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Synthesis and 2nd order nonlinear optical properties of soluble polyimides bearing nitroazobenzene type chromophore pendants attached in side-on mode†

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An organic soluble polyimide was prepared from 3,3′-dihydroxybenzidine and 2,2-bis(phthalic anhydride)hexafluoropropane. The two hydroxy groups in the repeating unit of the polyimide thus prepared were utilized in attaching 4-nitro-4′-diphenylaminoazobenzene chromophores onto the main chain perpendicularly (or in an end-on fashion) or laterally (or in a side-on fashion) through either the oxydimethylene or oxyhexamethylene spacer. All the polymers revealed two strong absorptions: one λ_{max} at 300 nm and the other λ_{max} at 493 nm. The polymers, when electrically poled, showed 2nd order nonlinear optical properties, $r_{33} = 9$–$23\ \mathrm{pm\ V^{-1}}$ at 1300 nm, $r_{33} = 102$–$194\ \mathrm{pm\ V^{-1}}$ at 633 nm, and $d_{33} = 59$–$109\ \mathrm{pm\ V^{-1}}$ at 1064 nm depending on their structure. The polymers bearing side-on attached chromophores revealed higher r_{33} values than those with end-on attached chromophores. Temporal stability of the former was also greater than that of the latter.

Introduction

A wide variety of polymers bearing chromophoric structures revealing nonlinear optical properties have been reported.[1–10] Especially, the second order nonlinear optical properties such as second harmonic generation and electro-optic properties of the polymers, have been studied in detail in relation to the structures of the polymer backbone and chromophores. Since noncentrosymmetrical orientation of dipolar chromophores is required in order to bring about 2nd order optical nonlinearity, electrical poling, either corona or contact poling, is usually applied to polymer thin films. There are exceptional examples where poling is not necessary. Representative examples are octupolar compounds[11] which, by symmetry, have zero-permanent dipole moment. Poled or aligned chromophores, however, tend to relax back to a disordered state, which has to be prevented from occurring for long-term utilization of the materials. Earlier, we[12] reported that poly(*p*-phenylenevinylene) derivatives having oriented chromophores, due to their very rigid backbones, did not exhibit any relaxation even at elevated temperatures. Polyamides[13,14] and crosslinkable polymers[15] also provide us with thermally stable NLO compositions. Polyimides[16–24] are another example of polymers with rigid backbones. Organic–inorganic composites,[25] especially silica composites prepared by sol–gel methods, have been attracting much attention too.

On the other hand, polymers[26] containing azobenzene chromophores are the subject of numerous reports due to their unique optical properties resulting from the ability of azo chromophores to undergo photoinduced orientation involving *cis*↔*trans* isomerization. Recently, we[27] have been trying to compare the dependence of photoinduced orientation of azobenzene type chromophores on their mode of attachment, *i.e.* either laterally (side-on) or perpendicularly (end-on), on polyoxetane backbones. In particular, we[27] observed extraordinarily fast photoinduced reorientation of chromophores and decay behaviour at room temperature, far lower than their glass transition temperatures. Polymers bearing the laterally attached chromophores revealed faster writing than polymers which bear the perpendicularly attached chromophores. Moreover, we[28] previously demonstrated that the following polyimide ($n = 6$) could control the orientational ordering of the 5CB liquid crystal by changing the incident angle of the pump beam utilized in the photoalignment of the azo chromophores.

In this report, we would like to describe the synthesis and 2nd order NLO properties of **SP-2** and **SP-6** (Fig. 1), where "**SP**" stands for side-on attachment of the chromophores and, 2 and 6 for the numbers of the methylene groups in the spacers. For the sake of comparison, discussion on the synthesis and properties of the homologous polymer (**EP-2** and **EP-6**, Fig. 1) bearing end-on or perpendicularly attached chromophores is also included in this paper. "**EP**" stands for end-on attachment of the chromophore pendants.

Experimental

Synthesis of polymers

The polymers were prepared *via* a three step synthetic route as shown in Scheme 1. Synthetic details for the preparation of compound **3** can be found elsewhere.[27] Other synthetic details are available from the Electronic Supplementary Information†.

Preparation of **SP-2**: **PI** (0.69 g; 1.1 mmol), compound **3**(**2**) (1.5 g; 3.3 mmol) and triphenylphosphine (1.4 g; 5.5 mmol) were dissolved in 30 mL of dry tetrahydrofuran under a dry nitrogen atmosphere. Diisopropyl azodicarboxylate (1.1 g; 5.4 mmol)[29] was added dropwise to the solution. The mixture was stirred for 2 days. The reaction mixture was added dropwise with vigorous stirring to a mixture of 500 mL of methanol and 10 mL of 2 M hydrochloric acid. The precipitate was collected by filtration. The crude product thus obtained

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†Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/jm/b1/b107553e/

