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Synthesis and characterization of novel polyamides carrying NLO moieties

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A series of novel polyamides carrying NLO chromophores were synthesized and their general properties were characterized. The electrooptic properties of a couple of selected compositions were studied. These polyamides were synthesized by direct polycondensation at 100°C of 4,4′-methylenedianiline or 4,4′-oxydianiline with 4-nitro-[*N*,*N*-bis(2-carboxyethyl)]aniline or 4-[*N*,*N*-bis(2-carboxyethyl)amino]-4′-nitrostilbene in the presence of a condensing agent composed of lithium chloride and triphenyl phosphite. All of the polymers were found to be amorphous and their glass transition temperatures were about 160°C. In contrast, the polymer that does not carry the nitro group in the phenyl ring of the side group revealed a T_g value of only 78°C. This difference strongly indicates that the nitro group is involved in the formation of hydrogen bonds and, thus, hinders the chain mobility resulting in the enhanced T_g values. This could be confirmed by the i.r.-spectroscopic analysis of the polymers. The u.v.-vis. absorption characteristics of the polyamides also were studied. The second-order nonlinear optical properties of the thin films of two selected polymers of better solubility were studied by measuring their electrooptic coefficients after being poled at the temperatures near their T_gs. When the polymer films were poled at the field strength of 0.4–0.6 $\mathrm{MV\,cm^{-1}}$, their electrooptic coefficients obtained for the incident beam of 1.3 μm were about 3 $\mathrm{pm\,V^{-1}}$ and they showed an excellent temporal stability even at 80°C. © 1997 Elsevier Science Ltd.

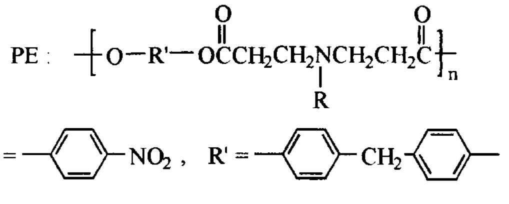
(Keywords: polyamides; NLO chromophore; 4-nitro[*N*,*N*,-bis(2-carboxyethyl)]aniline)

INTRODUCTION

Organic polymers carrying chromophores of nonlinear optical (NLO) characteristics are attracting much scientific interest because of their potential applications in various electrooptic devices[1–9]. Their advantages over inorganic materials are easier processability and high NLO activities. In order to achieve a high second order NLO activity, one usually has to rely on poling of thin polymer films inducing an alignment of chromophores. Such an alignment of chromophores will provide us noncentrosymmetric structures necessary for the second-order NLO activity. The long term stability of orientation of chromophores, however, is rather poor due to their relaxative reorientation at room and elevated temperatures, unless relaxation movements of chromophores are suppressed through special approaches such as crosslinking of polymer chains[10–15], increase in chain rigidity[16] and reduction of chain mobility by interchain hydrogen bondings[17,18]. The last approach, however, has not yet been explored intensively.

In this report, we would like to describe the synthesis of a series of polyamides (PA-1–PA-5, see *Table 1*) carrying NLO chromophores and their properties. Since PA-1 and PA-3 could produce high quality, poled thin films, the second-order NLO properties of the films thereof were studied by measuring their electrooptic coefficient for the incident light of 1.3 μm. PA-5 was included in this study for the sake of comparison of structural characteristics which does not carry the nitro group in the side pendent.

The following polyester, PE, was also synthesized in order to compare its properties with the corresponding polyamide, PA-1.



$$\mathrm{PE}:\ \left[\!-\mathrm{O{-}R'{-}O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_2CH_2}\underset{\mathrm{R}}{\underset{|}{\mathrm{N}}}\mathrm{CH_2CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\right]_n$$

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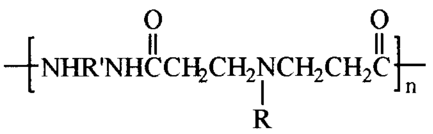
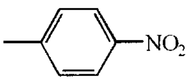
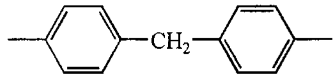
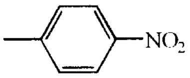
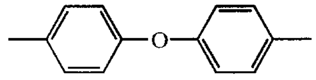
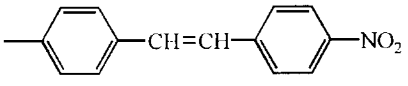
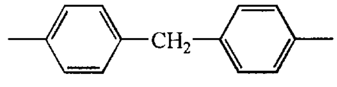
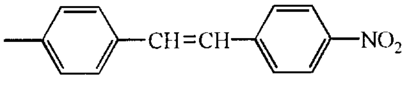
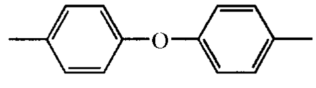
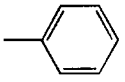
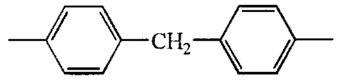
Table 1 Polyamides PA-1–PA-5



$$\left[NHR'NH\overset{O}{\overset{\|}{C}}CH_2CH_2\underset{R}{\underset{|}{N}}CH_2CH_2\overset{O}{\overset{\|}{C}} \right]_n$$

