JOURNAL OF
Materials
CHEMISTRY

Novel nonlinear optical polymers based on poly(1,4-phenylenevinylene)

Chong-Bok Yoon and Hong-Ku Shim*†

Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon 305–701, Korea

A novel poly(1,4-phenylenevinylene) (PPV) derivative containing a nonlinear optical (NLO) moiety was synthesized *via* the methoxy-precursor pathway to give a highly rigid structure which still maintained good processability. Poly[2-butoxy-5-(2-{ethyl-[4-(4-nitrophenyldiazenyl)phenyl]amino}ethoxy)-1,4-phenylenevinylene] (PBDR1PV), containing a Disperse Red 1 (DR1)-type chromophore, was characterized by conventional spectroscopic methods (UV–VIS, FT-IR, NMR) and by thermal analyses. The synthetic approach has been applied for the preparation of high optical quality films for nonlinear optical applications. PBDR1PV films showed a high resonant d_{33} value of 50 pm V^{-1} when measured using the second harmonic generation (SHG) method. The nonlinearity of PBDR1PV was very stable at 90 °C for a month without detectable loss. In addition to second-order NLO properties, the PBDR1PV film showed third-order NLO properties simultaneously and the measured $\chi^{(3)}$ value was found to be 2.5×10^{-12} esu.

Nonlinear optical (NLO) materials which can alter the character of light have applicability in future optical technologies such as telecommunications, computation, and information processing.[1–3] Recently, poled polymers have received much attention because of their high second-order nonlinearities and easy processability, and high bandwidth devices have been demonstrated.[4,5] Many second-order NLO polymers have been studied, but the thermal stability of the poled state has been one of the major problems which requires improvement for practical device applications.[5] Poling is usually conducted near the glass transition temperature (T_g) of the polymers. But maintenance of the poled state is extremely difficult even at room temperature because of the relaxation of the polymer chains as well as side chain chromophore units, which can destroy the orientation of poled dipoles. Many methods have been proposed to prevent the relaxation of poled chains including crosslinking them during or after poling to form three-dimensional networks[6–8] and the incorporation of NLO chromophores into high T_g polymer backbones.[9–12] Each approach has its own set of advantages and disadvantages. For crosslinking systems, the crosslinking reaction is very hard to control, and uniform crosslinking is even more difficult, which makes it inappropriate for producing high optical quality. For high T_g polymer matrices, the difficulty in poling at very high temperatures is substantial.

Recently, poly(1,4-phenylenevinylene) (PPV) systems have been studied for organic semiconductor devices such as light emitting diodes (LED) and electrically conducting materials.[13,14] The PPV system is π-conjugated and the backbone is quite rigid. As a result, PPV shows no glass transition temperature up to the decomposition temperature and this polymer is insoluble in any solvent after elimination.[15] The structural rigidity of the PPV system could lead to very thermally stable polar structures. Besides the second-order NLO properties, third-order NLO properties could be observed due to the conjugated segment of the PPV backbone. So it is possible to demonstrate second- and third-order NLO activity simultaneously by combining the PPV backbone and a dye segment. We have introduced push–pull dipoles into the main chain of the PPV system.[16] But due to synthetic difficulties associated with the introduction of powerful donors into such systems, low second-order NLO activity was achieved. The largest values obtained in PPV systems such as poly-[2-(4-cyanophenyl)ethenyl-5-methoxy-1,4-phenylenevinylene] (PCEMPV)[17] and poly[2-methoxy-5-(4-nitrophenyl)ethenyl-1,4-phenylenevinylene] (PNEMPV)[16] were only 1.2 pm V^{-1} (r_{33}) and 10 pm V^{-1} (d_{33}) respectively. We now report the introduction of tethered NLO chromophores as side chains on the rigid polyconjugated PPV backbone to enhance the nonlinearity. In this regard, we have tethered Disperse Red 1, a popular NLO chromophore, to a PPV backbone *via* an ether linkage and a flexible ethylene unit. In this report, we present the results of the second and third harmonic generation studies on poly[2-butoxy-5-(2-{*N*-ethyl-*N*-[4-(4-nitrophenyldiazenyl)phenyl]amino}ethoxy)-1,4-phenylenevinylene] (PBDR1PV) synthesized by an organic-soluble precursor polymer pathway.

