F. R.; Pasillas, P. L.; Hoover, J. M.; Lindsay, G. A.; Henry, R. A. *J. Appl. Phys.* **1990**, *68*, 456.
(29) Isoshima, T.; Wada, T.; Zhang, Y. D.; Brouyere, E.; Bredas, J. L.; Sasabe, H. *J. Chem. Phys.*, in press.
(30) *Orientationally Ordered Electro-Optic Materials*; Singer, K. D., Kuzyk, M. G., Sohn, J. E., Eds.; Plenum Press: New York, 1988.
(31) Wang, L. M.; Zhang, Y. D.; Yamakado, M.; Wada, T.; Sasabe, H. *Mol. Cryst. Liq. Cryst.* **1994**, *255*, 131.
(32) Goodson, T., III; Gong, S. S.; Wang, C. H. *Macromolecules* **1994**, *27*, 4278.
(33) Guan, H. W.; Pauley, M. A.; Brett, T.; Wang, C. H. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 2615.
(34) Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. *Macromolecules* **1990**, *23*, 3640.
(35) Eich, M.; Sen, A.; Looser, H.; Bjorklund, G. C.; Swalen, J. D.; Twieg, R.; Yoon, D. Y. *J. Appl. Phys.* **1989**, *66*, 2559.
(36) Winkelhahn, H. J.; Schrader, S.; Neher, D.; Wegner, G. *Macromolecules* **1995**, *28*, 2882.
(37) Kang, C. S.; Heldmann, C.; Winkelhahn, H. J.; Schulze, M.; Neher, D.; Wegner, G. *Macromolecules* **1994**, *27*, 6156.

MA950585V