	R	R'
PA-1 :		
PA-2 :		
PA-3 :		
PA-4 :		
PA-5 :		

EXPERIMENTAL

Materials and methods

The reagents such as 4,4′-methylenedianiline (MDA), 4,4′-oxydianiline (ODA), 4-nitroaniline, 4-nitrobenzylbromide, 4-acetamidobenzaldehyde, lithium chloride and sodium hydride were purchased from Aldrich Chemical Co. Acrylic acid, pyridine, 1-methyl-2-pyrrolidone (NMP), triphenylphosphite (TPP) and triethylphosphite (TEP) were purified by vacuum distillation before use. ^{1}H n.m.r. and i.r. spectra were recorded on a FT-80A 300 MHz instrument and on a Schimadzu IR-435 spectrophotometer, respectively. Elemental analyses were performed using the Perkin–Elmer EA-240 instrument. U.v.-vis. spectra were recorded on a Schimadzu UV-240 spectrophotometer. D.s.c. measurements were performed on a Du Pont 910 under nitrogen at a heating rates of 10°C min^{-1}. T.g.a. measurements were carried out on a Du Pont 951 under nitrogen at a heating rate of 10°C min^{-1}. Wide angle X-ray diffractrograms were obtained using nickel-filtered Cu*Kα* ($\lambda = 1.5409$ Å) radiation on a Rigaku Geiger X-ray diffractometer. Inherent viscosities were measured at a polymer concentration of 0.5 g dl^{-1} in *N,N*-dimethylformamide (DMF) at 25°C using a Cannon–Fenske viscometer. Thicknesses of the polymer films were measured by using an Alpha step 200 profilometer. Refractive indices were measured by prism coupling method[19].

Synthesis of monomers

N,N-Bis(2-carboxyethyl)amino-4-nitrobenzene (**1**, BANB). This compound was synthesized from 4-nitroaniline and acrylic acid via simple addition reaction[20]. The crude product was recrystallized from ethyl acetate/*n*-hexane (1/1 by vol.). Its structure was confirmed by elemental analysis and ^{1}H n.m.r.-spectroscopy; mp 168–169°C.

Anal. Calcd. for **1** ($C_{12}H_{14}N_2O_6$): C 51.06, H 4.96, N 9.93%. Found: C 51.27, H 4.85, N 9.85%. ^{1}H n.m.r. (acetone-d_6, ppm) δ 8.20 (*d*, 2H, ArH), 6.75 (*d*, 2H, ArH), 3.85 (*t*, 4H, NCH_2), 2.72 (*t*, 4H, $COCH_2$).

4-[*N,N*-Bis(2-carboxyethyl)amino-4′-nitrostilbene (**2**, BANS). 4-Amino-4′-nitrostilbene[21] (2.4 g; 0.01 mol) was dissolved in acrylic acid (7.2 g; 0.1 mol). The mixture was heated to and maintained at 95°C for 3 h, after which it was cooled to room temperature. The resulting precipitate was collected on a filter followed by washing with water. The crude product was recrystallized from acetic acid. Yield was 3.3 g (85%); mp 187–190°C.

Anal. Calcd for **2** ($C_{20}H_{20}N_2O_6$): C 62.50, H 5.21, N 7.29%. Found: C 62.25, H 5.17, N 7.35%. ^{1}H n.m.r. (DMSO-d_6, ppm) δ 8.20 (*d*, 2H, ArH), 7.75 (*d*, 2H, ArH), 7.55 (*d*, 2H, ArH), 7.45 (*d*, 1H, $-C=CH$), 7.15 (*d*, 1H, $-CH=C$), 6.85 (*d*, 2H, ArH), 3.75 (*t*, 4H, $2NCH_2$), 2.65 (*t*, 4H, $2COCH_2$).

N,N-Bis(2-carboxyethyl)aminobenzene (**3**, BAB). This compound was prepared from aniline and acrylic acid at 65°C in the similar manner as described in the preparation of **2**; mp 116–117°C. Its structure was confirmed by elemental and spectroscopic analyses.

Anal. Calcd for **3** ($C_{12}H_{15}NO_4$): C 60.76, H 6.33, N 5.92%. Found: C 60.36, H 6.31, N 5.71%. ^{1}H n.m.r. ($CDCl_3$, ppm) δ 12.29 (*s*, 2H, 2COOH), 7.17 (*d*, 2H, 2ArH), 6.65 (*m*, 3H, 3ArH), 3.56 (*t*, 4H, $2NCH_2$), 2.48 (*t*, 4H, $2COCH_2$).

