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Simple synthetic route to soluble polyimides *via* nitro-displacement reaction and their second-order nonlinear optical properties

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Nonlinear optical (NLO) functionalized polyimides were directly synthesized using the nitro-displacement reaction between an alkanediol monomer and a diimide monomer without a thermal curing step. The polyimides were soluble in aprotic polar solvents such as DMSO, DMAc, DMF and NMP, and showed glass transitions at temperatures between 172 and 198 °C. We observed good thermal stability up to around 300 °C (at 5% weight loss) for the polymers. The weight average molecular weights of the resulting polymers were determined to be 10 400–15 100 ($M_w/M_n = 1.84$–2.00). The poled polymer films showed good nonlinearity ($d_{33} = 76$ pm V^{-1}) in the Maker fringe method for the second harmonic generation (SHG).

In recent years, nonlinear optical (NLO) polymers have become a potential candidate material for applications such as frequency modulators, linear electro-optic devices and optical storage because of advantages such as good processability, large nonlinearity, facile molecular design and low price.[1,2] Much research in NLO polymers to realize new advanced polymeric systems with better thermal and temporal stabilities of the dipole alignment has been carried out for polymer systems such as side chain polymers,[3] crosslinked polymers[4] and organic–inorganic hybrid systems.[5] Polyimides in NLO polymers have high thermal stabilities and can maintain the dipole alignment of NLO chromophore pendants attached on the polymer backbone at high temperatures.[6b] However, most aromatic polyimides require processing at high temperatures for the imidization from a precursor polyamic acid and show limited solubility in common organic solvents.[1] Polyetherimides with an ether linkage are a better polymeric system with enhanced processability and solubility while maintaining the meritorious properties of polyimides.[7] Since the one-step polymerization of polyimides by nitro-displacement reaction without thermal imidization was first introduced,[8] some groups lately reported poly(etherbenzimidazole)s[9] with heat-resistance and poly(arylene ether ketone)s[10] containing trifluoromethyl groups. However, efforts to prepare polyimides by nitro-displacement using alkyl oxide instead of aryl oxide have not been reported yet.

In this paper, we introduce a simple synthetic route to NLO-functionalized polyetherimides using the nitro-displacement reaction. Nitro-displacement reaction using alkyl oxide as a nucleophile has been carried out at a mild temperature without a thermal curing step as in Scheme 2. The aromatic carbon to which the nitro group is attached is very electron deficient because of the electron-withdrawing properties of the nitro group and the imide group, and as a result, the aromatic nucleophilic attack by the nucleophile gives the step polymerization by a nitro-displacement. We synthesized monomers with a dialkylaminonitrostilbene (DANS) unit to give second-order NLO activity to the resulting polymers.

