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Communications to the Editor

Synthesis of a New Poly(1,4-phenylenevinylene) Derivative Containing Disperse Red 1

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Recently, poled polymers have received much attention due to their high second-order nonlinearity and easy processability. High-bandwidth devices are achievable with them.[1,2] However, thermal stability has been one of the major problems to be improved for practical device applications. In order to realize potential application, the polymers must endure temperatures exceeding 300 °C and prolonged operation temperatures of up to 100 °C without loss of their optical properties.[3] Attempts to prevent relaxation of poled order in polymers, have included cross-linking after poling[4,5] and introduction of a rigid backbone such as polyimide.[3,6] Verbuest et al. incorporated a thermally stable NLO chromophore into the side chain of a polyimide chain and obtained long-term stability of the polar orientation at 170 °C.[3]

Lately the poly(1,4-phenylenevinylene) (PPV) system has been applied to organic semiconductor devices such as light emitting diodes (LED) or electrical conducting materials. The PPV system is conjugated with π-electrons, so it can have a very rigid backbone. It has no glass transition temperature up to its decomposition temperature and is insoluble in any solvent after elimination.[7] These characteristics of the PPV system can be applied to second-order nonlinear optical materials. We tried to enhance its temporal stability by introducing a NLO chromophore into its hard polyconjugated structure. Promising results have already been published by us.[8] Poly[2-((4-cyanophenyl)ethenyl)-5-methoxy-1,4-phenylenevinylene)-*co*-(1,4-phenylenevinylene)], poly(CEMPV-*co*-PV), which contains an electron donor and an electron acceptor in the phenylene ring of the PPV main chain, showed an r_{33} value of 1 pm/V and no relaxation even at 100 °C. However, due to the difficulty of introducing a powerful electron donor in the PPV main chain, the second-order nonlinear optical susceptibility was lower than that of a conventional second-order NLO polymer. Thus the introduction of a nonlinear optical chromophore into the main chain of the PPV system has been limited, though it gives very stable nonlinearity at high temperature. Disperse Red 1 has often been used as a dispersing guest NLO material or attached to the nonconjugated polymer backbone as a side-chain NLO group. Therefore these systems could not prevent the relaxation of second-order nonlinearity at high temperature. In this study, we present the synthesis and the second-order NLO property of the PPV derivative containing Disperse Red 1 as a side chain of the phenylene ring, named poly(2-butoxy-5-(2′-{ethyl[4′-[4′-nitrophenylazo]phenyl]amino}ethoxy)-1,4-phenylenevinylene) (PBDR1PV). The amino group could be used as a powerful electron donor group of dipoles and the nitro group as an electron acceptor, which gave a higher β value than those of incorporated chromophores in PPV as before. This higher β value and the rigidity of the PPV backbone were expected to exhibit a large second-order nonlinear optical susceptibility and temporal stability of nonlinearity.

The synthetic procedures are shown in Figure 1. The mesylated Disperse Red 1 (**1**) was obtained by reacting Disperse Red 1 with an equivalent of methanesulfonyl chloride and triethylamine. The mesylated compound was reacted in butoxyphenol with potassium bicarbonate in acetone by refluxing for 12 h. Butoxyphenol was used because its compounds show better solubility than methoxy-substituted compounds. This alkylated product (**2**) was chloromethylated by formaldehyde and dry HCl to give bischloromethylated compound **3**. Then it was converted to tetrahydrothiophenium salt **4** by reacting with tetrahydrothiophene in methanol. These