Experimental

Instrumentation

^{1}H NMR spectra were recorded on a Bruker AM 200 spectrometer. FT-IR spectra were obtained with a Bomem Michelson series FT-IR spectrophotometer and UV–VIS spectra were measured on a Shimadzu UV-3100S. Thermogravimetric analyses (TGA) were performed with a Dupont 9900 analyzer under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) data were obtained on a Perkin-Elmer DSC-7 with a heating rate of 10 °C min^{-1}. The refractive index was determined using a Rudolph Ellipsometry (Auto EL-IV) and fitted by the Selmeyer equation.[18] The second-order nonlinearity of these polymer samples was measured by the second harmonic generation (SHG) method using 1064 nm laser radiation. A polarized Q-switched Nd:YAG laser with an 8 ns pulse width and a 10 Hz repetition rate was used as the light source. The second harmonic signal was detected by a photomultiplier tube and averaged over 300 pulses in a boxcar integrator. For third-harmonic generation (THG) measurements, the light ($\lambda =$ 1064 nm) generated by a Q-switched Nd:YAG laser was converted into 1907 nm, fundamental wavelength, using a H_2 Raman shifter to perform these measurements in a transparent region where polymers have no absorption. The sample was mounted on the rotational stage and third harmonic intensities

---

† E-mail: hkshim@sorak.kaist.ac.kr

were measured using a PM-tube and a Boxcar integrator at each degree. Collected data were processed, and maximum and minimum intensities at zero degree were obtained.

Monomer synthesis

2-{Ethyl[4-(4-nitrophenyldiazenyl)phenyl]amino}ethyl methanesulfonate 1. In a 250 ml round bottomed flask, 10 g (32 mmol) of Disperse Red 1 dye and 4.0 g (35 mmol) of methanesulfonyl chloride were dissolved in 100 ml of dichloromethane and cooled with an ice bath. Triethylamine (3.5 g, 35 mmol) was added to the solution dropwise to prevent overheating of the mixture. The reaction mixture was reacted for 24 h at room temp. and extracted with dichloromethane. The resulting solid, after evaporation of solvent, was purified by recrystallization from methanol. The product yield was 11 g (91%). Mp 138 °C. δ_H ($CDCl_3$) 1.24 (t, 3H), 2.98 (s, 3H), 3.52 (q, 2H), 3.79 (t, 2H), 4.39 (t, 2H), 6.78 (d, 2H), 7.85 (d, 2H), 7.91 (d, 2H), 8.28 (d, 2H).

***N*-[2-(4-*n*-Butoxyphenoxy)ethyl]-*N*-ethyl-4-(4-nitrophenyldiazenyl)phenylamine 2.** To a 250 ml round-bottomed flask containing 50 ml of acetone and 50 ml of *N*,*N*-dimethylformamide (DMF), 10 g (25 mmol) of **1** and 4.4 g (26 mmol) of 4-butoxyphenol were added and 3.6 g (26 mmol) of potassium hydrogen carbonate was added to this solution. The reaction mixture was refluxed for 24 h and then poured into ice–water. The red precipitate formed was collected by filtration. The red solid was also purified by recrystallization from methanol to yield 9.5 g (82%) of product. Mp 84 °C. δ_H ($CDCl_3$) 0.94 (t, 3H), 1.24 (t, 3H), 1.50 (m, 2H), 1.74 (m, 2H), 3.60 (q, 2H), 3.84 (m, 4H), 4.11 (t, 2H), 6.76 (d, 2H), 6.80 (s, 4H), 7.85 (d, 2H), 7.91 (d, 2H), 8.29 (d, 2H).

***N*-{2-[4-*n*-Butoxy-2,5-bis(chloromethyl)phenoxy]ethyl}-*N*-ethyl-4-(4-nitrophenyldiazenyl)phenylamine 3.** A mixture of 9.5 g (21 mmol) of **2**, 15 ml of concentrated aqueous HCl and 10 ml of 37 wt% aqueous formaldehyde was dissolved in 1,4-dioxane. This mixture was refluxed for 8 h with the continuous addition of dry HCl gas. After addition of excess cold aqueous NaOH, a red solid was precipitated and recrystallized from methanol. The product yield was 7.0 g (60%). Mp 119 °C. δ_H ($CDCl_3$) 0.95 (t, 3H), 1.23 (t, 3H), 1.50 (m, 2H), 1.77 m, 2H), 3.59 (m, 10H), 3.88 (m, 4H), 4.21 (t, 2H), 4.56 (d, 4H), 6.90 (m, 4H), 7.90 (d, 4H), 8.30 (d, 2H).