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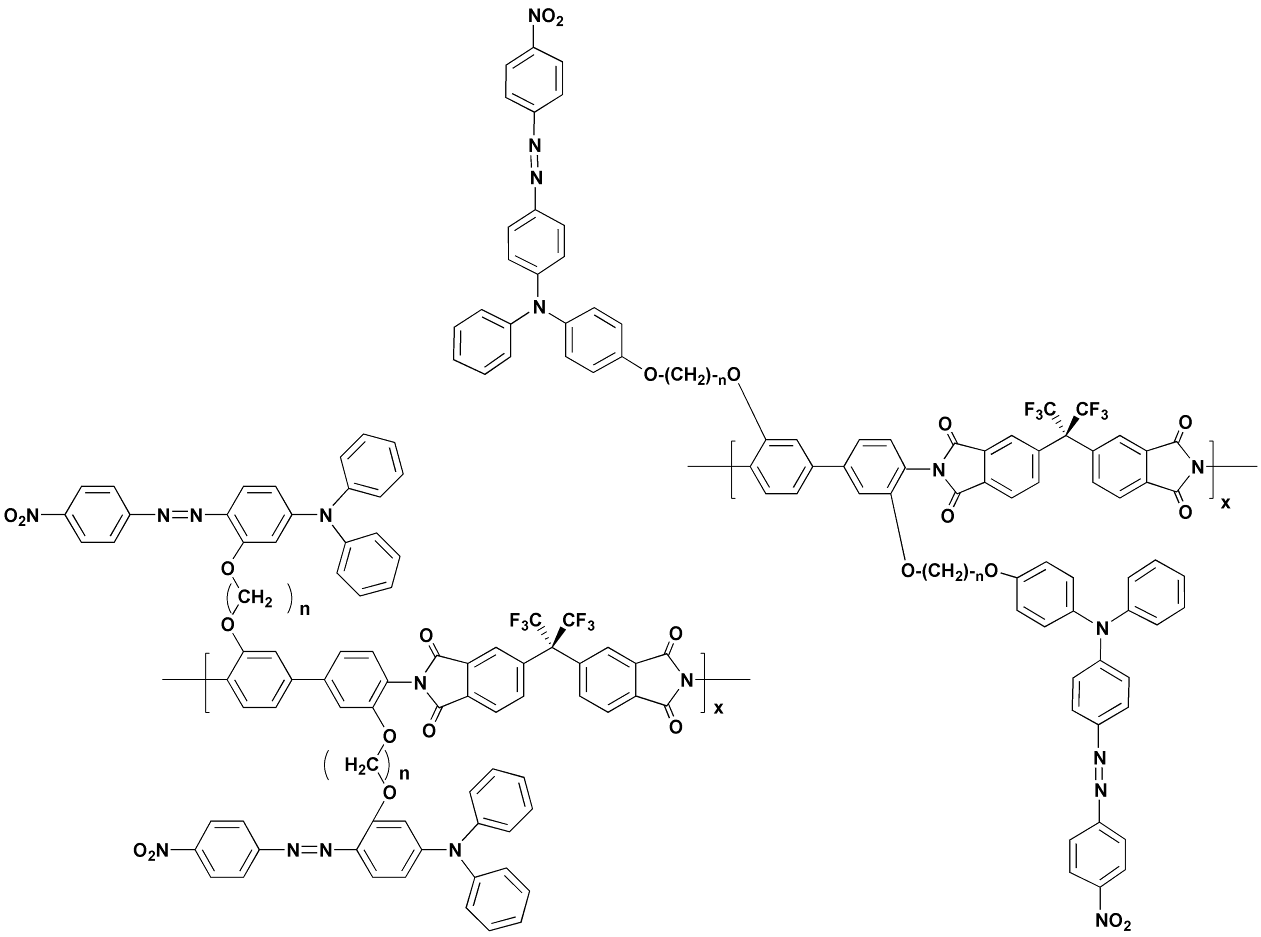


n = 2 and 6 (SP-2 and SP-6)

n = 2 and 6 (EP-2 and EP-6)

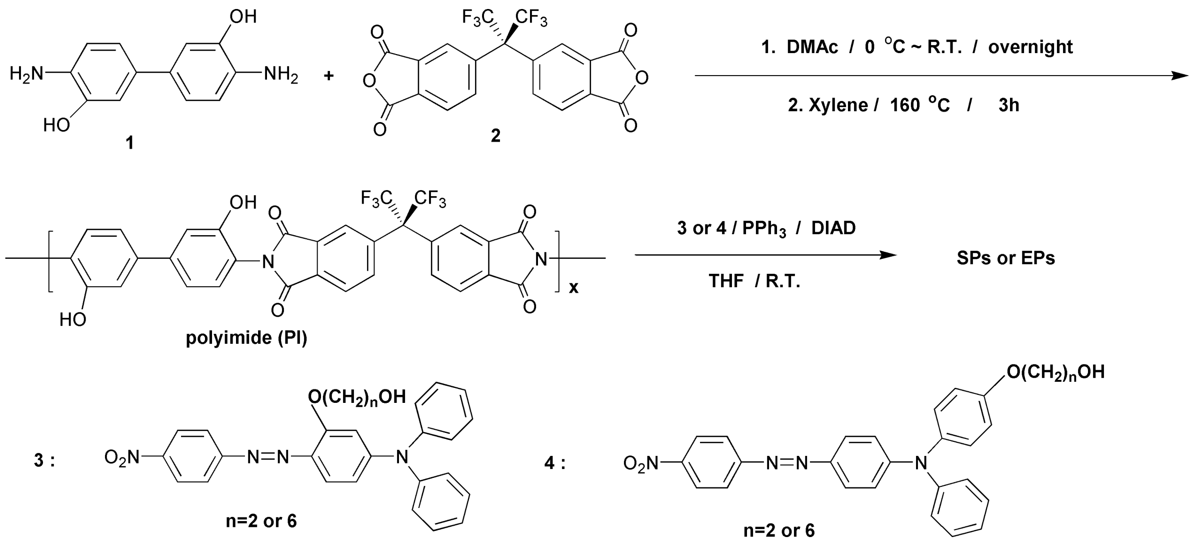
Fig. 1 Structures of polymers (**SP-2**, **SP-6**, **EP-2** and **EP-6**).

was subjected to Soxhlet extraction with methanol for 2 days. The product yield was 1.4 g (85%).

^{1}H NMR spectrum (CDCl$_3$, δ ppm): 4.3–4.6 (br d, 8H, $-OCH_2CH_2O-$), 6.5–8.2 (m, 46H, *Ar-H*). FT-IR spectrum (KBr, cm^{-1}): 1787, 1732 (stretching of amide), 1504, 1343 (N–O stretching), 1241, 1102 (C–O stretching). Anal. Calcd. for $C_{83}H_{54}N_{10}O_{12}F_6$: C 66.58, H 3.63, N 9.35%. Found: C 65.91, H 3.99, N 8.98%.

