A new synthetic approach for polymers containing a high density of second-order nonlinear optical chromophores

Yadong Zhang, Liming Wang, Tatuso Wada and Hiroyuki Sasabe

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

A new synthetic approach has been developed to incorporate a high density of second-order nonlinear optical chromophores into the polyester main chain in which two kinds of chromophores are aligned as a slipped shoulder-to-shoulder arrangement.

Organic nonlinear optical (NLO) polymers have recently attracted considerable interest due to their potential applications in integrated electro-optic devices.[1,2] Several design strategies have been developed for the synthesis of NLO polymers, such as guest–host systems,[3–5] side chain systems,[6–10] and main chain systems.[11–14] The magnitude of the second-order nonlinearity is mainly dependent on three factors; molecular hyperpolarisability (β) of chromophore, concentration of chromophore and the degree of electric poling. Generally, a polymer with a high percentage of chromophores poled by an electric field has a large macroscopic second-order NLO response $\chi^{(2)}$. In order to reach a maximum concentration of NLO chromophores, NLO moieties with suitable arrangements could be linked by small spacer units into a polymeric main chain or side chain.[12,15] In our synthetic approach, NLO chromophores are placed into a polymeric main chain in which the two kinds of chromophores are aligned as a slipped shoulder-to-shoulder arrangement (as shown in Fig. 1). In this arrangement, the dipole alignment should be easier to achieve by applying an electric field than in structures where the dipole moments are aligned along the polymeric main chain.[11,14] Theoretical studies on the dependency of nonlinearity on the distance and orientation of a number of NLO chromophores shows that a slipped cofacial conformation is an advantageous arrangement for enhancing nonlinearity.[16] Here we report a new approach to the synthesis of polymers with a high density of NLO chromophores in a polymeric main chain by a two-stage Knoevenagel polycondensation. Two kinds of NLO chromophores, carbazole substituted with two acceptor groups and disperse red 19 (DR-19), have been used as synthetic building

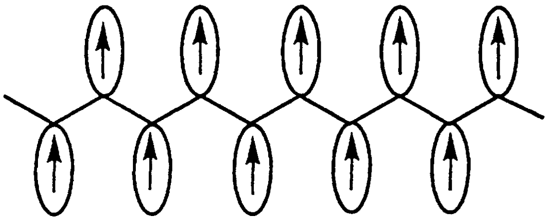
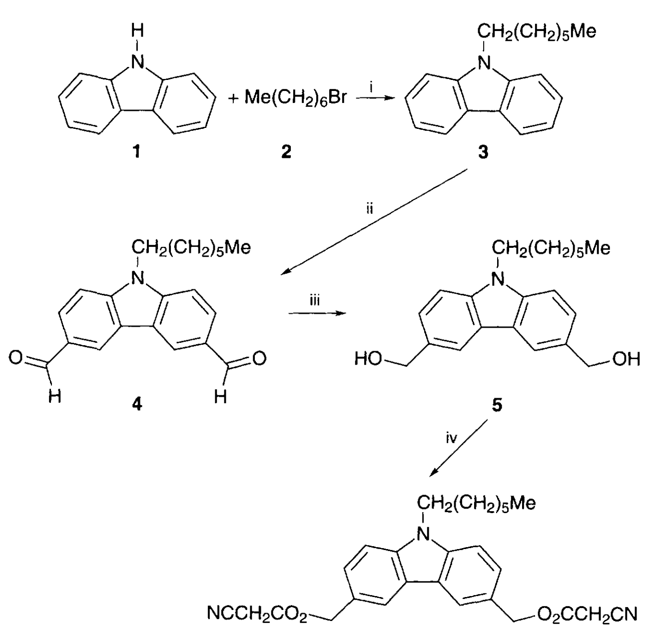
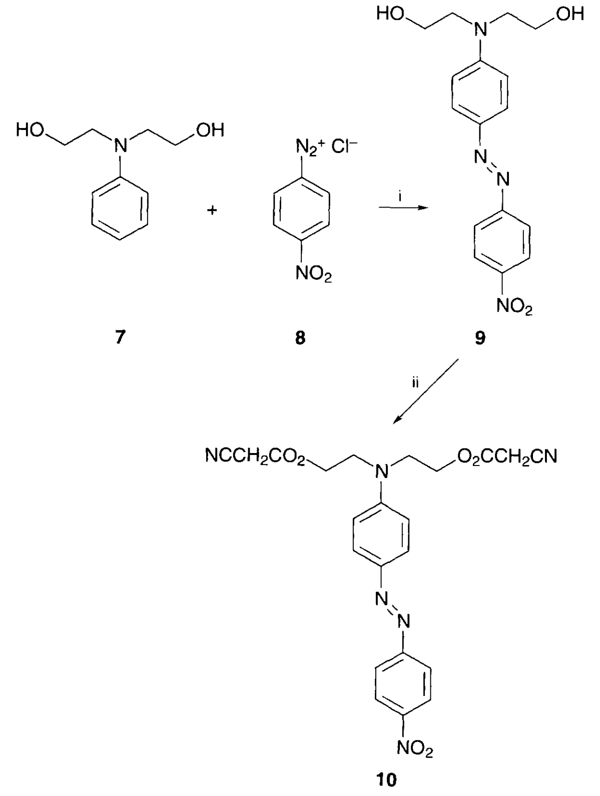