Synthesis of polyamides and a polyester

All of the polyamides were prepared by direct polycondensation of dicarboxylic acids and aromatic diamines[22,23]. A typical polymerization procedure is given for the synthesis of PA-1. BANB (**1**) (0.50 g, 2.0 mmol), LiCl (0.40 g), TPP (1.2 g) and MDA (0.396 g, 2.0 mmol) were placed into a 100 ml three-necked flask equipped with a magnetic stirrer, nitrogen inlet and a septum. Pyridine (2 ml) and NMP (8 ml) were introduced into the flask using a syringe. The reaction mixture was stirred at 100°C for 24 h under a nitrogen atmosphere and cooled to room temperature. And then, the mixture was poured into excess ice water. The precipitate was washed with acetone, dried in vacuum to yield the yellowish polymer, PA-1 (0.615 g, 85%); ^{1}H n.m.r. (DMSO-d_6, ppm) δ 10.0 (*s*, 2H, 2NH), 8.05 (*d*, 2H, 2ArH), 7.45 (*d*, 4H, 4ArH), 7.10 (*d*, 4H, 4ArH), 6.85 (*d*, 2H, 2ArH), 3.8 (*m*, 6H, $2NCH_2$ + Ar–CH_2–Ar), 2.65 (*t*, 4H, $2C(O)CH_2$); i.r. (KBr, cm^{-1}) 3400 (N-H stretching), 1663 (C = O stretching), 1512 and 1312 (N-O stretching).

PA-2 was synthesized from BANB (**1**) and ODA by the same procedure. It is a yellowish polymer. The yield was 92%. ^{1}H n.m.r. (DMSO-d_6, ppm) δ 10.10 (*s*, 2H, 2NH), 8.05 (*d*, 2H, 2ArH), 7.55 (*m*, 4H, 4ArH), 6.90 (*m*, 4H, 4ArH), 6.70 (*d*, 2H, 2ArH), 3.80 (*t*, 4H, $2NCH_2$), 2.70 (*m*, 4H, $2C(O)CH_2$); i.r. (KBr, cm^{-1}) 3314 (N-H stretching), 1663 (C = O stretching), 1501 and 1312 (N-O stretching).

Reddish brown PA-3 was obtained from BANS (**2**) and MDA, and the yield was 92%. ^{1}H n.m.r. (DMSO-d_6, ppm) δ 9.85 (*s*, 2H, 2NH), 8.10 (*d*, 2H, 2ArH), 7.65 (*d*, 2H, 2ArH), 7.42 (*m*, 7H, 6ArH + C = CH), 7.00 (*m*, 5H, 4ArH + CH = C), 6.70 (*d*, 2H, 2ArH), 3.60–3.70 (*m*, 6H, Ar–CH_2–Ar + $2CH_2N$), 2.50 (*t*, 4H, $2CH_2C(O)$); i.r. (KBr, cm^{-1}) 3387 (N–H stretching), 1663 (C = O stretching), 1610 (C = C stretching), 1512 and 1331 (N–O stretching), 960 (= C–H out-of-plane bending).

The yield of reddish brown PA-4 obtained from BANS (**2**) and ODA was 90%. ^{1}H n.m.r. (DMSO-d_6, ppm) δ 10.05 (*s*, 2H, 2NH), 8.05 (*d*, 2H, 2ArH), 7.70 (*d*, 2H, 2ArH), 7.45–7.55 (*m*, 7H, 6ArH + CH = C), 6.95 (*m*, 5H, 4ArH + CH = C), 6.70 (*d*, 2H, 2ArH), 3.65 (*t*, 4H, $2CH_2N$), 2.55 (*t*, 4H, $2CH_2C(O)$); i.r. (KBr, cm^{-1}) 3267 (N–H stretching), 1662 (C = O stretching), 1605 (C = C stretching), 1497 and 1331 (N–O stretching), 971 (= C–H out-of-plane bending).

Yellowish PA-5 was prepared from BAB (**3**) and MDA, and the yield was 95%. ^{1}H n.m.r. (DMSO-d_6, ppm) δ 9.93 (*s*, 2H, 2NH), 8.05 (*d*, 2H, 2ArH), 7.45 (*d*, 4H, 4ArH), 7.10 (*d*, 4H, 4ArH), 6.85 (*d*, 2H, 2ArH), 3.80 (*s*, 2H, Ar–CH_2–Ar), 3.62 (*s*, 4H, $2NCH_2$), 2.50 (*s*, 4H, $2C(O)CH_2$); i.r. (KBr, cm^{-1}) 3260 (N-H stretching), 1659 (C = O stretching).

Polyester PE was synthesized by polycondensation of BANB (**1**) and 4,4′-dihydroxydiphenylmethane at 80°C using thionyl chloride in pyridine according to the literature procedure[24]. PE is yellowish in colour and its yield was 60%. ^{1}H n.m.r. (DMSO-d_6, ppm) δ 8.06 (*d*, 2H, 2ArH), 7.60 (*d*, 4H, 4ArH), 7.23 (*d*, 4H, 4ArH), 6.53 (*d*, 2H, 2ArH), 3.80 (*s*, 2H, Ar–CH_2–Ar), 3.00 (*m*, 4H, $2OCH_2$), 2.65 (*t*, 4H, $2C(O)CH_2$); i.r. (KBr, cm^{-1}) 1749 (C = O stretching), 1509 and 1336 (N–O stretching), 1163 (C–O stretching).