SP-6 was prepared in the exact same manner from **PI** and the corresponding chromophore, **3**(**6**). Its structure was confirmed spectroscopically and by elemental analysis. Recovered yield after Soxhlet purification was 89%.

Preparation of **EP-2** and **EP-6**: the polymers were prepared from **PI** and **4**(**2**) or **4**(**6**) in the same manner as described above for the preparation of **SP-2**. The structures of the polymers are confirmed spectroscopically and by elemental analysis. Recovered yields after Soxhlet purification were 85 and 80%, respectively.



Scheme 1

Characterization of polymers

^{1}H NMR and FT-IR spectra of intermediates and polymers were recorded on a Varian AM 300 spectrometer and on a Bomem Michelson instrument, respectively . UV-Vis spectra were recorded on a Hewlett Packard HP 8452A Diode Array spectrophotometer. Elemental analysis was performed by the Center for Organic Reactions, Sogang University, Seoul, Korea, using an Eager 200 elemental analyzer. Molecular weights of the polymers were determined by a Waters 745 GPC instrument with a refractive index detector against a polystyrene reference. Tetrahydrofuran was employed as an eluent. Thermal properties of the polymers were examined under a nitrogen atmosphere on a Mettler 821^e and TGA 50 at a heating and cooling rate of 10 °C min^{-1}.

Measurement of 2nd order optical nonlinearity

The 2nd order nonlinear optical properties of polymer films (0.60–0.75 μm thick) were measured by the reflection method[30,31] and the Maker fringe method.[32,33] The polymer solutions (5 wt%) in 1,1,2,2-tetrachloroethane were filtered through 0.2 μm Teflon filters and then the films were prepared by spin-coating onto ITO coated glasses and onto glasses for the reflection method and the Maker fringe method. The first method provides us with electro-optic coefficient (r_{33})[34] and the second method, the second harmonic coefficient[34] (d_{33}; the values were calculated by using Herman and Hayden's theory[35] where the absorption effect was considered at the second harmonic generated frequency of 532 nm). Experimental details of the methods can be found in our previously published papers.[12,13,36,37] The first and the second methods require contact poling and corona poling, respectively. For contact poling, an electric field of 1.0–1.2 MV cm^{-1} was applied to the polymer films between ITO and gold electrodes for 15 min at the glass transition temperature (T_g) of each sample. For corona poling, an electric field of 3.5 kV was applied to the polymer film for 10 min and the distance from a tungsten tip to the sample was 1.5 cm. Poling was conducted at the T_g temperature of each sample. In both cases, the electric field was kept on until the samples were cooled to room temperature after poling. Three lasers (He-Ne, diode, and Nd : YAG) were utilized in this experiment for the wavelengths 633, 1300, 1064 nm, respectively. Refractive indices of polymer films were determined using an ellipsometer (Rudolps-2000, USA) at the Korea Basic Science Institute — Seoul branch. The d_{33} values were estimated relative to the intensity of the second harmonics by a Y-cut quartz plate of 1.025 mm thickness. The d_{11} value of Y-cut quartz plate was taken to be 0.96 × 10^{-9} esu.[38] The temporal stability of some of the poled polymer films was studied either by measuring the decrease in the r_{33} value at 80 °C or by observing the decrease in the intensity ($\sqrt{I_{2\omega}}$) of the second harmonics as the films were stepwise heated from room temperature to 160 °C. The samples were kept at each temperature for 1 h.