2-*n*-Butoxy-5-(2-{ethyl[4-(4-nitrophenyldiazenyl)phenyl]amino}ethoxy)-1,1′-(1,4-phenylenebismethylene)bis(tetrahydrothiophenium) dichloride 4. Compound **3** (55.0 g, 9 mmol) and excess tetrahydrothiophene (3.0 ml, 34 mmol) were reacted for 24 h at 50 °C in methanol. The desired monomer salt **4** was obtained by concentration of the reaction solution, precipitation in cold acetone, filtration, and vacuum drying. The product yield was 4.0 g (60%). Mp 112 °C (decomp.). δ_H ([$^2H_6$]DMSO) 0.95 (t, 3H), 1.19 (t, 3H), 1.49 (m, 2H), 1.74 (m, 2H), 2.23 (m, 8H), 3.48 (m, 10H), 4.01 (m, 4H), 4.23 (t, 2H), 4.52 (d, 4H), 6.99 (d, 2H), 7.55 (d, 2H), 7.85 (d, 2H), 7.91 (d, 2H), 8.33 (d, 2H).

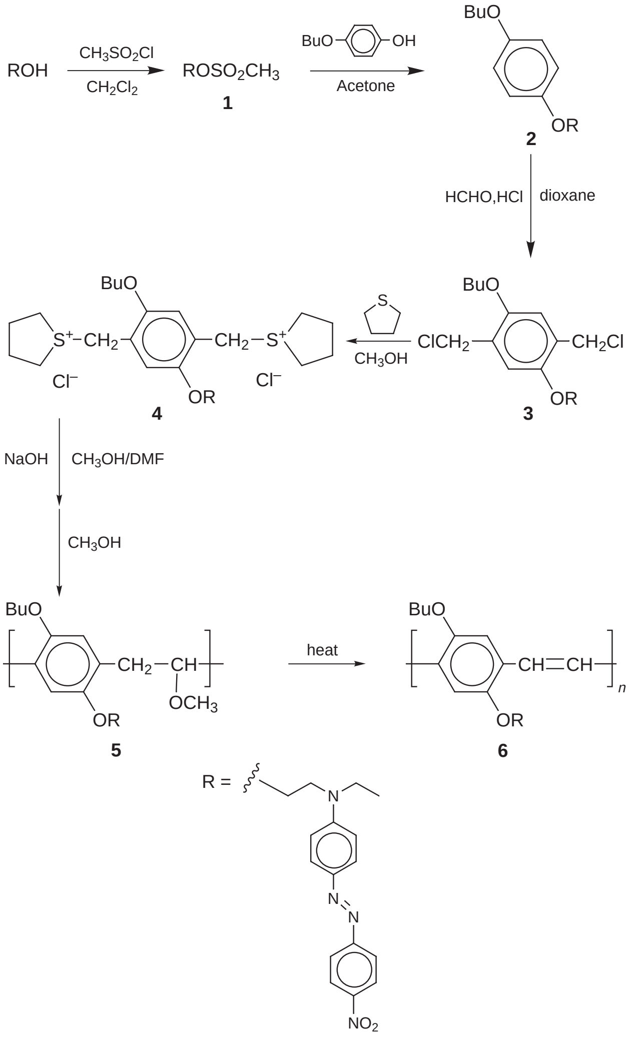
Polymerization

Polymerization was performed with 1.0 M aqueous sodium hydroxide using methanol–DMF cosolvent. To remove oxygen and other gases from reaction solvents to obtain high molecular masses, the reaction vessel was attached to the vacuum line for several minutes and flushed with oxygen-free nitrogen prior to the polymerization reaction. After 1 h stirring, a viscous reddish solution was placed in a dialysis tube with a molecular mass cutoff at 12 000. This polymer solution was kept in methanol for 24 h, and the red precipitate **5** formed was collected by filtration and purified by Soxhlet extraction with methanol.