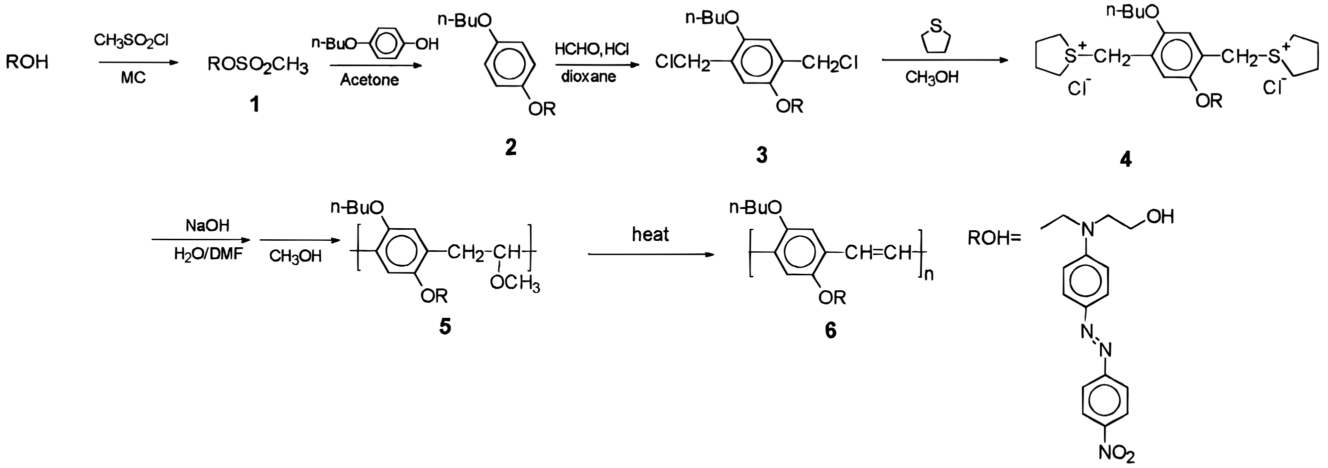

Figure 1. Synthetic route and structure of PBDR1PV.

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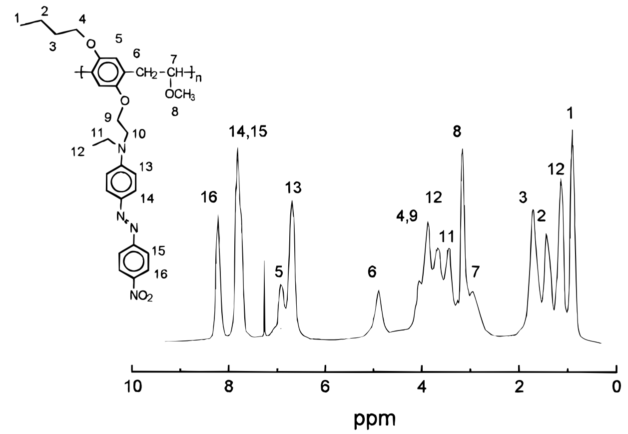

Figure 2. ^{1}H NMR ($CDCl_3$) spectrum of the PBDR1PV precursor polymer.