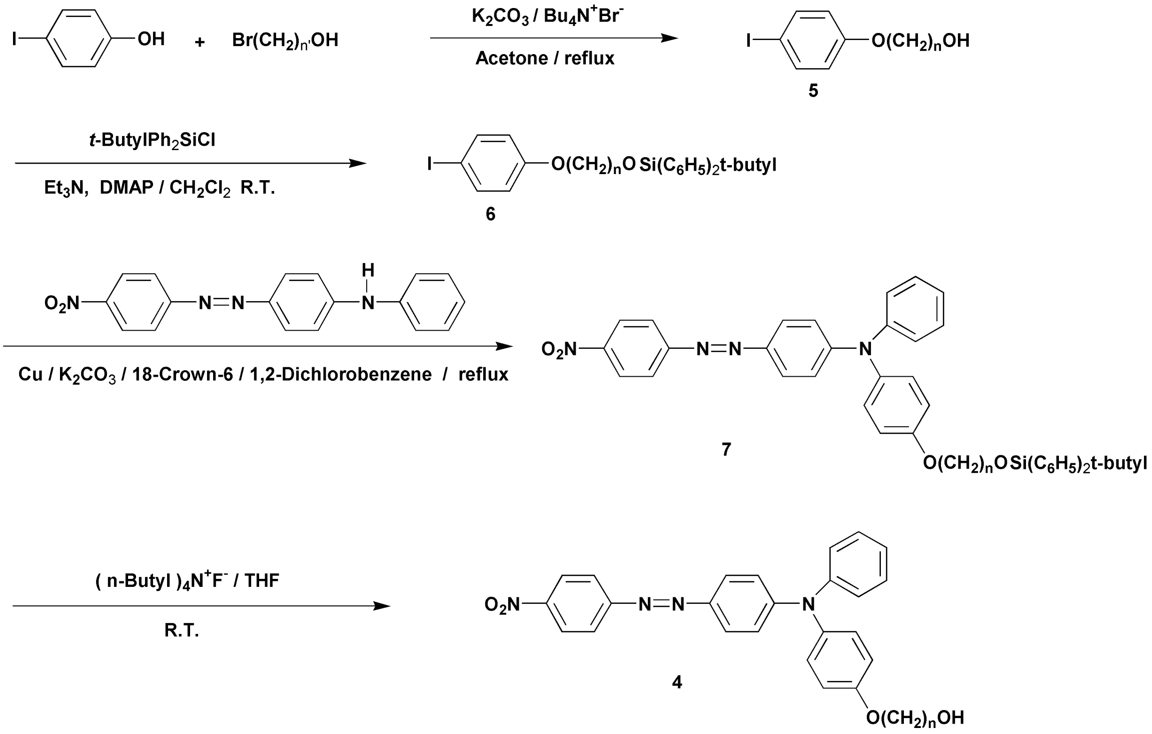
Results and discussion

Synthesis and general properties of SP and EP polymers

In order to prepare the four polyimides, **SP-2**, **SP-6**, **EP-2** and **EP-6**, bearing chromophores as pendants, we had to synthesize separately **PI** (Scheme 1) and the chromophores, [**3**(**2**), **3**(**6**), **4**(**2**), and **4**(**6**)], and then coupling between **PI** and chromophores followed.

As far as the synthesis of the second chromophoric compounds, **4**(**2**) and **4**(**6**), is concerned, the synthetic route (Scheme 2) had to be altered from the route[27,39] to compounds **3**(**2**) and **3**(**6**) as discussed above in Experimental. 4-(ω-Hydroxyalkoxy)iodobenzenes (**5**) were reacted with *tert*-butyldiphenylsilyl chloride to protect the terminal hydroxy group in **5**. The Ullmann coupling[40] between **6** and the azo compound, Disperse orange 1, produced compound **7**, whose silyl protecting group was then removed by fluoride[41] to result in the final chromophore **4**.

The **SP** and **EP** polymers could be readily prepared from **PI** and chromophoric compounds. Condensation between phenolic hydroxy compounds and aliphatic alcohols can be readily performed by using the condensing agent pair, triphenylphosphine and diisopropyl azodicarboxylate. Such condensations are called the Mitsunobu reaction.[29] **PI** contains two phenolic hydroxy groups per repeating unit and the chromophoric azo compounds contains one aliphatic hydroxy



Scheme 2

Table 1 General properties of polymers

Polymer	$M_n{}^a \times 10^3$	$M_w/M_n{}^a$	$(DP)_n{}^a$	T_g/°C^b	T_d/°C^b
PI	20.8	2.2	33	375	—
SP-2	37.7	2.1	25	193	265
SP-6	43.7	2.9	27	152	270
EP-2	44.4	2.8	30	193	305
EP-6	52.5	3.0	32	152	305

[a] Determined against a polystyrene standard by GPC using tetrahydrofuran as an eluent. [b] T_g and T_d stand for the glass transition and initial decomposition temperature, respectively: estimated from the DSC or TGA thermograms, respectively, at the heating rate of 10 °C min^{-1}. The temperature where the initial slope change occurred was taken to be the transition or decomposition temperature.

group. In order to ensure complete reaction, the chromophoric aliphatic alcohols were used in an excess of 50 mole%. Structures of the intermediates and the final polymers were confirmed by ^{1}H-NMR and FT-IR spectroscopy and also by elemental analysis as detailed in the Experimental section.

All the SP and EP polymers were soluble in common organic solvents such as THF, chloroform, 1,1,2,2-tetrachloroethane, and *N*,*N*-dimethylformamide. Average molecular weights of **PI**, **SP** and **EP** polymers were determined by GPC against a polystyrene reference. THF was employed as an eluent. The number average molar mass (M_n) and the weight average molar mass (M_w) of **PI** were 20800 and 45900, respectively. This corresponds to the average degree of polymerization of 33 and polydispersity index of 2.2. Molecular weights of the final **SP** and **EP** polymers determined by GPC were M_n = 37700–52500 and M_w = 80000–162600. As shown in Table 1, these values correspond to an average degree of polymerization of 25–32 and polydispersity indices of 2.1–3.0. Discrepancies between molecular weights and polydispersity indices of **PI** and those of **SP** or **EP** polymers can be ascribed to the fact that all the data for molecular weights were obtained by GPC against polystyrene. Since the chromophores in the **SP** and **EP** polymers are quite bulky and polar, it is highly conceivable that chain conformations, and thus molecular hydrodynamic volumes, of the polymers in THF solutions are not only much different from that of **PI** but also differ greatly between each of the **SP** and **EP** polymers.

All the **SP** and **EP** polymers are amorphous as shown by the X-ray diffractograms in Fig. 2. The diffractograms show only a very broad diffraction in the wide-angle region centered around $2\theta = 20°$ (4.4 Å), which reflects interchain spacing. The starting polymer, **PI**, is also amorphous. The glass transition temperatures given in Table 1 were obtained using DSC at a heating rate of 10 °C min^{-1}. The T_g value of **PI** is the highest, 375 °C, among the polymers. The polymers bearing the chromophore pendants exhibit much lower T_g values due to the increase in their free volume by the presence of the bulky pendants. The longer, hexamethylene spacer in **SP-6** and **EP-6** reduces the T_g value to a greater extent when compared with the shorter, dimethylene spacer in **SP-2** and **EP-2**. One interesting point to note is that the two pairs of **SP-2** and **EP-2**, and **SP-6** and **EP-6** exhibit the same T_g values, 193 and 152 °C, respectively, regardless of the difference in the mode (side-on *vs.* end-on) of binding of the chromophore pendants. The presence of the same polymethylene spacers between the backbone and the chromophore pendants must be the major reason for this observation. Thermal stability of the present polymers is rather poor because the azobenzene moieties undergo thermal decomposition to produce nitrogen and other products. The initial decomposition temperature (265–270 °C) of the **SP** polymers appear to be significantly lower than that (305 °C) of the **EP** polymers: probably side-on attachment of the chromophoric unit to the spacer makes the surroundings around the thermally labile azo group more congested leading to easier decomposition. However, the initial decomposition temperatures (Table 1, 265–305 °C) are much higher than the T_g values. This ensures safe poling of the present polymers at or near their T_g temperatures. At the same time, high T_g values of the polymers are expected to bring about improved temporal stability of molecular orientation of poled polymer films, which is discussed in the next Section.