Results and Discussions

Our strategy in synthesizing NLO-functionalized PPV was to introduce the NLO-active moiety as a side chain on the PPV backbone.[19] Because Disperse Red 1 itself has limited solubility in common organic solvents, we introduced the *n*-butoxy substituent into the phenylene ring as a flexible side chain for better solubility (Scheme 1). The monomer **4** was soluble in methanol–DMF and gave a dark red solution once polymerized. The precursor polymer obtained, **5**, was soluble in various organic solvents such as 1,2-dichloroethane, tetrahydrofuran (THF), and dichloromethane. The well defined ^1H NMR ($CDCl_3$, ppm) spectrum of the polymer **5** is shown in Fig. 1. The precursor polymer solution could be spin-coated to produce homogeneous, pinhole-free thin films of thickness approximately 1 µm. The chromophore content by mass was 68% in the PBDR1PV, which represents a very high dye loading level in the NLO active polymer.[12]

As mentioned above, PPV itself is a highly conjugated structure which is insoluble in common organic solvents, so it should be processed at the precursor polymer stage, and then thermally eliminated to the final fully conjugated structure. Some methods such as FT-IR and UV–VIS spectroscopy were developed to show the conversion of the precursor polymer to the final eliminated structure. We could see the characteristic absorption peak of the *trans*-vinylene moiety at 965 cm^{-1} (the



Scheme 1

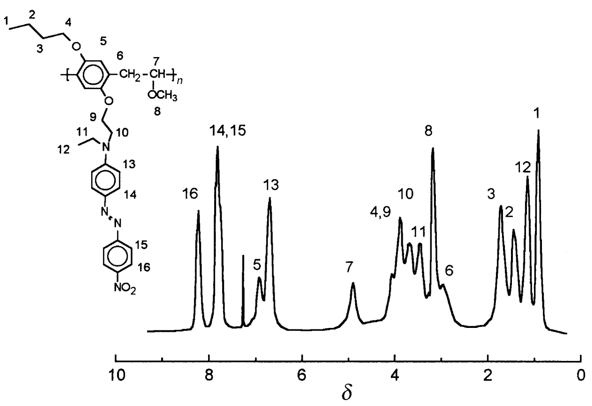


Fig. 1 ^{1}H NMR spectrum of precursor polymer **5**

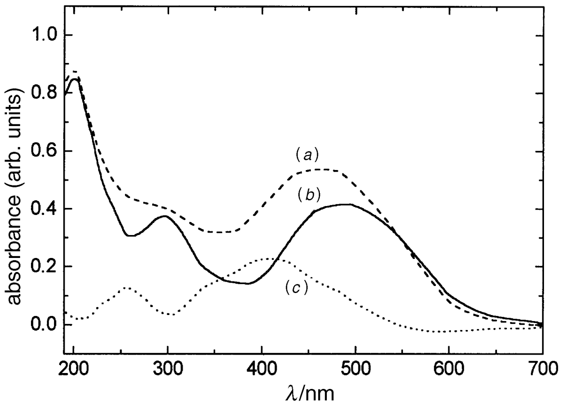


Fig. 2 UV–VIS spectra of (*a*) PBDR1PV, (*b*) its precursor polymer, and (*c*) the spectral difference between them

out-of-plane bending mode of the *trans*-vinylene group) in the FT-IR spectrum of PBDR1PV indicative of the formation of the phenylenevinylene unit during thermolysis. Fig. 2 shows the UV–VIS spectra of PBDR1PV **6** and its precursor polymer **5**. In the precursor polymer, absorption occurs mainly at 480 nm corresponding to the characteristic absorption of Disperse Red 1 chromophore.[20] The shoulder around 300 nm is due to the aromatic benzene moiety both in the precursor polymer and in PBDR1PV. The absorption difference between the precursor polymer **5** and PBDR1PV **6** [Fig. 2(*c*)] shows a maximum at around 410 nm, indicating that elimination to give a π-conjugated structure has occurred. Since the absorption maxima of dialkoxy-substituted PPV derivatives in the UV–VIS region occur at around 460 nm,[21] it can be presumed that methoxy groups in the PBDR1PV precursor polymer were not completely eliminated during thermolysis. We also performed the elimination at a higher temperature (Fig. 3) and observed a strong absorption change due to the crosslinking reaction of the azo-dye moiety. After elimination at 225 °C for 1 h, the characteristic absorption of Disperse Red 1 was significantly decreased and above 250 °C the UV absorption of Disperse Red 1 had mostly disappeared. For pyrolysis at 200 °C, the characteristic absorption originating from Disperse Red 1 in **5** was largely retained. These results show that the elimination reaction should be performed near 200 °C.