Experimental

Analytical instrumentation

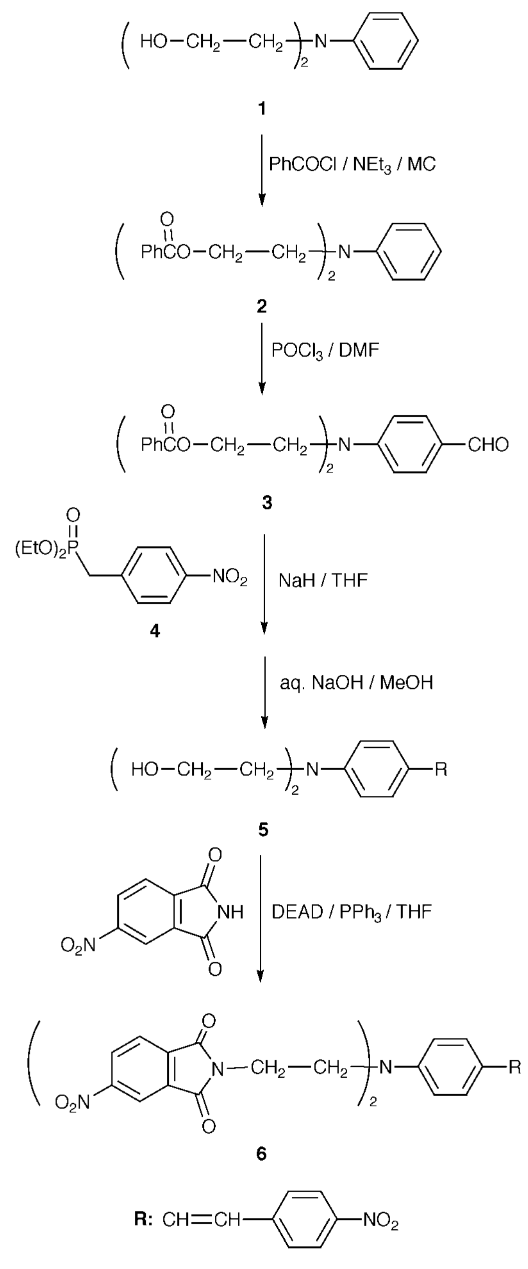
Melting points were uncorrected and were measured with an Electrothermal 9100 model (England). Synthesized compounds were characterized by ^{1}H-NMR spectra on a Bruker AM 200 or AM 300 spectrometer. FT-IR spectra were obtained with a Bomem Michelson series FT-IR spectrophotometer (on KBr plates) and UV–visible spectra were measured on a Shimadzu UV-3100S. Differential scanning calorimetric (DSC) analysis and thermogravimetric analysis (TGA) were performed under nitrogen atmosphere at a heating rate of 10 °C min^{-1} with a Dupont 9900 analyzer. The number and weight average molecular weights of polymers were estimated by a gel permeation chromatography (GPC) instrument, Waters 2690 model, using dimethylacetamide (DMAc) as eluant. The setup for performing the corona poling was designed to heat up to 300 °C and to apply the poling voltage in the range of 0–10 kV under nitrogen atmosphere. The second harmonic generation coefficients (d_{33}) of these polymer samples were measured using the Maker fringe method for second harmonic generation (SHG) from 1064 nm laser radiation.[11b] The polarized *Q*-switched Nd : YAG laser (Lumonics HY750) with a 10 ns pulse width and a 10 Hz repetition rate was used as the light source. The second harmonic signal was detected by the photomultiplier tube (Hamamatsu R-928) and averaged over 300 pulses in a boxcar integrator (Stanford SRS250) to increase the signal to noise ratio. Film thickness was determined using a Tencor Alpha-Step 500 surface profiler.

Materials

3-Nitrophthalic anhydride (98%), 4-nitrophthalic anhydride (92%), diethyl azodicarboxylate (DEAD) (97%), 4,4′-methylenedianiline (MDA) (97%), anhydrous *N*,*N*-dimethylformamide (DMF) (99.8%), 1-methylpyrrolidin-2-one (NMP) (99.5%) and sodium hydride (60% dispersion in oil) were purchased from Aldrich Co. and used without further purification. Triphenylphosphine (99%) was purchased from Fluka Co. and *N*-phenyldiethanolamine (min. 95%) was purchased from TCI Co. (Japan) and both of them were used without further purification. Anhydrous tetrahydrofuran (THF) was obtained by distillation using sodium as drying agent. All other solvents and reagents were analytical-grade quality, purchased commercially and used as received unless otherwise stated.