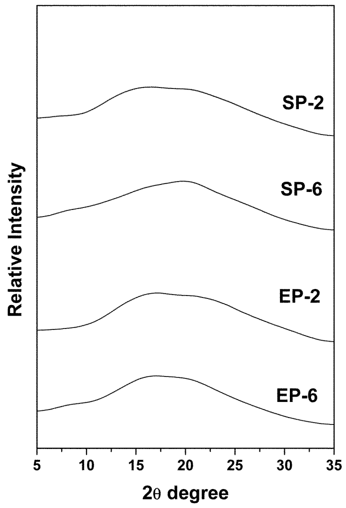


Fig. 2 Wide angle X-ray diffractograms of polymers at room temperature.

Fig. 3 compares the UV-Vis absorption spectra of **SP-6** and **EP-6**. Since spectra of **SP-6** and **EP-6** are exactly the same as those of shorter spacers, only the spectra of these two representative polymers are given. The two spectra given in Fig. 3 are practically the same. They reveal two strong absorptions, one at λ_{max} = 300 nm and the other at λ_{max} = 500 nm. The first absorptions arise from the π–π* transitions of substituted benzenes and the second from π–π* transitions of the delocalized π-systems all over the chromophore structures.

The 2nd order nonlinear optical properties

Fig. 4 show the dependence of the electro-optic coefficient $(r_{33})^{1a}$ values on the applied poling field for the four polymers. The data for r_{33} values were obtained for an incidence wavelength of 633 nm (He-Ne laser, *p*-polarized wave), which is absorbed by the polymers to some extent (7–18%, see Table 2 and Fig. 3). Therefore, the data shown in Fig. 4 are all resonance-enhanced values. At a poling field of 1.0–1.2 MV cm^{-1}, they reveal r_{33} values higher than 100 pm V^{-1} with the value for **EP-2** polymer being particularly greater than that for the **SP-2** polymer at a poling field 1.2 MV cm^{-1}. When the wavelength of the incident light was changed to 1300 nm (diode laser) from 633 nm, significantly lower r_{33} values were obtained. Moreover, the polymer (**SP-2**) bearing the side-on attached chromophore through the shorter dimethylene spacer exhibited a significantly higher r_{33} value of 23 pm V^{-1} at a

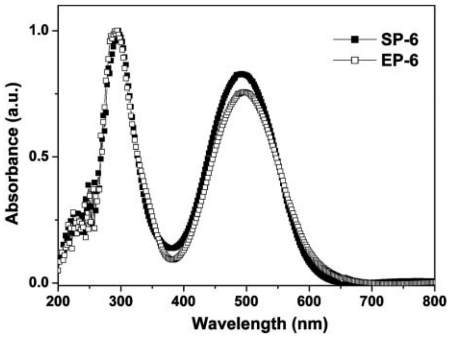


Fig. 3 UV-Visible absorption spectra of **SP-6** and **EP-6**.

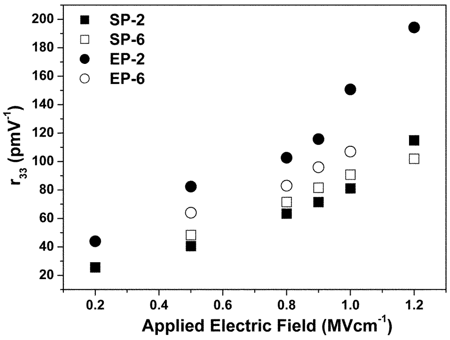


Fig. 4 The electro-optic coefficient r_{33} values of the contact poled polymers obtained for an incident wavelength of 633 nm. The values are relative to that for the Y-cut quartz plate.

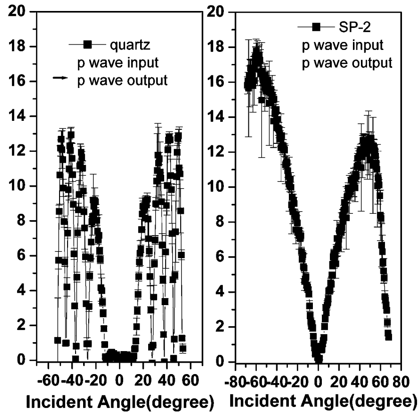


Fig. 5 Maker fringe pattern of the corona poled **SP-2** film and quartz.

poling field of 1.2 MV cm^{-1}, when compared with 16 pm V^{-1} for **EP-2**, that is, the corresponding polymer bearing the end-on attached chromophore. In other words, mode of attachment of the chromophore to the spacer influences NLO properties of the polymers. Since all the polymers do not absorb any light at 1300 nm, the higher r_{33} value for **SP-2** indicates that side-on attachment of the NLO chromophore brings about more efficient orientation than end-on attachment. This effect is not observed when the spacer becomes much longer, from dimethylene to hexamethylene. In other words, the maximum r_{33} values obtained for **SP-6** and **EP-6** are about the same. This must be due to a much higher degree of conformational freedom possible for the longer polymethylene spacers regardless of the mode of attachment of the chromophores.

The second harmonic coefficients, d_{33},[1a] of the **SP-2** and **EP-2** polymers were obtained by the Maker fringe method[32,33] using a Nd : YAG laser beam (1064 nm) with a pulse width of 7 nm. The incident angle was varied from −70° to +70°. Fifty data points were obtained stepwise for every 0.6°. All the data points were calibrated against the second harmonic intensity of Y-cut quartz (1.025 mm thick).

