6714 *Macromolecules* **1992,** *25,* 6714–6715

Novel Double-End Cross-Linkable Chromophores for Second-Order Nonlinear Optical Materials

Chengzeng Xu, Bo Wu, and Larry R. Dalton*

Department of Chemistry, University of Southern California, Los Angeles, California 90089-1062

Yongqiang Shi, Peter M. Ranon, and William H. Steier

Department of Electrical Engineering, University of Southern California, Los Angeles, California 90089-0483

Received July 21, 1992
Revised Manuscript Received September 17, 1992

Polymeric second-order nonlinear optical (NLO) materials have been studied extensively in recent years for applications in electrooptic devices. To achieve a large and stable second-order optical nonlinearity for poled polymers, four important objectives must be realized: A high number density of the incorporated chromophores with large first hyperpolarizability (β) must be attained; a high electric poling efficiency is desirable; the temporal stability, thermal stability, and photostability of the poling-induced order must be excellent; and the polymers must exhibit appropriate processibility. Incorporating NLO moieties covalently into polymers, as pendants or part of the main chain, is effective in improving the number density and the processibility.[1] Cross-linking reactions have been proven useful in stabilizing the macroscopic second-order optical nonlinearity.[2–12]

Several approaches have been taken in exploring cross-linkable NLO polymer materials. The first is to synthesize thermosetting prepolymers containing NLO chromophores.[2–4] The second is to synthesize polymers with NLO chromophores in the side chain and cross-linking units on the main chain.[5–7] The third is to synthesize polymers with both NLO moieties and cross-linking groups in the main chain.[8] The fourth approach is to prepare guest–host composites having cross-linkable groups either on the guest NLO chromophores or in the host polymer materials.[9–12] All these approaches have shown to be successful in stabilizing the macroscopic second-order optical nonlinearities of the resulting polymers. In this communication we report a new family of double-end cross-linkable (DEC) NLO chromophores and their polymers. A preliminary study of the NLO properties of the polymers is presented.

In the DEC chromophores, as shown in Figure 1a, one of two different types of polymerizable functional groups is introduced at each end of a dipole. The vinyl group can be polymerized by addition polymerization, and the hydroxy groups can be polymerized by condensation polymerization. The different reaction mechanisms of the two functional groups make it possible for the DEC chromophores to undergo two-step polymerization, condensation and addition. Either the condensation reaction or the addition reaction can be carried out first. This enabled us to design and synthesize cross-linkable NLO polymers of type I (Figure 1b) by condensation polymerization and type II (Figure 1c) by addition polymerization (first-step polymerization). The cross-linking groups (XL) in the main chain can be introduced by copolymerization. Type I and type II polymers can be spin cast from their solutions into optical-quality thin films. The films can be subsequently poled by an electric field and cross-linked (second-step polymerization) by photoreactions or thermal reactions to lock in the dipole orientation. This scheme is intriguing because the poled and cross-linked films are expected to provide improved temporal NLO stability facilitated by their potentially high cross-linking densities and by the fixing of both ends of the chromophore dipoles. Moreover, the fixing of the dipole ends will limit the trans–cis isomerization or reorientation of azo and stilbene type NLO chromophores and therefore will improve the photostability of nonlinearities.

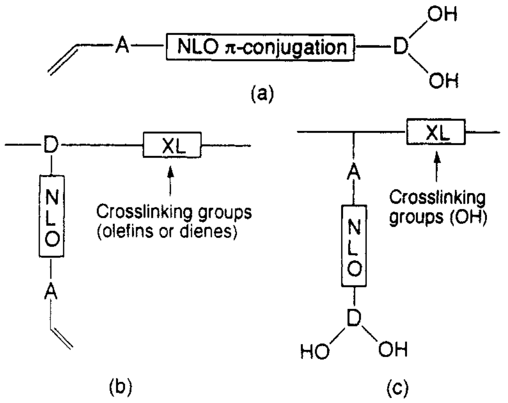
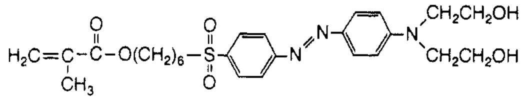


Figure 1. General structures of DEC chromophores and their polymers: (a) DEC chromophores; (b) type I polymers; (c) type II polymers.



DEC-1

Figure 2. Structure of one of the DEC NLO chromophores synthesized.