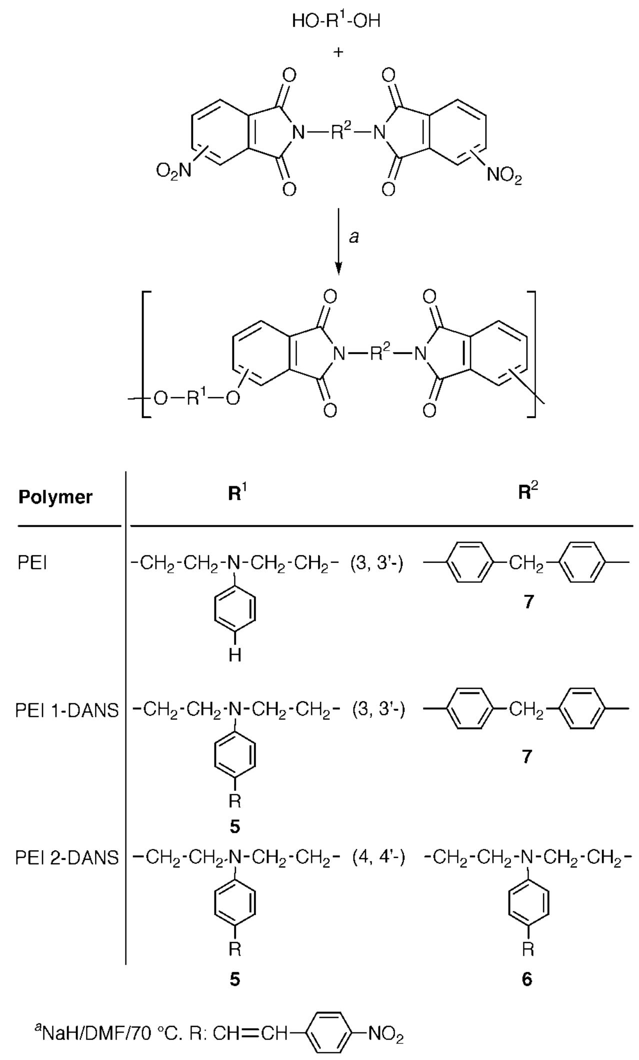
Synthesis of monomers

Compound **2** comes from the protection of alkanediol of *N*-phenyldiethanolamine (**1**) with benzoyl chloride (Scheme 1).



Scheme 1 Synthetic route to the monomers.

Compound **3** was obtained by Vilsmeier reaction from **2**. Compound **5** was synthesized by Horner–Emmons–Wittig reaction between **3** and **4**, and by deprotection to the alcohol. Compound **6** was obtained by Mitsunobu reaction of a diol and a phthalimide.[12] Compound **7** was obtained by acid-catalyzed imidization of 3-nitrophthalic anhydride and 4,4′-methylenedianiline with acetic acid using a Dean–Stark apparatus for removal of the residual water.



Scheme 2 Synthetic route to the polyetherimides.

2-[Phenyl(2-benzoyloxyethyl)amino]ethyl benzoate (2). *N*-Phenyldiethanolamine (20 g, 110 mmol) and benzoyl chloride (27.3 mL, 242.7 mmol) were put into a 2-necked 250 mL round-bottomed flask with methylene chloride (19.5 mL, 112.2 mmol). Triethylamine (32.8 mL, 242.7 mmol) was added dropwise and the resultant mixture was stirred for 3 h in an ice bath (at 0 °C). Water (20 mL) was poured into the mixture and it was extracted with methylene chloride three times. After removing the residual solvent by evaporator, a yellowish liquid was obtained and the solvent was removed under vacuum. The liquid changed to a white solid. The solid was recrystallized in methanol to yield a white powder as product (37 g, 95 mmol, 86%). UV–vis (CH_2Cl_2) λ_{max}/nm: 231; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 8.02 (t, 4H, ArH), 7.54 (m, 2H, ArH), 7.41 (t, 4H, ArH), 7.30 (t, 2H, ArH), 6.90 (d, 2H, ArH), 6.75 (t, 1H, ArH), 4.52 (t, 4H, $-NCH_2C\mathit{H}_2O-$), 3.83 (t, 4H, $-NC\mathit{H}_2CH_2O-$). Calcd. for $C_{24}H_{23}NO_4$: C, 74.02; H, 5.95; N, 3.60; Found: C, 74.06; H, 6.02; N, 3.61%.

2-[(4-Formylphenyl)(2-benzoyloxyethyl)amino]ethyl benzoate (3). 2-[Phenyl(2-benzoyloxyethyl)amino]ethyl benzoate (10 g, 25.7 mmol) and DMF (92 mL, 123.4 mmol) were put into a 2-necked 250 mL round-bottomed flask. Phosphorus oxychloride (47 g, 30.9 mmol) was added dropwise and the resultant mixture was stirred for 3 h at 80 °C. The solution color changed to dark green. Water (20 mL) was poured into the mixture and it was extracted with ethyl acetate three times. Then the pH of the solution mixture was adjusted to basic using NaOH solution. After removing the residual solvent by evaporator, a white solid was obtained and the solid was recrystallized from methanol to yield a white powder product (8.4 g, 20.0 mmol, 78%). UV–vis (CH_2Cl_2) λ_{max}/nm: 318, 236; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 9.74 (s, 1H, $-C\mathit{H}O$), 7.95 (d, 4H, ArH), 7.72 (d, 2H, ArH), 7.51 (t, 2H, ArH), 7.39 (t, 4H, ArH), 6.90 (d, 2H, ArH), 6.75 (t, 1H, ArH), 4.54 (t, 4H, $-NCH_2C\mathit{H}_2O-$), 3.90 (t, 4H, $-NC\mathit{H}_2CH_2O-$). Calcd. for $C_{24}H_{23}NO_4$: C, 71.93; H, 5.55; N, 3.36; Found: C, 71.86; H, 5.65; N, 3.38%.