Fig. 5 presents a representative example of a Maker fringe pattern obtained for a corona poled **SP-2** film. The d_{33} values (Table 2) of **SP-2** and **EP-2** were 110 and 86 pm V^{-1}, respectively, for the polymer films poled for 10 min at a corona field of 3.5 kV. Here again, the value for **SP-2** is greater than that for **EP-2**, implying that poling is more efficient for the side-on attached chromophore.

Although we did not try to optimize the poling conditions for the present polymer films in order to achieve as high r_{33} or d_{33} values as possible, the 2nd order NLO coefficients obtained are comparable to those reported for polyimides bearing the same or similar chromophore pendants. For example, a copolymer of disperse red 1 (**DR 1**)-substituted methacrylate and methyl methacrylate, when poled by a corona field, gave d_{33} = 43 pm V^{-1} at 1064 nm and r_{33} = 18 pm V^{-1} at 633 nm.[42]

Recently, Davey *et al.*[16] reported the synthesis of NLO chromophore-embedded polyimides that reveal very high thermal stability in 2nd-order nonlinear optical properties. These polymers, after corona poling, exhibited $\chi^{(2)}$ responses as high as 82 pm V^{-1} and negligible decay at 100 °C over 1000 h. Ueda *et al.*[17] have reported various polyimides bearing two NLO chromophore pendants per repeating group. One of their polymers exhibited a d_{33} value of 138 pm V^{-1} at a wavelength of 1064 nm, which remained unchanged for 360 h even at 160 °C. Shen *et al.*[18] recently prepared a series of polyimides bearing different types of azobenzene or azothiophene type NLO chromophoric pendants. Although the d_{33} values of the polymers are not very high, they appear to be fairly thermally stable. It[19] is also noted that NLO polyimides with dipole moments aligned transverse to the imide linkage show very good temporal stability even at elevated temperatures.

We studied temporal stability of poled polymers by examining the decrease of the r_{33} values at 80 °C as a function of time (Fig. 6) and also by *in situ* observation of decrease in SHG intensity with increasing temperature (Fig. 7). In the latter experiment the polymer films were kept for one hour at each temperature during which time the SHG intensity was continuously monitored. From the former experiments the relaxation rate of the poled NLO chromophores was found to increase in the order of **SP-2** < **EP-2** < **SP-6** < **EP-6**. After 24 hours at 80 °C, they retained 89, 80, 75 and 67% of their original r_{33} values, respectively (see Fig. 6), and the dependence of the relaxation on temperature (Fig. 7) clearly demonstrates a lower thermal stability of chromophore orientation in **EP-2** than in **SP-2**. In other words, longer spacers and end-on attachment of NLO chromophores are less efficient in the stabilization of oriented chromophores. Since the azo

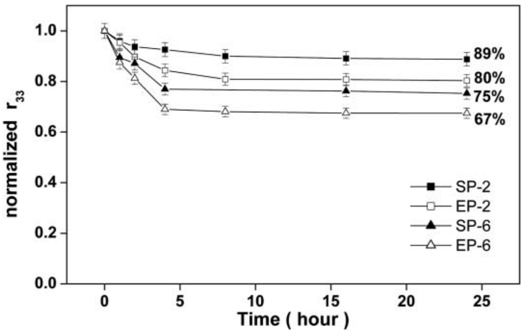


Fig. 6 Thermal stability of the contact poled polymers at 80 °C by the reflection method.

Table 2 Optical properties of polymers

Polymer	Transmittance (%) at 633 nm	r_{33} (pm V^{-1}) at 633 nm	r_{33} (pm V^{-1}) at 1300 nm	d_{33}^{c} (pm V^{-1})	n (532 nm)	n (1064 nm)
SP-2	88	115[a]	23[a]	110	1.78	1.71
SP-6	93	102[a]	8.6[a]	77	1.55	1.55
EP-2	82	194[a]	16[a]	86	1.74	1.63
EP-6	84	107[b]	9.5[b]	59	1.55	1.55

[a]Contact poling at 1.2 MV cm^{-1} for 15 min. [b]Contact poling at 1.0 MV cm^{-1} for 15 min. [c]Corona poling at 3.5 kV cm^{-1} for 10 min.

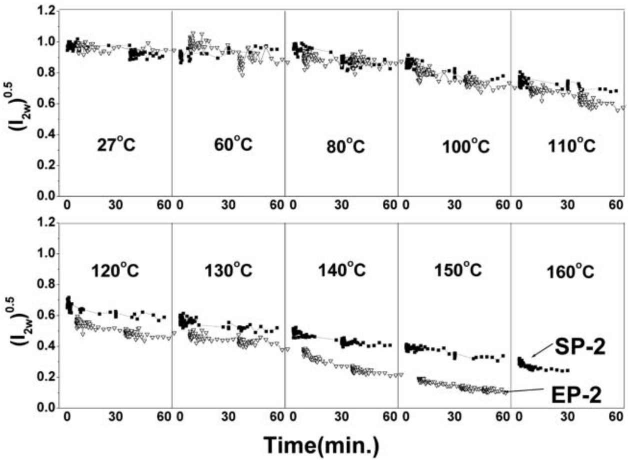


Fig. 7 Thermal stability of the corona poled **SP-2** and **EP-2** polymers at various temperatures by SHG measurement.

chromophores can undergo photo-induced isomerization between the *cis* and *trans* forms, we are presently studying the detailed kinetics of this isomerization, which will be published in the near future.

It is rather puzzling why side-on attachment of chromophores to the spacer results in higher 2nd order NLO values and slower relaxation in chromophore orientation. At the present time, it is conjectured[27] that side-on attachment favours the orientation of the chromophores because both terminal ends are not tied and the central binding site acts as a molecular axle for easier rotation. Once oriented, the chromophores may be in a better orientation for a beneficial interaction with the polyimide main chain, which, in turn, would stabilize the poled state. As stated above, too long a spacer, however, can reduce this positive aspect due to easier conformational changes of the spacer.