Measurement of electrooptic coefficients

Polymer films were prepared by spin-coating polymer solutions in DMF onto ITO glass plate. The polymer solutions (20 wt%) were first filtered through a 0.45 μm Teflon membrane filter to remove insoluble particles, then spun in a spin coater at 800–2000 rpm for 5–15 s depending on the desired thickness. And the films obtained were finally dried in a vacuum oven at 150°C for 24 h. After an aluminium electrode was built on the polymer films by thermal evaporation, electrode poling was conducted near T_g of polymers at an applied voltage of 0.2–0.3 kV with a poling current less than 0.2 mA.

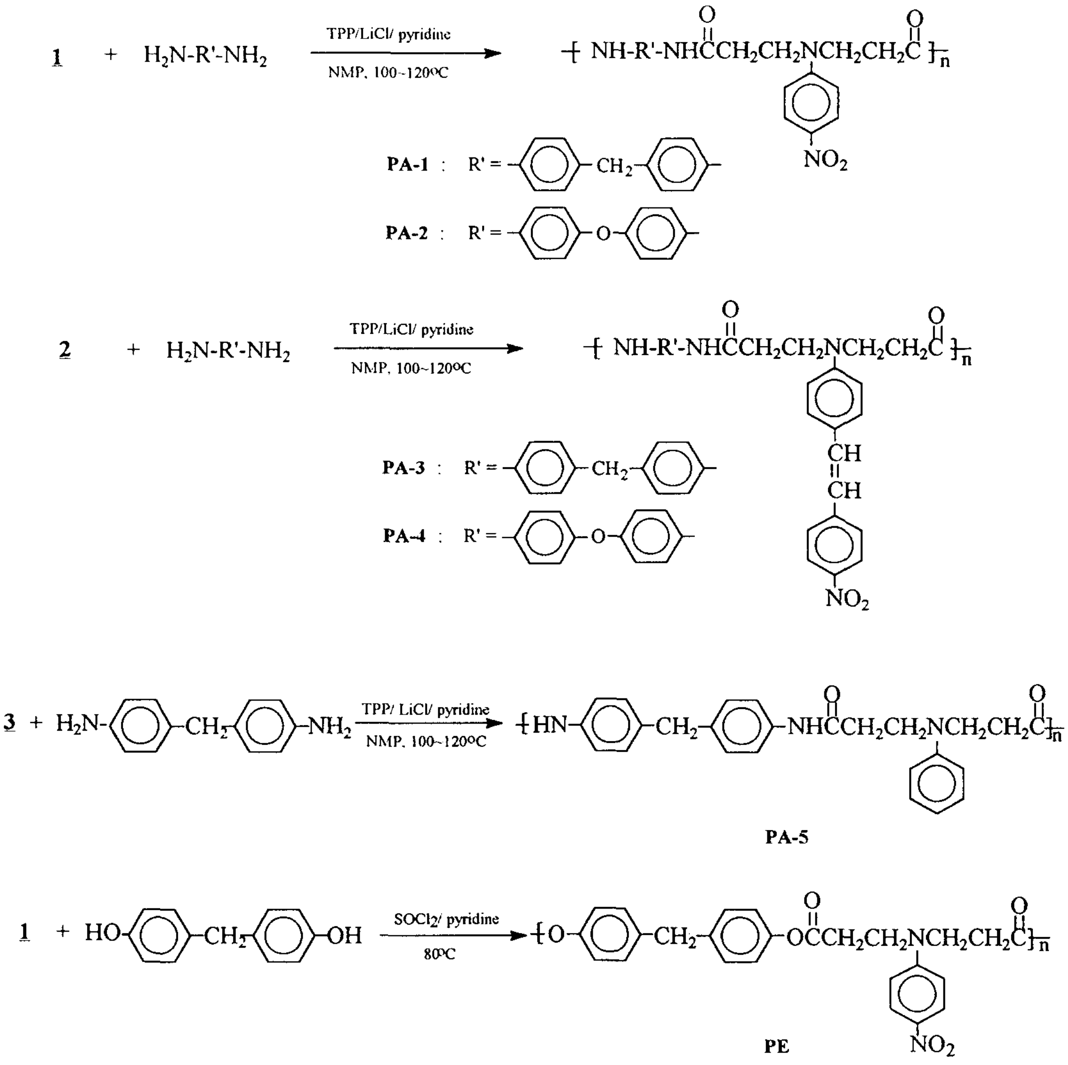
Electrooptic coefficients of the poled polymers were measured by the reflection measurement technique[25,26]. A He–Ne laser beam (632.8 nm) was employed as the incident light. The input beam was set at 45° to the plane of incidence so that the parallel (*p*-wave) and perpendicular (*s*-wave) components of the optical field were equal in amplitude. The reflected beam propagated through a Solei–Babinet compensator, an analyser and into a detector. The modulation in the beam was measured using a lock-in amplifier.