Our representative example of the double-end cross-linkable NLO chromophores synthesized is shown in Figure 2. The structure was confirmed by NMR, elemental analysis, etc. ^{1}H-NMR (250 MHz, CDCl$_3$), δ from TMS: 7.96 (m, 4 H), 7.91 (d, J = 8.0, 2 H), 6.84 (d, J = 8.8, 2 H), 6.07 (d, J = 0.6, 1 H), 5.54 (m, 1 H), 4.10 (t, J = 6.5, 2 H), 3.96 (t, J = 4.4, 4 H), 3.76 (t, J = 4.2, 4 H), 3.11 (t, J = 7.7, 2 H), 1.92 (s, 3 H), 1.77–1.38 (m, 8 H). Anal. Calcd for $C_{26}H_{35}N_3O_6S$: C, 60.31; H, 6.77; N, 8.12; S, 6.19. Found: C, 60.13; H, 6.79; N, 8.04; S, 6.16. This chromophore (DEC-1) has one methacrylate group at one end and two hydroxy groups at the other end. Monomer DEC-1 was polymerized with terephthaloyl chloride by refluxing in dioxane and pyridine to prepare a type I cross-linkable polymer (polymer I). The FTIR ester carbonyl stretch (1719 cm^{-1}) and ^{1}H-NMR COOCH$_2$ peak (4.59 ppm) gave evidence for the formation of polymer I. DEC-1 was also polymerized with methyl methacrylate (MMA) at a 1:3 molar ratio in DMSO at 70 °C, using AIBN as the initiator, to obtain a type II polymer (polymer II). The formation of the copolymer, polymer II, was demonstrated by the vanishing of the FTIR vinyl band (1636 cm^{-1}) and the ^{1}H-NMR methacrylate peaks (6.07, 5.54, and 1.92 ppm) and the retention of the characteristic NMR peaks from DEC-1 (as listed above) and MMA (COOCH$_3$, 3.59 ppm). For both polymers, the molecular weights measured by size exclusion chromatography using a polystyrene reference are typically 3000–6000. Detailed results of the synthesis and characterization of DEC-1 and its polymers will be presented in a separate publication. Copolymerizations of the monomer DEC-1 with unsaturated diacyl chlorides (condensation polymerization) and 2-hydroxyethyl methacrylate (addition polymerization) to introduce cross-linking groups (XL) onto the polymer backbones are in progress.

0024-9297/92/2225-6714$03.00/0

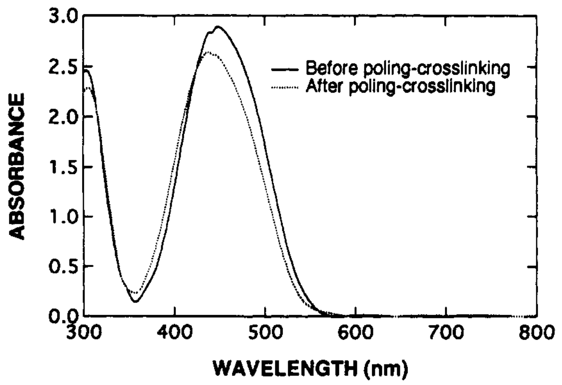


Figure 3. UV–vis spectra of polymer II film of 1.5-μm thickness coated on an ITO glass slide before and after poling and cross-linking.

Both polymer I and polymer II are orange powders and are readily soluble in common organic solvents. Optical-quality thin films of these materials were prepared by spin casting onto indium–tin oxide (ITO) coated glass slides from 10% solutions of polymer I in chloroform and polymer II in tetrahydrofuran/chloroform (3:1 v/v), respectively. The polymer films were poled by a corona-discharge setup at 115 °C for polymer I and 165 °C for polymer II. The poling voltage was ~5 kV with a tip-to-plane distance of 1.5 cm. Second-harmonic generation (SHG) was employed to study the NLO properties of the films. Second-order susceptibilities, $\chi^{(2)}$, of 60 pm/V for polymer I and 100 pm/V for polymer II were obtained at 1.064-μm fundamental wavelength. A Y-cut quartz crystal (d_{11} = 0.5 pm/V) was used as reference.

The methacrylate groups in polymer I can be thermally initialized with the assistance of initiators to form cross-linked three-dimensional networks. The hydroxy (OH) groups in polymer II can react with isocyanate (NCO) or epoxy groups in the cross-linkers to form cross-linked polymer systems. To study the feasibility of stabilizing the electric field-induced order by cross-linking reactions, a polymer II film was cross-linked and the NLO stability of the film was studied. An in-situ cross-linking method was employed; thus a polymer II film incorporated with the cross-linker 3,3′-dimethoxy-4,4′-biphenylene diisocyanate, at a 1:1 molar ratio, was poled and cured simultaneously at temperatures ranging from 160 to 180 °C for 2 h. FTIR spectra, which permit monitoring of the cross-linking reaction, showed that the characteristic peak of the isocyanate group (2272 cm^{-1}) decreased with reaction time and completely disappeared after 2 h of curing. The cured film is not soluble in organic solvents, indicating that polymer II in the film is cross-linked.

The ultraviolet–visible (UV–vis) spectra, shown in Figure 3, were taken using the same polymer II thin film coated on an ITO glass slide. It is noted that an absorbance change occurred after the film was poled and cross-linked. The absorbance decrease is a result of the alignment of the chromophore dipoles.[13] A peak blue shift after poling and cross-linking, which is similar to that in other cross-linked NLO polymer systems,[4,7,11] is also observed.