Conclusion

We have successfully prepared soluble aromatic polyimides bearing azo NLO chromophores bound to polymethylene spacers either by a side-on or an end-on attachment fashion. The so-called Mitsunobu reaction[29] between the hydroxy-substituted polyimides and aliphatic alcohols bearing chromophores were found to be very useful in preparing the title polymers. All the polyimides were amorphous and exhibited high glass transition temperatures higher than 150 °C. The T_g values did not depend on the mode of binding of the chromophores. The average degree of polymerization was not very high, DP = 25–32, but the polymers were able to form high quality films by spin-coating the solutions in 1,1,2,2-tetrachloroethane. Since the chromophores carry an electron-donating group at one end and an electron-attracting group at the other, their 2nd order nonlinear optical properties were studied by measuring electro-optic coefficients (r_{33}) and second harmonic coefficients (d_{33}) after their films were poled at their T_g. This study demonstrates that side-on attachment of NLO chromophores improves 2nd order optical nonlinearity and temporal stability of their orientation when compared to the case where they were bound in an end-on fashion. This can be explained by easier rotational orientation of the chromophores in the former case. Side-on attachment of chromophores also appears to stabilize their orientation by stronger interactions with the polymer backbone due to parallel alignment.

Acknowledgement

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References

1 (*a*) D. J. Williams (ed.), *Nonlinear Optical Properties of Organic and Polymeric Materials*, ACS Symposium Series, Vol. 233, American Chemical Society, Washington, D. C., 1983; (*b*) P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, John Wiley & Sons, New York, 1991; (*c*) D. C. Chelma and J. Zyss (ed.), *Nonlinear Optical Properties of Molecules and Crystals, vol. 1 and 2*, Academic Press, New York, 1987.

2 G. A. Lindsay and K. D. Singer (ed.), *Polymers for Second-Order Nonlinear Optics*, ACS Symposium Series, Vol. 601, American Chemical Society, Washington, D. C., 1995.

3 D. M. Burland, R. D. Miller and C. A. Walsh, *Chem. Rev.*, 1994, **94**, 31.

4 S. Miyata and X. T. Tao, *Synth. Met.*, 1996, **81**, 99.

5 H. Saadeh, L. Wang and L. Yu, *Macromolecules*, 2000, **33**, 1570.

6 S. R. Marder, B. Kippelen, A. K.-Y. Jen and N. Peyghambarian, *Nature*, 1997, **388**, 845.

7 (*a*) Z. Liang, Z. Yang, S. Sun, B. Wu, L. R. Dalton, S. Garner, S. Kalluri, A. Chen and W. H. Steier, *Chem. Mater.*, 1996, **8**, 2681; (*b*) S. S. H. Mao, Y. Ra, L. Guo, C. Zhang, L. R. Dalton, A. Chen, S. Garner and W. H. Steier, *Chem. Mater.*, 1998, **10**, 146; (*c*) H. Ma, A. K.-Y. Jen, J. Wu, X. Wu, S. Liu, C.-F. Shu, L. R. Dalton, S. R. Marder and S. Thayumanavan, *Chem. Mater.*, 1999, **11**, 2218; (*d*) C. Wang, C. Zhang, M. S. Lee, L. R. Dalton, H. Zhang and W. H. Steier, *Macromolecules*, 2001, **34**, 2359; (*e*) C. Zhang, C. Wang, L. R. Dalton, H. Zhang and W. H. Steier, *Macromolecules*, 2001, **34**, 253.

8 K. S. Lee, K.-J. Moon, H. Y. Woo and H.-K. Shim, *Adv. Mater.*, 1997, **9**, 978.

9 L. P. Yu, W. K. Chan, Z. H. Peng and A. Gharavi, *Acc. Chem. Res.*, 1996, **29**, 13.

10 P. N. Prasad and B. A. Reinhardt, *Chem. Mater.*, 1990, **2**, 660.

11 (*a*) J. Zyss and I. Ledoux, *Chem. Rev.*, 1994, **94**, 77; (*b*) S. Brasselet, F. Cherioux, P. Audebert and J. Zyss, *Chem. Mater.*, 1999, **11**, 1915; (*c*) B. R. Cho, S. B. Park, S. J. Lee, K. H. Son, S. H. Lee, M.-J. Lee, J. Yoo, Y. K. Lee, G. J. Lee, T. I. Kang, M. Cho and S.-J. Jeon, *J. Am. Chem. Soc.*, 2001, **123**, 6421.

12 (*a*) J.-I. Jin and H.-K. Shim, Chapter 17 in ref. 2; (*b*) J.-I. Jin, Y.-H. Lee, B.-K. Nam and M. Lee, *Chem. Mater.*, 1995, **7**, 1897; (*c*) D.-H. Hwang, K.-S. Lee, H.-K. Shim, W.-Y. Hwang, J.-J. Kim and J.-I. Jin, *Macromolecules*, 1994, **27**, 6000; (*d*) J.-I. Jin and Y.-H. Lee, *Mol. Cryst. Liq. Cryst.*, 1994, **247**, 67.

13 Y.-W. Kim, J.-I. Jin, M.-Y. Jin, K.-Y. Choi, J.-J. Kim and T. Zyung, *Polymer*, 1997, **38**, 2269.

14 C. Weder, P. Nenenschwander, U. W. Suter, P. Pretre, P. Kaatz and P. Gűnter, *Macromolecules*, 1994, **27**, 2181 and 1995, **28**, 2377.