RESULTS AND DISCUSSION

Synthesis and general properties

All of the polyamides were prepared by direct polycondensation of dicarboxylic acids, **1–3**, carrying NLO moieties and aromatic diamines in the presence of a mixture consisting of lithium chloride, pyridine and triphenylphosphite, which was reported by Yamazaki *et al.*[22] to be an excellent condensing agent. The synthetic routes to the polymers are shown in *Scheme 1*. This synthetic approach is rather simple and was found to be satisfactory in the present synthesis. All of the polymers are soluble in such common solvents as DMF, NMP, DMSO and *N,N*-dimethylacetamide (DMAc), but insoluble in benzene, chloroform and acetonitrile. However, the MDA-based polymers (PA-1, PA-3 and PA-5) appeared to be more readily soluble than the ODA-based counterparts. Although the solution viscosity values (0.2–0.3 dl g^{-1}; *Table 2*) of the polymers obtained are not very high suggesting that their molecular weights are not very high, PA-1 and PA-3 produced thin films of high quality suitable to measurements of optical properties. Therefore, we did not try to optimize synthetic conditions to improve their molecular weights any further. The only polyester, PE, was prepared by directly condensing dicarboxylic acid, **1** (BANB) with MDA in the presence of a condensing agent composed of pyridine and thionyl chloride[24] (refer to *Scheme 1*). This polymer does not contain any amide group along the chain and it was prepared to compare its properties with those of the corresponding polyamide PA-1.

According to wide angle X-ray diffractometry (*Figure 1*) and differential scanning calorimetry (*Figure 2*) of the polymers, all of them appear to be amorphous, although we have not tried to induce their crystallization by thermal annealing. Cooling the polymer samples in the d.s.c. cell did not, however, exhibit any crystallization peak (exotherm) implying their poor crystallizing tendency, if any. The glass transition temperatures (T_gs) of PA-1 through PA-4 are about 160°C or slightly higher. In contrast, the T_g values of PA-5 and PE are much lower, 78 and 83°C, respectively. The major structural difference between these two groups lies in the fact the former contains nitro substituents in the pendant phenyl rings, whereas the latter either do not carry nitro pendent groups (PA-5) or do not contain amide protons along the chain (PE). This strongly indicates that the nitro groups in the former are involved in intra- and inter-chain hydrogen bondings with the amide protons along the chains and cause diminished chain mobility. This would result in enhanced T_g values as observed. It is rather surprising that the T_g value of PA-5, a polyamide, is



Scheme 1

Table 2 Synthetic results and physical properties of polyamides and polyester

Polymers	Yield (%)	Viscosity[a] [η] (dl^{-1} g)	T_g^b (°C)	U.v.-vis. data[c] λ (nm)	ε ($mol^{-1} cm^{-1}$)	Edge (nm)
PA-1	85	0.23	157	404	14320	480
PA-2	92	0.21	165	403	19090	480
PA-3	92	0.28	164	458	47750	600
PA-4	90	0.26	167	456	43290	600
PA-5	95	0.30	78	–	–	–
PE	60	0.15	83	387	12000	460

[a] Measured at the concentration of 0.5 g dl^{-1} in DMF solution at 25°C
[b] Determined by d.s.c. analysis at the heating rate of 10°C min^{-1} under nitrogen
[c] Measured for DMF solutions

more or less the same as the value of PE, a polyester. PE is not able to form hydrogen bonds either of inter- or intra-chain fashion. On the other hand, PA-5, a polyamide, contains amide groups along the chain, which are expected to be involved in the formation of hydrogen bonds. The low T_g value of PA-5 that is almost the same as the PEs T_g, however, suggests that the amide groups in PA-5 somehow are not able to do so. Or they may be able to do so only to a slight extent. The most

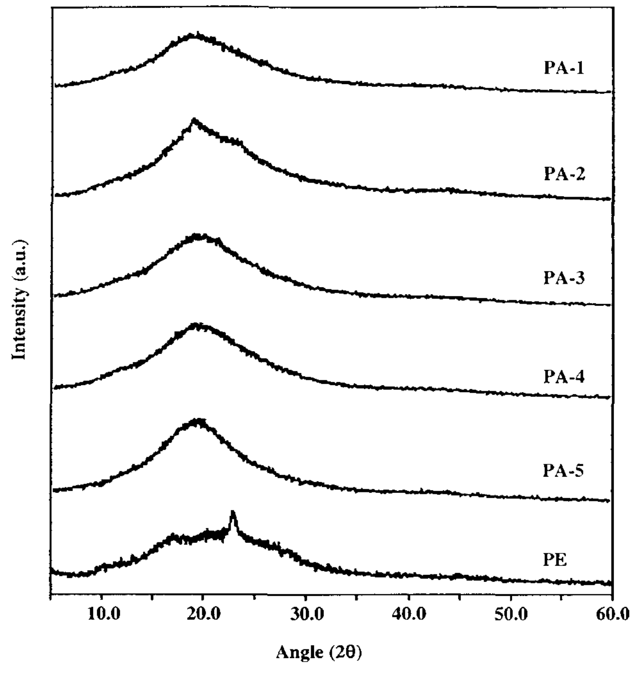


Figure 1 Wide angle X-ray diffractograms of polymers

plausible explanation for this can be found in the bulkiness of the phenyl group on the nitrogen atom in the dicarboxylic acid moiety, which prevents the amide groups from forming hydrogen bonds or at least lessens the amide groups' tendency to form them.

Participation of nitro groups in the formation of hydrogen bonds is reflected in *FT*i.r. spectra of the polymers. For example, the absorption owing to the symmetric N–O stretching of PE occurs at 1336 cm^{-1}, while that of PA-1 is red-shifted and appears at 1310 cm^{-1} (*Figure 3*). It is well known that, when the NO_2 group is involved in hydrogen bond formation, its i.r. absorption for the symmetric stretching mode is shifted to red[27] as observed for PA-1 relative to PE.