The measurement of the SHG coefficients after removing the poling electric field showed that the cross-linking reactions indeed improved the NLO stability of polymer II. Figure 4 illustrates the comparison of the temporal stability between the cross-linked and un-cross-linked polymer II films. The SHG coefficients measured at time t, $d(t)$, are normalized using the SHG coefficient measured at 0.5 h after poling, d(0.5 h). This is because the initial SHG signal decays within the first half an hour, ranging from 1 to 10%, are strongly affected by the corona poling histories. As can be seen from Figure 4, the cross-linked sample shows no temporal decay of SHG coefficients for at least 400 h, while the un-cross-linked sample shows a continuing decay at room temperature. It is worth pointing out that the cross-linked films are under continued observation, and no SHG decay is detected for more than 2000 h at room temperature and 95% of $\chi^{(2)}$ is retained after 100 h of annealing at 90 °C.

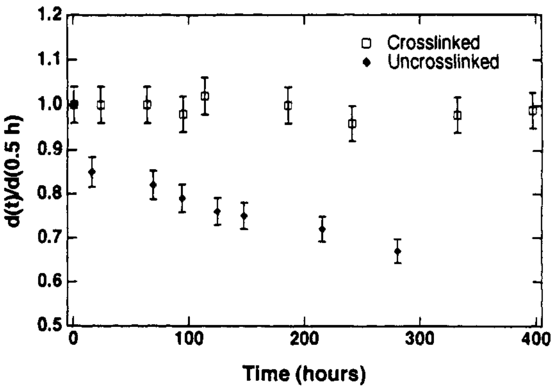


Figure 4. Temporal stability of the normalized SHG coefficients of the cross-linked and un-cross-linked polymer II films.

In conclusion, we have designed and synthesized a new family of NLO dyes, namely, double-end cross-linkable (DEC) chromophores. Chromophore-end cross-linkable polymers have been made from the DEC monomers. This scheme is desirable from the standpoint that high cross-linking density and the locking-in of both ends of the dipoles can be realized without sacrificing the number density of the NLO dyes and the processibility of the polymers. The preliminary NLO stability results demonstrate the feasibility of this versatile design for stabilizing macroscopic second-order optical nonlinearities.

Acknowledgment. This research is supported by Air Force Office of Scientific Research Contracts F49620-91-C-054 and F49620-91-C-0138 and by National Science Foundation Grant DMR-9107806. We also acknowledge the support from the National Center for Integrated Photonic Technology.

References and Notes

(1) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; John Wiley & Sons: New York, 1991.

(2) Eich, M.; Reck, B.; Yoon, D. Y.; Willson, C. G.; Bjorklund, G. C. *J. Appl. Phys.* **1989**, *66*, 3241.

(3) Jungauer, D.; Reck, B.; Tweig, R.; Yoon, D. Y.; Willson, C. G.; Swalen, J. D. *Appl. Phys. Lett.* **1990**, *56*, 2610.

(4) Shi, Y.; Steier, W. H.; Chen, M.; Yu, L. P.; Dalton, L. R. *Appl. Phys. Lett.* **1992**, *60*, 2577.

(5) Park, J.; Marks, T. J.; Yang, J.; Wong, G. K. *Chem. Mater.* **1990**, *2*, 229.

(6) Chen, M.; Yu, L. P.; Dalton, L. R.; Shi, Y.; Steier, W. H. *Macromolecules* **1991**, *24*, 5421.

(7) Yu, L. P.; Chan, W.; Dikshit, S.; Bao, Z.; Shi, Y.; Steier, W. H. *Appl. Phys. Lett.* **1992**, *60*, 1655.

(8) Xu, C.; Wu, B.; Dalton, L. R.; Ranon, P. M.; Shi, Y.; Steier, W. H. *Macromolecules*, following paper in this issue.

(9) Hubbard, M. A.; Marks, T. J.; Yang, J.; Wong, G. K. *Chem. Mater.* **1989**, *1*, 167.

(10) Wu, J. W.; Valley, J. F.; Ermer, S.; Binkley, E. S.; Kenney, J. T.; Lipscomb, G. F. *Appl. Phys. Lett.* **1991**, *58*, 225.

(11) Mandal, B. K.; Chen, Y. M.; Lee, J. Y.; Kumar, J.; Tripathy, S. *Appl. Phys. Lett.* **1991**, *58*, 2459.

(12) Allen, S.; Bone, D. J.; Carter, N.; Ryan, T. G.; Sampson, R. B.; Devonald, D. P.; Hutchings, M. G. In *Organic Materials for Non-linear Optics II*; Hann, R. A., Bloor, D., Eds.; The Royal Society of Chemistry: London, 1991; p 235.

(13) Mortazavi, M. A.; Knoesen, A.; Kowel, S. T.; Higgins, B. G.; Dienes, A. *J. Opt. Soc. Am. B* **1989**, *6*, 733.