Thermal analysis is also a convenient tool for studying the conversion to **6**. Fig. 4 shows the TGA and DSC thermograms for the precursor polymer **5**. Two endothermic peaks were observed in the DSC thermogram, corresponding to the loss of residual solvent and elimination of methanol. We observed an intense exothermic peak above 200 °C associated with a side reaction of the Disperse Red 1 moiety. Thus as mentioned above, thermal elimination should be performed under 200 °C to minimize the thermal crosslinking or decomposition reactions.

To prepare high quality films for the second harmonic measurements, the precursor polymer solution in 1,2-dichloroethane was first filtered through a 0.45 μm filter and then spin-coated onto indium–tin oxide (ITO) coated glass slides. The films were dried in an oven at room temp. under vacuum for 6 h. Films of **5** were electric field-poled by using a corona discharge. The poling process was performed in two steps. After the poling field had been applied to the film of the precursor polymer at 120 °C for 1 h, the elimination step to give the conjugated structure was conducted at 200 °C for an additional 1 h maintaining the electric field under a nitrogen atmosphere. To measure the NLO activity of our poled polymer samples, the second harmonic generation method was used[12] and the d_{33} value of this polymer was measured using the angular dependence method with a Y-cut quartz crystal (0.8 mm thickness) as the reference. The d_{33} value was found to be 50 pm V^{-1} with compensation for absorption in the calculation.[22,23] This value is the highest one reported for functionalized PPV derivatives, which is a feature ascribed to both the high poling efficiency of the tethered chromophore and the high nonlinearity of the DR1-type chromophore. Since the second harmonic wavelength (532 nm) is in the absorptive region of the polymer, there is a large resonant contribution to the d_{33} value. It is known that, for device applications, a large nonresonant value is important. Since we do not have a longer wavelength laser source, we evaluated the nonresonant value of this material by using an approximate model, a two-level model.[24] It was determined that the disperseless d_{33} value of the PBDR1PV was 10 pm V^{-1}.

Relaxation of the poled NLO chromophores depending on the temperatures was observed by monitoring the decrease in the SHG signal originating from the samples as a result of the decay in the poled order. Fig. 5 shows the plots of normalized d_{33} values *versus* time at various temperatures. Up to 90 °C,

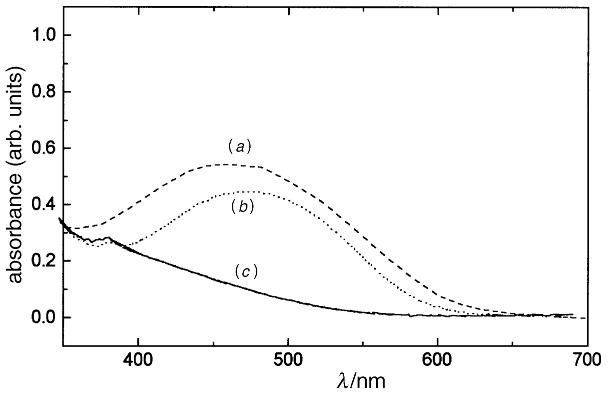


Fig. 3 UV–VIS spectra of polymer films (**5**) after pyrolysis at (*a*) 200, (*b*) 225 and (*c*) 250 °C

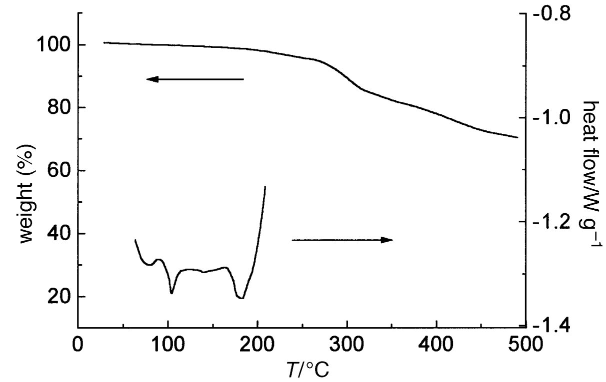


Fig. 4 Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) thermograms of PBDR1PV precursor polymer