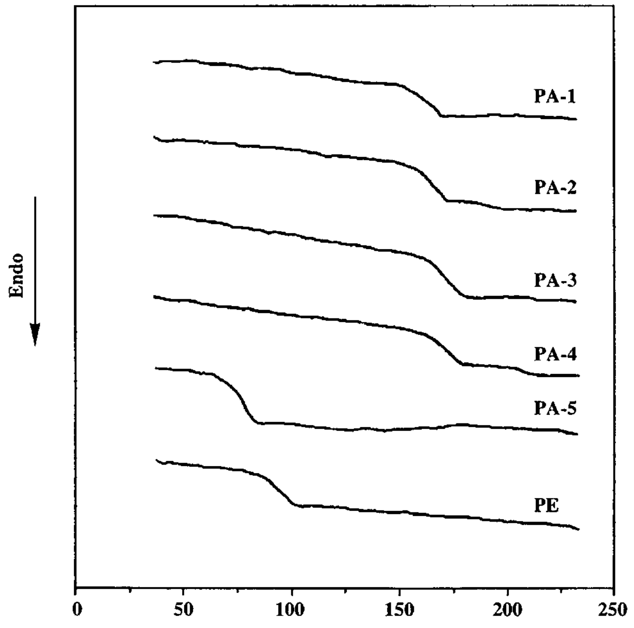


Figure 2 D.s.c. thermograms of polymers (heating rate 10°C min^{-1} under nitrogen)

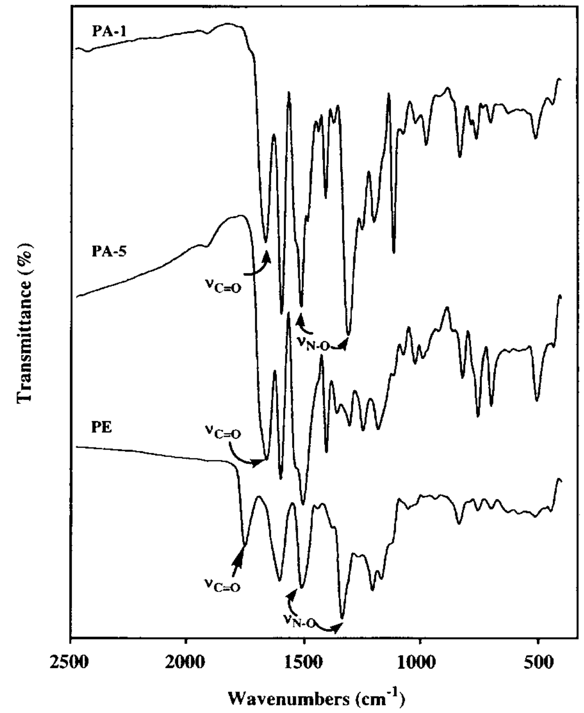


Figure 3 I.r. spectra of polymers

Figure 4 compares the u.v.-vis spectra of the polymers: PA-3 and PA-4 exhibit absorptions corresponding to π–π* transition of the 4-amino-4′-nitrostilbene[28] moiety, whose maxima are located at about 455 nm. The λ_{max} positions of PA-1 and PA-2 appear at much shorter wavelength, 403 nm. This absorption is due to the π–π* transition of the *p*-nitroaniline[28] moiety. The absorption of the polyester PE is significantly shifted to blue when compared with PA-1 and PA-2. As one can expect, the molar absorptivities of PA-3 and PA-4 are much higher than others (*Table 2*) due to the stilbene structures.

Nonlinear optical properties of PA-1 and PA-3

For the electrooptic experiment, only PA-1 and PA-3 that are MDA-based polyamides were chosen because of their better solubilities. Polymer films 1–4 μm thick were prepared from 20 wt% DMF solutions by spin-coating on ITO glasses and dried at 150°C. The refractive indices of the polymer films were measured by *m*-line method at various wavelength[19]. The values for PA-3 thus obtained are 1.688 at 0.83 μm and 1.660 at 1.3 μm. The values for PA-1 are slightly lower: 1.659 at 0.83 μm and 1.641 at 1.3 μm. After the polymer films were poled at a poling electric field of 0.4–0.6 MV cm^{-1} for 10 min, the electrooptic coefficients were measured using simple reflection measurement technique[25,26] and were estimated by using[25]

$$r_{33} = \frac{3\lambda I_m}{4\pi V_m I_c n^2} \frac{(n^2 - \sin^2\theta)^{3/2}}{(n^2 - 2\sin^2\theta)} \frac{1}{\sin^2\theta}$$

where λ is the optical wavelength, I_m the amplitude of the modulation, I_c the half-intensity point, V_m the modulating voltage, and n the refrative index.