monomer and intermediate compounds were identified with NMR spectra. Polymerization was performed with 1.0 N sodium hydroxide aqueous solution in methanol−water−dimethylformamide cosolvent. To remove oxygen and other gases from reaction solvents for high molecular weight, the cosolvent was attached to the vacuum line for several minutes and flushed with oxygen-free nitrogen prior to the polymerization reaction. After 1 h of stirring, the reddish solution was put into a dialysis tube with a molecular weight cutoff at 12 000. This polymer solution was kept in methanol for 24 h, and then the red precipitate (**5**) formed was collected by filtration. The ^{1}H NMR ($CDCl_3$, ppm) spectrum of this precursor polymer is shown in Figure 2. This methoxy-substituted precursor polymer was dissolved in 1,2-dichloroethane and cast onto indium tin oxide (ITO) layers to form thin films of 1−3 μm. In general, the elimination of methanol from the methoxy-substituted precursor polymer occurs from 150 to 200 °C.[10] Thus poling was performed into two steps. After the poling field was applied to the polymer sample at 120 °C for 2 h, the elimination step (210 °C for 1 h, holding electric field under a nitrogen flow,)was carried out. Due to the decomposition of Disperse Red 1 dye, we maintained the elimination temperature not higher than 210 °C. The second-order nonlinearity of these polymer samples was measured with the second harmonic generation (SHG) method at the 1064 nm, fundamental wavelength. The d_{33} value of this polymer measured using the angular dependence method with a quartz crystal as the reference was found to be 20 pm/V.[11] It shows a higher d_{33} value than those of other previously reported PPV derivatives,[12] but lower than those of other Disperse Red 1 substituted polymer systems.[9,12] Although not shown in this communication, the FT-IR spectrum of the PBDR1PV precursor polymer prior to the poling process shows a weak peak at 960 cm^{-1}, which corresponds to the *trans*-vinylene (−CH=CH−) bonds. This premature generation of vinylene units may block the full alignment of nonlinear optical chromophores. However, alignment can be optimized by varying poling process parameters such as the poling temperature and poling time. PBDR1PV shows no relaxation of second-order nonlinearity at room temperature for longer than 3 months (Figure 3). The final PBDR1PV is thought to be extremely rigid due to the polyconjugated backbone structure.. This rigidity of the polymer chains and bulkiness of Disperse Red 1 should exert a very high rotational energy barrier to the aligned dipoles, keeping their alignment as poled. Further study of the temporal stability at higher temperature is in progress.

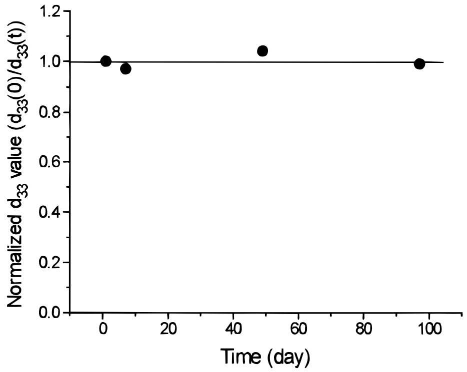

Figure 3. Normalized d_{33} values versus time at room temperature.

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References and Notes

(1) Norwood, R.; Khanarian, G. *Electron. Lett.* **1990**, *26*, 1265.
(2) Girton, D.; Kwiatowski, S.; Lipscomb, G.; Lytel, R. *Appl. Phys. Lett.* **1991**, *58*, 1730.
(3) Verbiest, T.; Burland, D. M.; Jurich, M. C.; Lee, V. Y.; Miller, R. D.; Volksen, W. *Science* **1995**, *268*, 1604.
(4) Hubbard, M. A.; Marks, T. J.; Yang, J.; Wong, G. K. *Chem. Mater.* **1994**, *1*, 167.
(5) Boogers, J. A. F.; Klasse, P. Th. A.; De Wlieger J. J.; Tinnemans, A. H. A. *Macromolecules* **1994**, *27*, 2095.
(6) Chem, T. A.; Jen, A. K. Y.; Cai, Y. *J. Am. Chem. Soc.* **1995**, *117*, 7295.
(7) Murase, I.; Ohnishi, T.; Noguchi, T.; Hiroka, M. *Synth. Met.* **1987**, *17*, 639.
(8) Hwang, D. H.; Lee, J. I.; Shim, H. K.; Hwang, W. Y.; Kim, J. J.; Jin, J. I. *Macromolecules* **1994**, *27* (21), 6000.
(9) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31.
(10) Shim, H. K.; Yoon, C. B.; Lee, J. I.; Hwang, D. H. *Polym. Bull.* **1995**, *34*, 161.
(11) Jerphagnon, J.; Kurtz, S. *Phys. Rev. B* **1970**, *1*, 1739.
(12) Jin, J. I.; Shim, H. K. *Polymers for Second-Order Nonlinear Optics;* ACS Symposium Series 601; American Chemical Society: Washington, DC, 1995; Chapter 17, p 223.

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