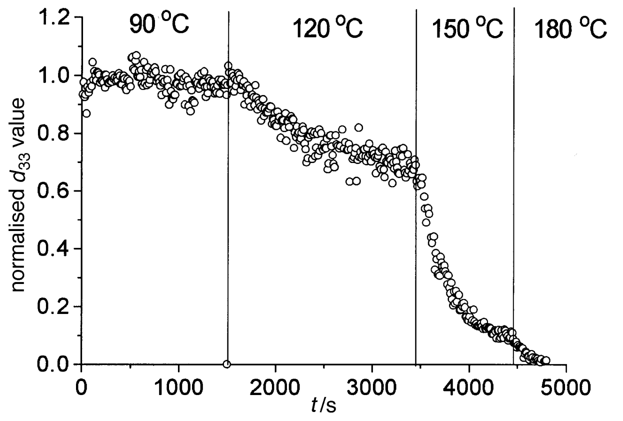
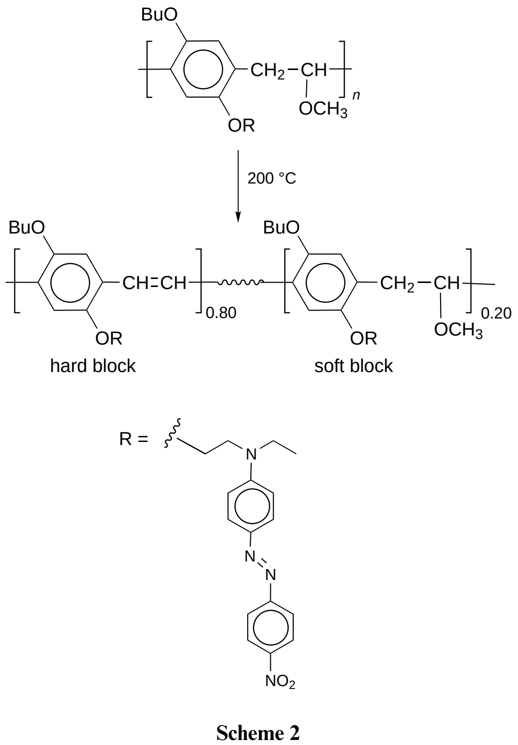


Fig. 5 The normalized d_{33} values *versus* time at various temperatures

poled PBDR1PV showed no detectable decay of SHG signal over 1500 s and gradual loss of nonlinearity occurred at 120 °C. The film retained about 70% of the original nonlinearity at 120 °C after 2000 s, and then the NLO activity disappeared completely at 180 °C. We think that the incomplete elimination of methanol is one of the main reasons for the decay of the nonlinearity at high temperatures. Normally, the methoxy-substituted PPV precursor polymer requires either an acid catalyst or a higher temperature above 250 °C for complete elimination.[21] But here, it is not possible to subject the polymer film to such conditions in order to protect the NLO chromophore. As a result, elimination was performed at lower temperatures (~200 °C) which results in a partially eliminated polymer (Scheme 2). We could estimate the uneliminated portion by comparing the mass after pyrolysis (200 °C in N_2 flow for 1 h) with the calculated mass when complete elimination occurred. The fraction of residual methoxy group was estimated to be around 20%. The uneliminated (soft) blocks should contribute to the mobility of NLO chromophores due to single bond rotation at high temperatures. So thermal stability of the NLO activity might be improved when fully eliminated structures are achieved, which could be possible either by developing other precursor routes[25] or by the introduction of a more thermally stable NLO chromophore.[10] We observed long-term stability of nonlinearity at room temp. and at 90 °C (Fig. 6). No measurable decay was detected after a month at 90 °C.