Fig. 1 Chromophore arrangement in main chain polyester after electric poling



Scheme 1 *Reagents and conditions*: i, NaOH, $(PhCH_2)Et_3N^+Cl^-$, PhH, H_2O, reflux, 6 h; ii, $POCl_3$–DMF, $ClCH_2CH_2Cl$, 90 °C, 24 h; iii, $NaBH_4$, NaOH, water, EtOH, room temp., 4 h; iv, $NCCH_2CO_2H$, DCC, CH_2Cl_2, <5 °C, 4 h



Scheme 2 *Reagents and conditions*: i, EtOH, water, room temp.; ii, $NCCH_2CO_2H$, DCC, THF, <5 °C, 5 h

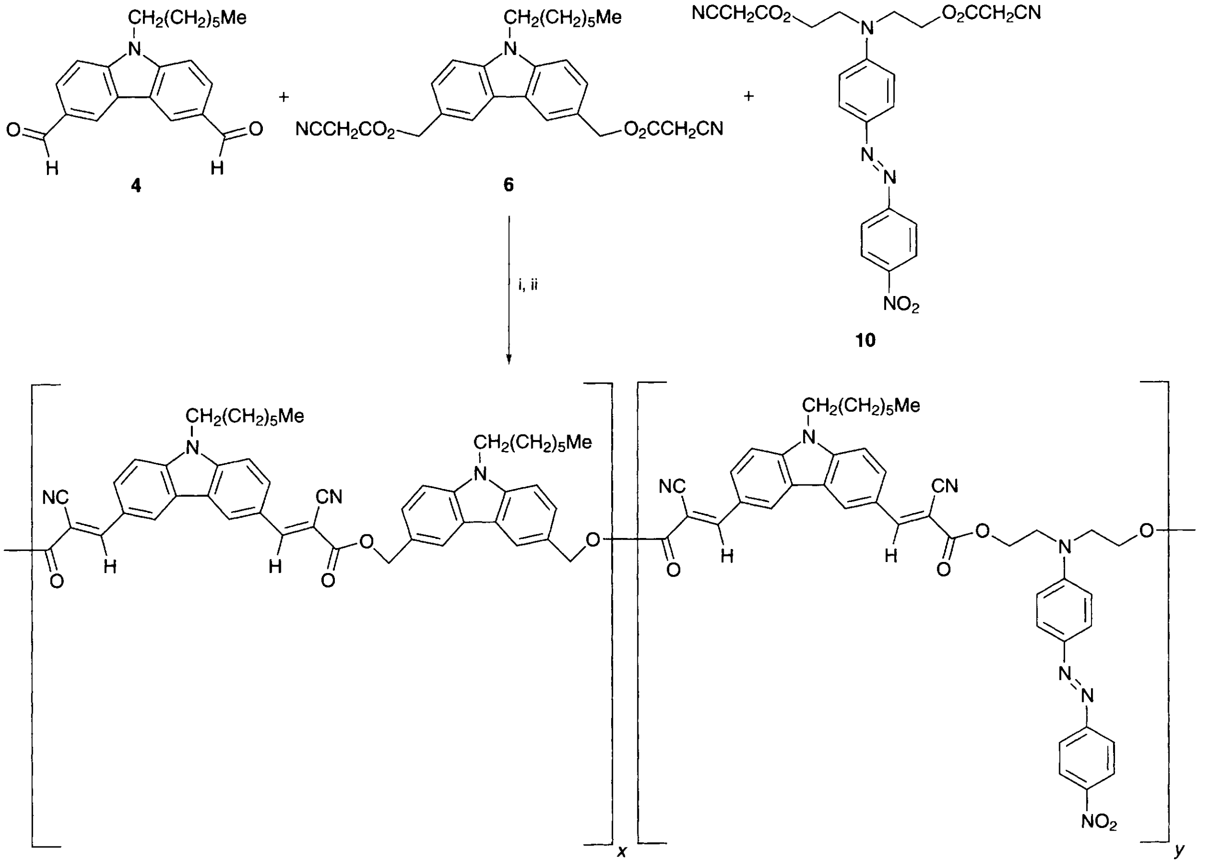
blocks and arranged into a slipped shoulder-to-shoulder arrangement.