Diethyl 4-nitrobenzylphosphonate (4). 1-(Bromomethyl)-4-nitrobenzene (20 g, 93.5 mmol) was put into a 2-necked 100 mL round-bottomed flask with triethyl phosphate

(19.5 mL, 112.2 mmol). This solution was stirred at 90 °C for 10 h. The resulting mixture was vacuum distilled after which a transparent yellowish liquid was obtained as product (21.3 g, 78.01 mmol, 83.5%). The product was preserved in a refrigerator. ^{1}H-NMR (200 MHz, $\mathrm{CDCl_3}$): δ 8.15 (d, 2H, ArH), 7.44 (dd, 2H, ArH), 4.00 (m, 2H, $-\mathrm{OC}H_2\mathrm{CH_3}$), 3.25 (d, 2H, $\mathrm{ArC}H_2-$), 1.21 (t, 6H, $-\mathrm{OCH_2C}H_3$). Calcd. for $\mathrm{C_{11}H_{16}NO_5P}$: C, 48.36; H, 5.90; N, 5.13; Found: C, 48.15; H, 6.33; N, 5.13%.

4-[Bis(2-hydroxyethyl)amino]-4′-nitrostilbene (5)^{6a}**.** 2-[(4-Formylphenyl)(2-benzoyloxyethyl)amino]ethyl benzoate (**3**) (6 g, 14.38 mmol) and sodium hydride (0.69 g, 17.26 mmol) were put into a 2-necked 250 mL round-bottomed flask with anhydrous tetrahydrofuran (*ca.* 100 mL). To this mixture, diethyl 4-nitrobenzylphosphonate (**4**) (3.94 g, 14.38 mmol) was added dropwise. The solution was stirred at 70 °C for 16 h. The solution changed to dark red as the nitrostilbene moiety was formed. After removing the solvent using the evaporator, the resulting solution was extracted with methylene chloride three times. The dried organic extracts were added to methanol (80 mL) and sodium hydroxide (2.53 g, 63.27 mmol) and the solution was stirred at 80 °C for 12 h. After completion of the reaction, some solvent was removed and water was poured into the reaction flask. After filtering, a red solid was obtained and dried over $\mathrm{P_2O_5}$ at 80 °C for 24 h *in vacuo*. The yield of compound **5** was 5.61 g (69%). Mp: 182–183 °C; UV–vis ($\mathrm{CH_2Cl_2}$): λ_{max}/nm: 434; FT-IR (KBr) $\tilde{\nu}_{\mathrm{max}}/\mathrm{cm^{-1}}$: 3320 (O–H), 1583 (C=C), 1338 (NO), 1108 (C–O); ^{1}H-NMR (200 MHz, DMSO-d_6): δ 8.16 (d, 2H, ArH), 7.74 (d, 2H, ArH), 7.45 (d, 2H, ArH), 7.39 (d, 1H, $\mathrm{CH{=}C}H$), 7.06 (d, 1H, $\mathrm{C}H\mathrm{{=}CH}$), 6.70 (d, 2H, ArH), 4.80 (br s, 2H, –OH), 3.53 (d, 4H, $\mathrm{NCH_2C}H_2\mathrm{O}$), 3.46 (d, 4H, $\mathrm{NC}H_2\mathrm{CH_2O}$). Calcd. for $\mathrm{C_{18}H_{20}N_2O_4}$: C, 65.84; H, 6.14; N, 8.53; Found: C, 65.50; H, 6.10; N, 7.82%.

4-{Bis[2-(4-nitrophthalimido)ethyl]amino}-4′-nitrostilbene (6). 4-[Bis(2-hydroxyethyl)amino]-4′-nitrostilbene (3 g, 9.13 mmol), 4-nitrophthalimide (3.72 g, 19.17 mmol), and triphenylphosphine (5.18 g, 19.17 mmol) were added to 60 mL of anhydrous tetrahydrofuran in a 2-necked round-bottomed flask and diethyl azodicarboxylate (DEAD) (3.34 g, 19.17 mmol) was added dropwise into the flask at room temperature. While DEAD was being added, thick brown-colored solids precipitated from the solution. The mixture was stirred for 24 h at room temperature. The resulting solid was recrystallized in methanol and the product was dried under vacuum to yield 3.34 g of reddish brown solid (80.4%). Mp: 259–260 °C; UV–vis ($\mathrm{CH_2Cl_2}$) λ_{max}/nm: 420; FT-IR (KBr) $\tilde{\nu}_{\mathrm{max}}/\mathrm{cm^{-1}}$: 1773, 1715 (C=O), 1583 (C=C), 1332 (NO); ^{1}H-NMR (200 MHz, DMSO-d_6): δ 8.57 (d, 2H, phthalimide), 8.44 (s, 2H, phthalimide), 8.17 (d, 2H, ArH), 8.08 (d, 2H, phthalimide), 7.70 (d, 2H, ArH), 7.37 (d, 2H, ArH), 7.21 (d, 1H, $\mathrm{CHC}H$), 7.04 (d, 1H, $\mathrm{C}H\mathrm{CH}$), 6.83 (d, 2H, ArH), 3.78 (br d, 4H, $\mathrm{NCH_2C}H_2\mathrm{N}$), 3.64 (br s, 4H, $\mathrm{NC}H_2\mathrm{CH_2N}$). Calcd. for $\mathrm{C_{34}H_{24}N_5O_8}$: C, 64.76; H, 3.84; N, 11.11; Found: C, 64.36; H, 3.54; N, 11.68%.