The r_{33} values thus obtained for the PA-1 film poled in the electric field of 0.4 MV cm^{-1} are 3.2, 2.3 and 2.1 pm V^{-1} respectively for the incident laser wavelength of 0.63 0.83 and 1.3 μm. In contrast, the r_{33} values of poled PA-3 film poled in 0.6 MV cm^{-1} are 4.6 and 3.3 pm V^{-1} respectively for the incident wavelength of 0.83 and 1.3 μm. The r_{33} values of PA-3 are higher because hyperpolarizability of BANS (**1**) should be similar to that of DANS which shows a higher value than that of dimethylaminonitrobenzene[29] whose moiety is the chromophore unit in PA-1. The r_{33} values of PA-3, however, are not so high as expected. The main reason for this can be found in the fact that the dipole orientation or poling is expected to be more difficult for PA-3 than PA-1, because PA-3 requires the rotation of much bulkier structural units than PA-1. Another point to be noted is the fact that the strength of poling fields utilized in the present investigation is rather low, which, in turn, resulted in rather low r_{33} values for PA-1 and PA-3. We, however, did not try to optimize the poling conditions, because the main objective of this investigation was to clarify the influence of hydrogen bond formation on the temporal stability of aligned chromophores. Wnek *et al.*[30] reported that a polyurethane carrying the same NLO chromophores as in PA-3 revealed a significant higher second harmonic generation property ($d_{33} = 23.7 \times 10^{-9}$ esu) than that ($d_{33} = 4.62 \times 10^{-9}$ esu) containing the *p*-nitroaniline unit. They poled their polymer films by corona treatment.

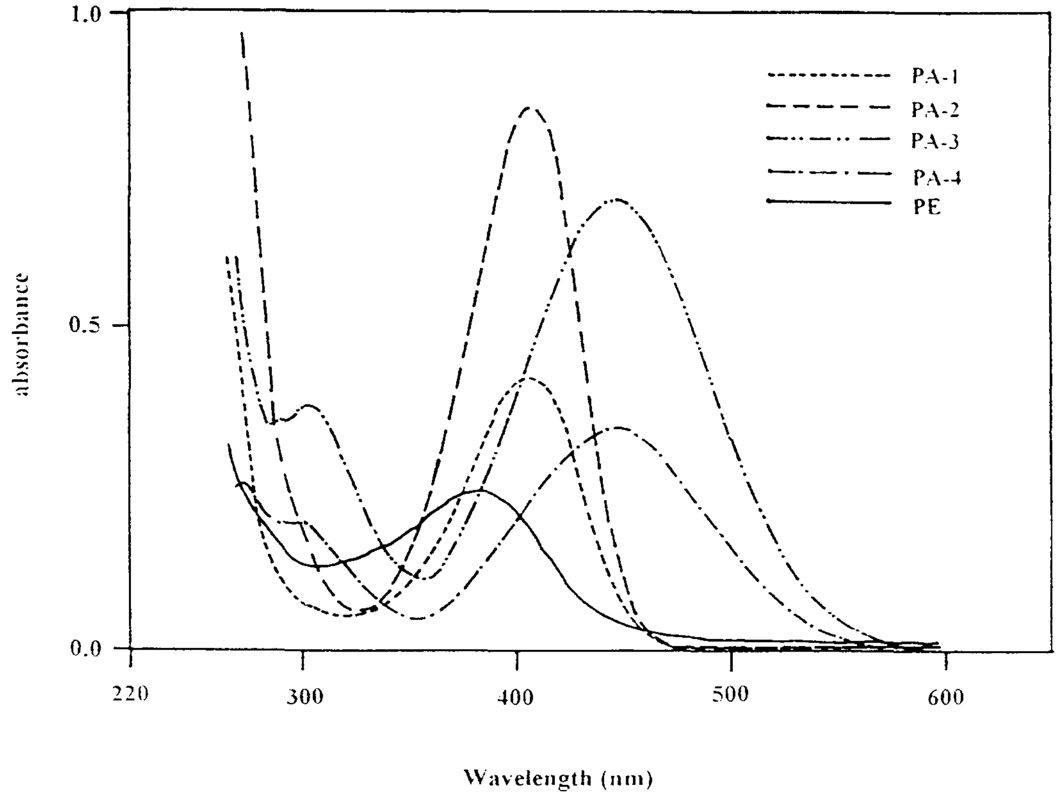


Figure 4 U.v.-vis spectra of polymers

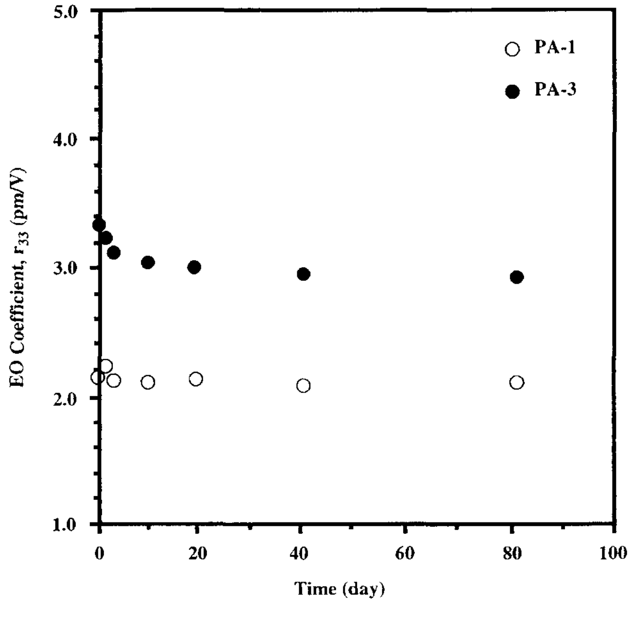


Figure 5 EO coefficients, r_{33}, of PA-1 and PA-3 measured at room temperature as a function of time