The co-monomers, 3,6-diformylcarbazole **4** and the bis(cyanoacetate) derivatives of **6** and **10**, were synthesized as shown in Schemes 1 and 2. Carbazole **1** reacted with 7-bromoheptane **2** in water–benzene using NaOH as a base and benzyltriethylammonium chloride as a phase transfer catalyst to afford 9-heptylcarbazole **3**. Two formyl groups could be introduced to the 3- and 6-positions of **3** to yield 3,6-diformyl-9-heptylcarbazole **4** by the Vilsmeyer formylation. 3,6-Dihydroxymethyl-9-heptylcarbazole **5** was obtained by treatment of **4** with $NaBH_4$. Compound **5** reacted with cyanoacetic acid in CH_2Cl_2 using *N,N'*-dicyclohexylcarbodiimide (DCC) as a water acceptor to give bis(cyanoacetate) **6**. Compound **9** was synthesized by the azo coupling of the diazonium salt of *p*-nitroaniline **7** with amine **8**. Esterification of **9** with cyanoacetic acid in THF using DCC as a water acceptor yielded bis(cyanoacetate) **10**. The chemical structures of all monomers were confirmed by ^1H NMR and IR spectroscopy, and elemental analysis.

Scheme 3 shows the synthesis of the polyesters **11a–d** by a two-stage Knoevenagel polycondensation starting from 3,6-diformylcarbazole **4** and bis(cyanoacetate)s **6** and **10** using 4-dimethylaminopyridine (DMAP) as a base. It was found that the molecular weights and yields of these polymers were very dependent on the conditions of the polycondensation. A one-stage Knoevenagel polycondensation in THF yielded the polymers **11a–d** with low molecular weight in low yields. In the case of the polycondensation of **4** and **6** in THF, a macrocyclic tetramer was obtained as the main product in high yield.[17] On the other hand, the two-stage polycondensation yielded the polyesters **11a–c** with high molecular weight in almost quantitative yields: reaction in THF for 1 h, followed by a solid state polycondensation for 4 h after removal of THF. It was found that the rate of solid state polycondensation was much more rapid than the polycondensation in THF. In the case of the two-stage polycondensation of **4** and **10**, an insoluble polyester **11d** was obtained in high yield. In order to obtain soluble polymers, the flexible moiety **6** has to be introduced.