15 (*a*) A. Hayashi, Y. Gato, M. Nakayama, H. Sato, T. Watanabe and S. Miyata, *Macromolecules*, 1992, **25**, 5094; (*b*) M.-Y. Jeong, J. W. Wu, J.-I. Jin and H.-G. Kim, *J. Korean Phys. Soc.*, 2000, **37**, 381; (*c*) J. A. F. Boogers, P. Th. A. Klaase, J.-J. de Vlieger, D. P. N. Akema and A. H. Tinnemans, *Macromolecules*, 1994, **27**, 197 and 205; (*d*) M. Ree, T. J. Shin, S. I. Kim, S. H. Woo and D. Y. Yoon, *Polymer*, 1998, **39**, 2521; (*e*) D. Jungbauer, B. Reck, D. Y. Yoon, C. G. Wilson and J. D. Swalen, *Appl. Phys. Lett.*, 1990, **56**, 2610; (*f*) S. Marturunkakul, J. I. Chen, L. Li, R. J. Jeng, J. Kumar and S. K. Tripathy, *Chem. Mater.*, 1993, **5**, 592; (*g*) C. Xu, B. Wu, L. R. Dalton, Y. Shi, P. M. Ranon and W. H. Steier, *Macromolecules*, 1992, **25**, 6714.

16 M. H. Davey, V. Y. Lee, L.-M. Wu, C. R. Moylan, W. Volksen, A. Knoesen, R. D. Miller and T. J. Marks, *Chem. Mater.*, 2000, **12**, 1679.

17 Y. Sakai, M. Ueda, T. Fukuda and H. Matsuda, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 1321.

18 Z. Li, Y. Zhao, J. Zhou and Y. Shen, *Eur. Polym. J.*, 2000, **36**, 2417.

19 N. Tsutsumi, M. Morishima and W. Sakai, *Macromolecules*, 1998, **31**, 7764.

20 D. Yu, A. Gharavi and L. Yu, *J. Am. Chem. Soc*, 1995, **117**, 11680.

21 R. D. Miller, D. M. Burland, M. C. Jurich, C. R. Moylan, J. R. Thackare, R. J. Twieg, T. Verbiest and W. Volksen, *Macromolecules*, 1995, **28**, 4970.

22 T.-A. Chen, A. K.-Y. Jen and Y. Cai, *Macromolecules*, 1996, **29**, 535.

23 A. K.-Y. Jen, V. P. Rao and J. Chandra'sekhar, ref. 2, Chapter 11.

24 H.-J. Lee, M.-Y. Lee, S. G. Han, H.-Y. Kim, J.-H. Ahn, E.-M. Lee

and Y.-H. Won, *J. Polym. Sci., Part A: Polym. Chem.*, 1998, **36**, 301.
25 (*a*) Y. H. Min, K. S. Lee, C. S. Yoon and L. D. Do, *J. Mater. Chem.*, 1998, **8**, 1225; (*b*) D. H. Choi, J. H. Park, T. H. Rhee, N. Kim and S. D. Lee, *Chem. Mater.*, 1998, **10**, 705; (*c*) K. S. Lee, C. J. Wung, P. N. Prasad, J.-C. Kim, C. K. Park, J.-I. Jin and H. K. Shim, *Mol. Cryst. Liq. Cryst.*, 1993, **224**, 33.
26 (*a*) D. H. Choi, J. S. Kang and H. T. Hong, *Polymer*, 2001, **42**, 793; (*b*) N. Tirelli, A. Altomare, R. Solaro, F. Follonier, C. Bosshard and P. Gunter, *Polymer*, 2000, **42**, 415; (*c*) M. Han, S. Morine and K. Ichimura, *Macromolecules*, 2000, **33**, 6360; (*d*) M. S. Ho, A. Natansohn and P. Rochon, *Macromolecules*, 1996, **29**, 44; (*e*) Z. Sekkat and M. Dumont, *Synth. Met.*, 1993, **54**, 373.
27 S. W. Cha, D. H. Choi and J.-I. Jin, *Adv. Funct. Mater.*, 2001, **11**, 355.
28 J. Ma, G. J. Lee, T. K. Lim, B.-J. Chun and J.-I. Jin, *Mol. Cryst. Liq. Cryst.*, 2000, **349**, 47.
29 O. Mitsunobu, *Synthesis*, 1981, 1.
30 C. C. Teng and H. T. Man, *Appl. Phys. Lett.*, 1990, **56**, 1734.
31 J. S. Schildkraut, *Appl. Opt.*, 1990, **29**, 2839.
32 P. D. Maker, R. W. Terhune, M. Nisenho and C. M. Savag, *Phys. Rev. Lett.*, 1962, **8**, 21.
33 J. Jerphagnon and S. Kurtz, *J. Appl. Phys.*, 1970, **41**, 1667.
34 A. F. Garito, K. D. Singer and C. C. Teng, *Molecular Optics: Nonlinear Optical Properties of Organic and Polymeric Crystals,* in ref. 1, Page 2.
35 W. N. Herman and L. M. Hayden, *J. Opt. Soc. Am. B*, 1995, **12**, 3.
36 K.-S. Lee, H. Y. Woo, M.-Y. Jeong, T. K. Lim, K.-J. Moon, H.-K. Shim and S.-W. Choi, *J. Opt. Soc. Am. B*, 1998, **15**, 393.
37 T. K. Lim, M.-Y. Jeong, C. Song and D. C. Kim, *Appl. Opt.*, 1998, **37**, 1223.
38 R. W. Boyd, *Nonlinear Optics*, Academic Press, Inc., San Diego, 1992, Page 52.
39 S. W. Cha, D. H. Choi and J.-I. Jin, *Adv. Funct. Mater.*, submitted.
40 R. D. Miller, D. M. Burland, M. Jurich, V. Y. Lee, C. R. Moylan, R. J. Twieg, J. Thackara, T. Verbiest, W. Volksen and C. A. Walsh, ref. 2, Chapter 10.
41 S. Hanessian and P. Lavallee, *Can. J. Chem.*, 1975, **53**, 2975.
42 Y. Shuto, M. Amano and T. Kaino, *Jpn. J. Appl. Phys.*, 1991, **30**, 320.