Bis[4-(3-nitrophthalimido)phenyl]methane (7). 3-Nitrophthalic anhydride (5.00 g, 26 mmol) and 4,4′-methylenedianiline (2.50 g, 13 mmol) were put into a 2-necked 250 mL round-bottomed flask with acetic acid (100 mL). The mixture was stirred at 55 °C for about 30 min and then a Dean–Stark separator was used to remove the by-product, water, over 120 °C for 24 h. The resulting mixture was precipitated by addition of methanol and after filtering, recrystallized from methanol. The purified product was a yellowish white solid and the yield was 3.32 g (6.05 mmol, 46.5%). Mp: 291–293 °C; UV–vis ($\mathrm{CH_2Cl_2}$) λ_{max}/nm: 225; FT-IR (KBr) $\tilde{\nu}_{\mathrm{max}}/\mathrm{cm^{-1}}$: 1784, 1720 (C=O); ^{1}H-NMR (200 MHz, DMSO-d_6): δ 8.31 (d, 2H, phthalimide), 8.24 (d, 2H, phthalimide), 8.09 (t, 2H, phthalimide), 7.43–7.37 (m, overlapped 8H, ArH), 4.08 (s, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$). Calcd. for $\mathrm{C_{29}H_{16}N_4O_8}$: C, 63.51; H, 2.94; N, 10.22; Found: C, 63.42; H, 2.86; N, 10.02%.

Synthesis of polyetherimides

The synthesis of polyimides was performed by step polymerization using an aromatic nucleophilic substitution of a 3- or 4-positioned activated nitro group of the phthalic imides as shown in Scheme 2. The reaction conditions of the polymerization were mild (70 °C) and sodium hydride, which is used as a base in aprotic polar solvents with high boiling point, was used. The synthesis of PEI 1-DANS and PEI 2-DANS followed the synthetic route of PEI.

PEI. *N*-Phenyldiethanolamine (0.52 g, 2.74 mmol) was put into a 2-necked 100 mL round-bottomed flask with anhydrous DMF (10 mL). To this, sodium hydride (0.274 g, 6.85 mmol) was added. Then, bis[4-(3-nitrophthalimido)phenyl]methane (1.5 g, 2.74 mmol) was added to the flask and the flask was maintained at 70 °C for 48 h. The crude polymer was extracted with a Soxhlet extractor for 2 days to remove low molecular weight polymers. The yield of a yellowish polymer was 1.16 g (66.6%). UV–vis ($\mathrm{CH_2Cl_2}$) λ_{max}/nm: 227 and 333; FT-IR (KBr) $\tilde{\nu}_{\mathrm{max}}/\mathrm{cm^{-1}}$: 1784, 1730 (C=O), 1284 ($\mathrm{ArC{-}O{-}CH_2}$); ^{1}H-NMR (200 MHz, DMSO-d_6): δ 7.9–7.5 (br m, 4H, ArH), 7.5–7.2 (br d, 8H, ArH), 7.2–6.8 (br s, 4H, ArH), 6.8–6.6 (br m, 2H, ArH), 6.6–6.4 (br m, 1H, ArH), 4.35 (s, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 4.2–3.6 (br d, 8H, $-\mathrm{NC}H_2\mathrm{CH_2}-$ and $-\mathrm{NCH_2C}H_2-$); M_{n}: 5200; M_{w}: 10 400; T_{g}/°C: 172.4; T_{d5}/°C: 303.