Table 1 shows the number average molecular weight (M_n), determined by gel permeation chromatography (GPC), and glass transition temperature (T_g), obtained by differential scanning calorimeter (DSC). The GPC columns (10^5, 10^4 and 500 Å) employed were calibrated by the polystyrene standards with molar masses from 1.32×10^3 up to 3.15×10^6 g mol^{-1}. It was found that the chloroform soluble polymers **11a–c** have very large molecular weights with a very wide distribution. The chemical structures of the polymers **11a–c** were confirmed by conventional spectroscopic techniques, IR, ^1H NMR and UV. The polymer **11d** was only characterized by IR due to its poor solubility in organic solvents.

X:*Y* (percentage of incorporation) was obtained from the molar ratio (*m*/*m*) of starting materials used for the polycondensation. The polymer **11d** with $x = 0$ has the highest density of NLO chromophores. Almost 100% *m*/*m* of NLO chromophores, 3,6-diacceptor-substituted carbazole and DR-19, are in the polyester main chain. However, such a polymer is insoluble in common organic solvents. From the polymer **11d**, thin films for NLO measurement and molecular weight could not be obtained. Two approaches can improve the solubility of the polymer **11d**. One is extension of the flexible alkyl chain on the 9-position, and another is the addition of some flexible



11a $x = 100$, $y = 0$
11b $x = 75$, $y = 25$
11c $x = 50$, $y = 50$
11d $x = 0$, $y = 100$

Scheme 3 *Reagents and conditions*: i, DMAP, THF, 40 °C, 1 h; ii, DMAP, 40 °C, 4 h moieties as shown in this synthesis work. Carbazole chromophores and carbazole flexible moieties were selected for the synthesis of this polymer because it is well known that the carbazole compounds have both photoconductive and second-order NLO properties.[18,19] Carbazole should be an ideal building block for both second-order NLO and photorefractive materials. The other polymers **11a–c** with different percentages of the carbazole flexible moiety are very soluble in common organic solvents, such as chloroform.

Thin films (about 1 μm) of the polymers **11a–c** could be obtained on a glass substrate by a spin coating method from their chloroform solutions filtered through a 0.2 μm syringe filter. The films were dried under high vacuum for 2 days. The samples were poled at 160 °C for 30 min with an applied DC electric field 10 kV cm^{-1}. The orientation of chromophores in the polymeric thin films could be monitored by the second harmonic generation (SHG). The poled thin films were cooled to room temperature and the poling field was subsequently removed. The second-order nonlinear optical studies were carried out with copolymer **11b**. The SHG measurements were performed using Q-switched Nd-YAG laser beam (λ = 1064 nm). The SHG intensity of a 1.3 μm film of the polymer **11b** was measured using standard Maker fringe technique. Fig. 2 shows the relation between the SHG intensity and the incident angle. The second harmonic coefficient (d_{33}) of the polymer **11b** could be calculated from the angular dependence of the SHG intensity using the formulae of Hayden for uniaxial materials.[20] A Y-cut quartz plate (d_{11} = 0.5 pm V^{-1}) was used as a reference material. From the calculation, we obtained a d_{33} value of 60 pm V^{-1}. Preliminary results showed that no significant relaxation of the dipoles was observed at ambient condition.

Table 1 Properties of main chain polymers **11a–d**

Polymer	$X:Y$	M_n	T_g/°C
11a	100:0	101000	134
11b	75:25	142000	152
11c	50:50	123000	154
11d	0:100	—	135