Scheme 2

To determine the third-order nonlinear optical susceptibilities ($\chi^{(3)}$) of the polymer, third harmonic intensities were measured as a function of incident angle between −10 and 40°. BK-7 glass was used as both reference and substrate. Fig. 7 shows the Maker fringe patterns of PBDR1PV and BK-7 glass. The $\chi^{(3)}$ value of the PBDR1PV was calculated by comparing the measured THG peak intensity of film with that of the substrate using eqn. (1)[26,27]

$$\chi^{(3)}=\frac{2}{\pi}\chi_s^{(3)}\frac{(I_{3\omega})^{1/2}/l}{(I_{3\omega,s})^{1/2}/l_{c,s}} \qquad (1)$$

where l is the sample thickness (assumed to be much thinner than the coherence length), $\chi_s^{(3)}$ and $l_{c,s}$ are the third-order nonlinear susceptibility and the coherence length of the BK-7 substrate, respectively, and $I_{3\omega}$ and $I_{3\omega,s}$ are the measured peak intensity values in the fringe patterns of the thin films and BK-7 glass. We assumed that the effect of the refractive index difference between the PBDR1PV and the substrate for $\chi^{(3)}$ calculation is negligible. The measured $\chi^{(3)}$ value of PBDR1PV

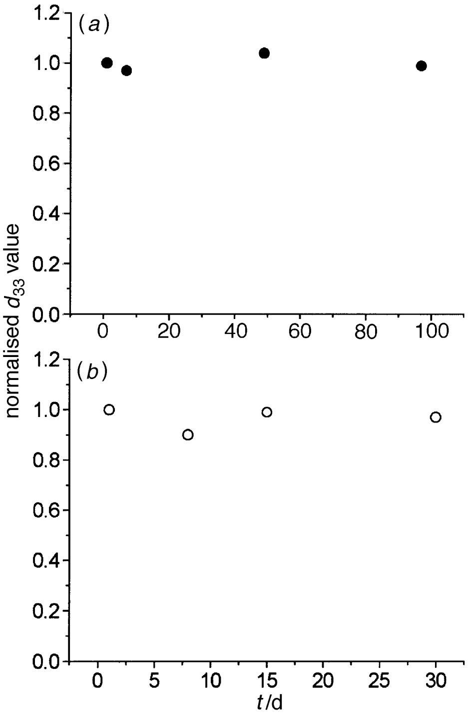


Fig. 6 The normalized d_{33} values *versus* time at (*a*) room temperature and (*b*) 90 °C

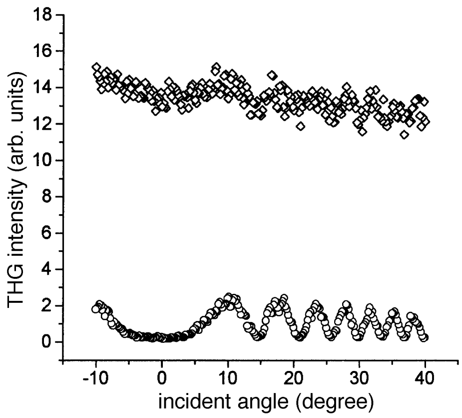


Fig. 7 Maker–Fringe pattern of (○) BK-7 glass (reference) and (◇) PBDR1PV

was 2.5×10^{-12} esu, which is smaller than that of poly(2,5-dimethoxy-1,4-phenylenevinylene) (PDMPV), 5.4×10^{-11} esu at 1.85 μm reported by Kaino *et al.*[27,28] This result is explained by the band gap difference of the PPV backbone. It is well known that the $\chi^{(3)}$ value is inversely proportional to the sixth power of band gap energy. PBDR1PV film was not fully eliminated as mentioned above. We could obtain the absorption profile due to the PPV backbone itself from the absorption difference. The measured absorption edge for conjugated backbone is around 560 nm [Fig. 2(*c*)], which is shorter than that of PDMPV(610 nm). So it can be deduced that PBDR1PV has a larger bandgap energy than PDMPV. This increase in bandgap energy leads to a lower $\chi^{(3)}$ value than that of PDMPV.

Conclusion

A new NLO-active PPV derivative containing Disperse Red 1 as a pendant second-order NLO chromophore was prepared. The organic-soluble route selected here gives improved optical quality films and the high second-order nonlinear optical properties compared to the other NLO functionalized PPV derivatives as well as the third-order NLO activity. The nonresonant d_{33} value of PBDR1PV film, which was stable at 90 °C, was 10 pm V^{-1} at 1064 nm and the $\chi^{(3)}$ value measured at 1907 nm was 2.5×10^{-12} esu.

This work was supported by the Korea Science and Engineering Foundation (95-0300-06-01-3).