PEI 1-DANS. The yield of reddish solid polymer was 3.20 g (81.0%). UV–vis (thin film on ITO) λ_{max}/nm: 433; FT-IR (KBr) $\tilde{\nu}_{\mathrm{max}}/\mathrm{cm^{-1}}$: 1774, 1716 (C=O), 1335 (NO), 1283 ($\mathrm{ArC{-}O{-}CH_2}$); ^{1}H-NMR (300 MHz, DMSO-d_6): δ 8.2–8.0 (br s, 2H, ArH), 7.9–7.5 (br s, 2H, ArH), 7.5–7.2 (br s, 8H, ArH), 7.2–6.9 (br s, 2H, $-\mathrm{C}H\mathrm{C}H-$), 6.9–6.6 (br s, 2H, ArH), 4.5–4.2 (br s, 2H, $-\mathrm{PhC}H_2\mathrm{Ph}-$), 4.2–3.6 (br d, 8H, $-\mathrm{NC}H_2\mathrm{CH_2O}-$ and $-\mathrm{NCH_2C}H_2\mathrm{O}-$); M_{n}: 8300; M_{w}: 15 200; T_{g}/°C: 197.3; T_{d5}/°C: 295.

PEI 2-DANS. The yield of reddish solid polymer was 0.34 g (61.15%). UV–vis (thin film on ITO) λ_{max}/nm: 438; FT-IR (KBr) $\tilde{\nu}_{\mathrm{max}}/\mathrm{cm^{-1}}$: 1767, 1709 (C=O), 1335 (NO), 1286 ($\mathrm{ArC{-}O{-}CH_2}$); ^{1}H-NMR (300 MHz, DMSO-d_6): δ 8.3–7.9 (br s, 4H, ArH), 7.9–7.7 (br s, 4H, ArH), 7.7–7.2 (br m, 10H, ArH and $-\mathrm{C}H\mathrm{C}H-$), 7.2–6.9 (br s, 4H, ArH), 6.9–6.6 (br s, 4H, ArH), 4.5–4.0 (br s, 4H, $-\mathrm{NCH_2C}H_2\mathrm{O}-$), 4.0–3.7 (br s, 4H, $-\mathrm{NCH_2C}H_2\mathrm{N}-$), 3.7–3.4 (br d, 8H, $-\mathrm{NC}H_2\mathrm{CH_2O}-$ and $-\mathrm{NC}H_2\mathrm{CH_2N}-$); M_{n}: 9000; M_{w}: 11000; T_{g}/°C: 172.0; T_{d5}/°C: 300.

Film preparation for SHG measurements

The purified polymers were dissolved in anhydrous NMP solvent at a concentration of 10 wt%. The polymer solutions were filtered through a 0.45 μm Teflon filter (Whatman) and the filtrates were spin coated on the precleaned (with sonication in isopropyl alcohol and acetone) indium-tin oxide (ITO) coated glass substrates to give films whose thickness was around 300 nm. The films obtained were put in a vacuum oven at 100 °C under reduced pressure for 24 h for the removal of residual solvent. After drying the polymer films, they were poled at around T_{g} for about 20 min and cooled to room temperature under an electric field of 3.5–4.5 kV. The distance between the corona electrode and polymer film was 1 cm and the thickness of the tungsten wire used as the corona electrode was 25 μm.