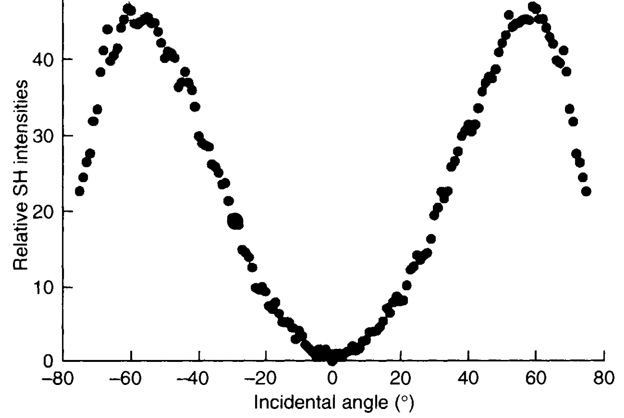


Fig. 2 Maker fringe data for a poled polymer **11b** film with 1.3 μm thickness

References

1 *Nonlinear Optical Properties of Organic and Polymeric Materials*, ed. D. J. Williams, ACS Symposium Series 233, American Chemical Society, Washington, DC, 1983.

2 *Nonlinear Optical Properties of Organic Molecules and Crystals*, ed. D. S. Chemla and J. Zyss, Academic Press, New York, 1987.

3 G. R. Meredith, J. G. Van Dusen and D. J. Williams, *Macromolecules*, 1982, **15**, 1385.

4 L. H. Hampsch, J. Yang, G. K. Wong and J. M. Torkelson, *Macromolecules*, 1988, **21**, 526.

5 K. D. Singer, J. E. Sohn and S. J. Lalama, *Appl. Phys. Lett.*, 1986, **49**, 248.

6 K. J. Drost, V. P. Rao and A. K. Y. Jen, *J. Chem. Soc., Chem. Commun.*, 1994, 369.

7 A. K. Y. Jen, Y. J. Lin, Y. M. Cai, V. P. Rao and L. R. Dalton, *J. Chem. Soc., Chem. Commun.*, 1994, 2711.

8 M. Eich, A. Sohn, H. Looser, G. C. Bjorklund, J. D. Swalen, R. Twieg and D. J. Yoon, *J. Appl. Phys.*, 1989, **66**, 2559.

9 N. P. Wang, T. M. Lealie, S. Wang and S. T. Kowel, *Chem. Mater.*, 1995, **7**, 185.

10 C. A. Walsh, D. M. Burland, V. Y. Lee, R. D. Miller, B. A. Smith, R. J. Twieg and W. Volksen, *Macromolecules*, 1993, **26**, 3720.

11 G. D. Green, J. I. Weinschenk, III, J. E. Mulvaney and H. K. Hall, Jr., *Macromolecules*, 1987, **22**, 722.

12 C. Weder, P. Neuenschwander, U. W. Suter, P. Pretre, P. Kaatz and P. Gunter, *Macromolecules*, 1994, **27**, 2181.

13 K. R. Carter, J. L. Hedrick, R. J. Twieg, T. J. Matray and C. A. Walsh, *Macromolecules*, 1994, **27**, 4851.

14 M. A. Mitchell, M. Tomida, A. B. Padias, H. K. Hall, Jr., H. S. Lackritz, D. R. Robello, C. S. Willand and D. J. Williams, *Chem. Mater.*, 1993, **5**, 1044.

15 I. McCulloch, H. T. Man, B. Marr, C. C. Teng and K. Song, *Chem. Mater.* 1994, **6**, 611.

16 S. D. Bella, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 1992, **114**, 5842.

17 T. Wada, Y. Zhang, L. Wang and H. Sasabe, *Nonlinear Optics*, 1995, **9**, 267.

18 B. Kppelen, K. Tamura, N. Peyghambarian, A. B. Padias and H. K. Hall, Jr., *Phys. Rev. B.*, 1993, **48**, 10 710.

19 T. Wada, Y. D. Zhang, Y. S. Choi and H. Sasabe, *J. Phys. D: Appl. Phys.*, 1993, **26**, B221.

20 L. M. Hayden, G. F. Sauter, F. R. Ore, P. L. Pasillas, J. M. Hoover, G. A. Lindsay and R. A. Henry, *J. Appl. Phys.*, 1990, **68**, 456.

Received, 31st August 1995; Com. 5/05762K