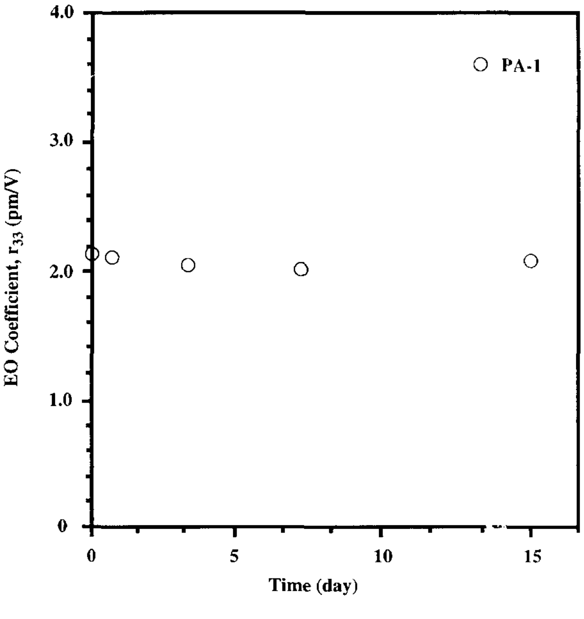


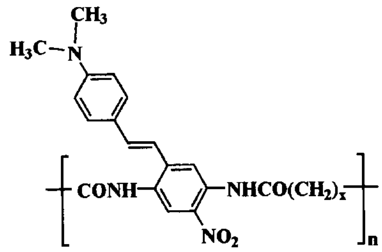
Figure 6 EO coeffients, r_{33}, of PA-1 measured at 80°C as a function of time

The r_{33} values of PA-3 remained constant over a period of more than 80 days at room temperature (*Figure 5*). Moreover, as shown in *Figure 6*, the electro-optic response of the poled PA-1 film retained its initial optical nonlinearity even after being kept at 80°C for 360 h.

This excellent temporal stability in the r_{33} values of these poled polymer films is attributed to the direct attachment of the chromophores to the polymer backbone. There is no spacer group between the chromophore and the polymer backbone, and, thus, molecular relaxation of the aligned chromophores is hindered. In addition, the presence of the secondary forces, or formation of hydrogen bondings, is another stabilizing factor. We[31–34] have clearly demonstrated recently that a rigid polymer backbone can lead to an improved temporal stability of aligned chromophores.

Suter *et al.*[35,36] recently reported the second-order nonlinear optical (second harmonic generation) properties of polyamides based on 2′,5′-diamino-4-(dimethylamino)-4′-nitrostilbene. These polymers contain the

NLO-phores as part of the polymer backbone with their dipoles oriented transversely to the polymer main chain, as shown below:



Second-order nonlinear optical coefficients (d_{33}) of up to 40 pm V^{-1} at a fundamental wavelength of 1542 nm were reported. The values are much higher than those obtained by us for the present polymers. One of the main reasons for the lower values reported in this report can be ascribed to the relatively low poling field strength utilized. We believe that improvement in the quality of polymer films and optimization of the poling condition will definitely provide us with higher values. Another interesting comparison to be made between the present polymer and those reported by Suter *et al.* lies in the fact that the positions of dialkylamino and nitro groups are reversed. In the present polymers nitro groups are located further apart from the backbone, which, in turn, is expected to promote more ready interchain hydrogen bond formation resulting in temporal stability of aligned chromophores as discussed above.

CONCLUSION

A series of new polyamides consisting of alternating aromatic and aliphatic structural moieties and having relatively high T_g values have been prepared and characterized. The dicarboxylic acid moieties of the polymers carry NLO chromophores either of *N*,*N*-dialkylamino-*p*-nitroaniline (DANA) residue or of 4′-(*N*,*N*-dialkylamino)-4-nitrostilbene (DANS) residue. For the sake of comparison, a corresponding polyester and a polyamide that do not carry the pendent nitro group on the chromophore also were prepared. According to the higher T_g values and i.r.-spectroscopic analysis of the polymers, it is believed that the pendent nitro groups are involved in the formation of hydrogen bonds with amide hydrogen atoms. Such a hydrogen bond formation in addition to the hydrogen bond formation between amide groups lead to the stabilizing or reduced relaxation of dipole alignment induced by electric poling. This conjecture can be supported by the temporal stability observed for NLO behaviour of two polymers, PA-1 and PA-3. PA-1 exhibits r_{33} value of about 2–3 pm V^{-1}, whereas PA-3 about 3–5 pm V^{-1}. These are understandable results because the DANS moiety should have a significantly higher permanent dipole moment than the DANA moiety, which in turn is expected to result in a higher r_{33} values for PA-3 as observed in this work.

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