References

1 P. N. Prasad and D. J. Williams, in *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley, New York, 1991.

2 R. W. Boyd, in *Nonlinear Optics*, Academic Press, New York, 1992.

3 J. Zyss and I. Ledoux, *Chem. Rev.*, 1994, **94**, 77.

4 L. R. Dalton, A. W. Harper, R. Ghosn, W. H. Steier, M. Ziari, H. Fetterman, Y. Shi, R. V. Mustacich, A. K.-Y. Jen and K. J. Shea, *Chem. Mater.*, 1995, **7**, 1060.

5 L. R. Dalton, A. W. Harper, B. Wu, R. Ghosn, J. Laquindanum, Z. Liang, A. Hubibel and C. Xu, *Adv. Mater.*, 1995, **7(6)**, 519.

6 J. A. F. Boogers, P. Th. A. Klasse, J. J. de Wlieger and A. H. A. Tinnemans, *Macromolecules*, 1994, **27**, 205.

7 R. Levenson, J. Liang and J. Zyss, *Polym. Prepr.*, 1994, **35**, 162.

8 B. K. Mandal, Y. M. Chen, J. Y. Lee, J. Kumar and S. Tripathy, *Appl. Phys. Lett.*, 1991, **58**, 2459.

9 T. A. Chen, A. K. -Y. Jen and Y. Cai, *J. Am. Chem. Soc.*, 1994, **117**, 7295.

10 T. Verbiest, D. M. Burland, M. C. Jurich, V. Y. Lee, R. D. Miller and W. Volksen, *Science*, 1995, **268**, 1604.

11 K. J. Moon, H. K. Shim, K. S. Lee, J. Zieba and P. N. Prasad, *Macromolecules*, 1996, **29(3)**, 861.

12 D. M. Burland, R. D. Miller and C. A. Walsh, *Chem. Rev.*, 1995, **94**, 31.

13 I. N. Kang, D. H. Hwang, H. K. Shim, T. Zyung and J. J. Kim, *Macromolecules*, 1996, **29(1)**, 165.

14 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn and A. B. Holmes, *Nature*, 1990, **347**, 539.

15 R. Ma. Gregorius, P. M. Lahti and F. E. Karasz, *Chem. Mater.*, 1991, **3**, 941.

16 J. I. Jin and H. K. Shim, in *Polymers for Second-order Nonlinear Optics* (ACS Symp. Ser.), 1995, p. 223.

17 D. H. Hwang, J. I. Lee, H. K. Shim, W. Y. Hwang, J. J. Kim and J. I. Jin, *Macromolecules*, 1994, **27(21)**, 6000.

18 B. Tatian, *Appl. Opt.*, 1984, **23**, 4477.

19 C. B. Yoon, K. J. Moon and H. K. Shim, *Macromolecules*, 1996, **29(17)**, 5754.

20 C. R. Moylan, R. J. Twieg, V. Y. Lee, S. A. Swanson, K. M. Betterton and R. D. Miller, *J. Am. Chem. Soc.*, 1993, **115**, 12 599.

21 H. K. Shim, C. B. Yoon, J. I. Lee and D. H. Hwang, *Polym. Bull.*, 1995, **34**, 161.

22 W. N. Herman and L. M. Hayden, *J. Opt. Soc. Am. B.*, 1995, **12**, 416.

23 J. Jerphagnon and S. K. Kurtz, *J. Appl. Phys.*, 1970, **41**, 1667.

24 M. Kauranen, T. Verbiest, C. Boutton, M. N. Teerenstra, K. Clays, A. J. Schouten, R. J. M. Nolte and A. Persoons, *Science*, 1995, **270**, 966.

25 B. R. Hsieh, H. Antoniadis, D. C. Bland and W. A. Feld, *Adv. Mater.*, 1995, **7(1)**, 36.

26 T. Kaino, K. Kubodera, S. Tomaru, T. Kurihara, S. Saito, T. Tsutsui and S. Tokito, *Electron. Lett.*, 1987, **23**, 1095.

27 T. Kaino, H. Kobayash, K.I. Kubodera, T. Kurihara, S. Saito, T. Tsutsui and S. Tokito, *Appl. Phys. Lett.*, 1989, **54**, 1619.

28 D. H. Hwang, J. I. Lee, M. Lee and H. K. Shim, *Bull. Korean Chem. Soc.*, 1994, **15**, 25.

Paper 7/07657F; *Received* 23rd *October*, 1997