Results and discussion

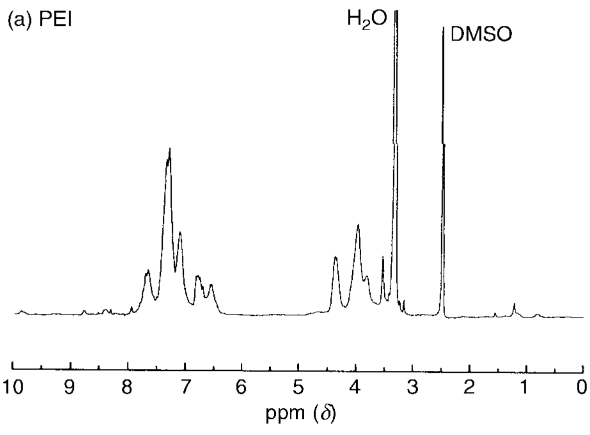
The synthetic routes of the monomers and the final polyetherimides are shown in Schemes 1 and 2. In Scheme 1, *N*-phenyldiethanolamine (**1**) was protected with benzoyl chloride in methylene chloride solvent in the presence of an equivalent amount of triethylamine as a catalyst. Following Vilsmeier formylation in DMF solvent, compound **2** yielded compound **3**. A subsequent reaction of **3** and phosphonate **4** by Horner–Emmons–Wittig reaction and deprotection with sodium hydroxide gave the diol monomer.[13b] Compound **5** and 4-nitrophthalimide produced the dinitroimide monomer **6** including a DANS moiety by Mitsunobu reaction using diethyl azodicarboxylate (DEAD) and triphenylphosphine as reagents in anhydrous tetrahydrofuran.[12] Bis[4-(3-nitrophthalimido)-phenyl]methane (**7**) was produced from the imidization of 4,4′-methylenedianiline (MDA) and 3-nitrophthalic anhydride.[8] All intermediates, including the monomers, were characterized by elemental analysis, and the measurement of melting points and common spectroscopic techniques such as ^{1}H-NMR, FT-IR, and UV–visible spectroscopies. Their results are in good agreement with the structures obtained in each step of the synthetic routes. The polyetherimides (PEIs), PEI, PEI 1-DANS and PEI 2-DANS, were synthesized by step polymerization between alkanediol and diimide monomers using sodium hydride as a base in an anhydrous DMF solvent at 70 °C for 48 h. Then, the final PEIs were purified by Soxhlet extraction in methanol for 2 days. The yields of the PEIs were 67% (a yellowish powder), 81% (a reddish powder) and 61% (a reddish powder) for PEI, PEI 1-DANS and PEI 2-DANS, respectively. Using this method it is possible to polymerize the 3,3′-isomer and 4,4′-isomer by the substitution of 3- or 4-nitrophthalimide. The final PEIs were readily soluble in aprotic polar solvents such as DMF, DMSO, DMAc, and NMP due to their alkoxide linkages. Their solubility was especially good in NMP.

The molecular weights were obtained from gel permeation chromatography (GPC) analysis using polystyrene as standard and DMAc as eluant. The weight average molecular weights of the polymers were determined to be 10 400 ($M_w/M_n = 2.00$) for PEI, 15 200 ($M_w/M_n = 1.84$) for PEI 1-DANS and 11 000 ($M_w/M_n = 1.26$) for PEI 2-DANS (using DMF solvent as eluant).

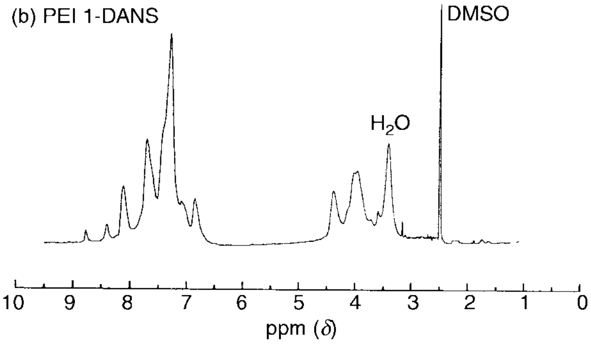
Fig. 1 is the ^{1}H-NMR spectra of the polymers, which show signal broadening due to polymerization, but the chemical shifts are well consistent with the proposed polymer structures. After purification of the polymers, we could observe neither the amide proton nor the proton ($\delta \sim 10$ ppm) of the aldehyde that could have been generated from the rupture of the imide ring by sodium hydride, in all polymers. In the NMR spectra of PEI and PEI-DANS 1, small peaks above δ 8.2 originate from the protons of the nitrophthalic imide group in the polymer end group.[14] The peak at 2.49 ppm comes from DMSO and the sizable peak at 3.3 ppm originates from H_2O molecules in DMSO-d_6 solvent. The FT-IR spectra of PEI also showed the formation of alkyl aryl ether bonds in all of PEI, PEI 1-DANS and PEI 2-DANS. After polymerization, a new medium peak around 1285 cm^{-1} appeared and it was due to the asymmetric stretching of ArC–O–CH$_2$ in the polymer backbone.[14] From this observation, we could deduce that the nitro-displacement reaction was successfully completed. In addition, the strong peak around 1715 cm^{-1} and the medium peak around 1775 cm^{-1} were due to the carbonyl asymmetric stretching in the imide ring. In the UV–visible spectra, PEI 1-DANS and PEI 2-DANS showed absorption maxima at $\lambda_{max} = 433$ and 438 nm (thin film on ITO glass substrate) respectively and these absorption peaks originated from the π–π^* transition of the conjugated 4,4′-aminonitrostilbene moiety.

Thermal characterization of the PEIs was carried out using TGA and DSC instruments. TGA studies indicated that the first decomposition (at 5% weight loss) of all polymers occurred around 300 °C under nitrogen atmosphere (Table 1 and Fig. 2). In DSC thermograms, the polymers did not show melting endothermic peaks, indicating that they represent a noncrystalline phase, but showed relatively high glass transition temperatures; T_g values are 172.4 °C for PEI, 197.3 °C for PEI 1-DANS and 172.0 °C for PEI 2-DANS. In the case of PEI 1-DANS, the glass transition occurred at a higher temperature (by *ca.* 25 °C) than others because of the rigidity of the NLO-functionalized chromophore and the aromatic group on the imide backbone of the polymer chain.

(a) PEI



(b) PEI 1-DANS



(c) PEI 2-DANS

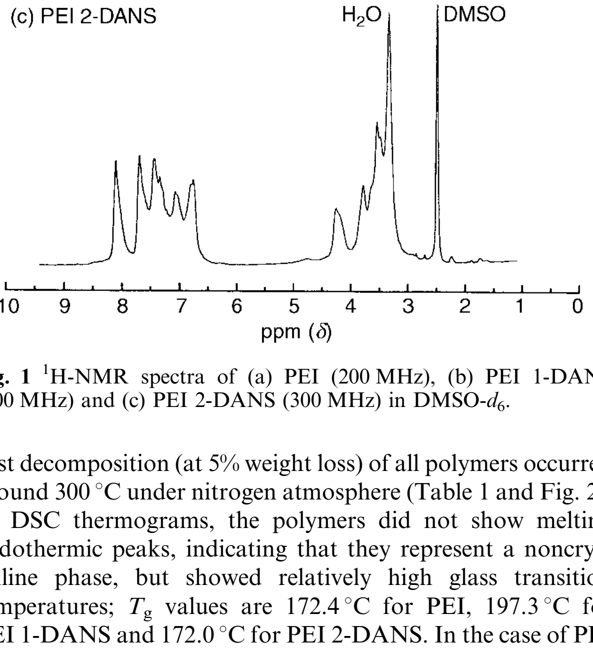


Fig. 1 ^{1}H-NMR spectra of (a) PEI (200 MHz), (b) PEI 1-DANS (300 MHz) and (c) PEI 2-DANS (300 MHz) in DMSO-d_6.

The final polyetherimides were dissolved in NMP and were processed into optically good quality films by spin coating with a heated polymer solution. For induced second order optical nonlinearity, the polymer films were poled at around T_g for about 20 min and cooled to room temperature under an applied electric field. After the corona discharge poling, the UV–visible spectra of PEI 1-DANS and PEI 2-DANS exhibited a slight blue shift and a decrease in absorption because of the birefringence caused by dipole alignment. The absorption changes are directly related to the orientation of the chromophores and can be used as a means of evaluating the degree of orientation. If one assumes that the molecular electronic transition moment is parallel to the permanent

Table 1 The physicochemical properties of the resulting polyetherimides

Polymers	M_n[a]	M_w[a]	M_w/M_n	T_g/°C	T_{d5}/°C[b]	λ_{max}/nm
PEI	5200	10400	2.00	172.4	303	227, 333 (CH_2Cl_2)
PEI 1-DANS	8300	15200	1.84	197.3	295	433.4 (on ITO glass)
PEI 2-DANS	(9000)	(11000)	(1.26)	172.0	300	438.1 (on ITO glass)

[a]Molecular weight of the final polymers is estimated by gel permeation chromatography using DMAc (DMF) as eluant. [b]Onset of 5% weight loss on TGA thermograms at a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

Table 2 The optical properties of the final polyetherimides

Polymers	Calcd. chromophore contents/wt%	Film thickness[a] /μm	Φ	$\alpha^{f}_{2\omega}$[b] at 532 nm/μm^{-1}	d_{33}/pm V^{-1} (d_{33}/d_{31})	$d_{33}(\infty)$ /pm V^{-1}
PEI 1-DANS	30.43	0.106	0.16	0.64	76 (3)	21
PEI 2-DANS	52.31	0.350	0.27	0.75	54 (3)	14

[a]Film thickness was measured on the alpha step surface profiler. [b]Absorption coefficient $\alpha^{f}_{2\omega}$ at 532 nm after poling.

ground-state dipole moment, one can obtain the order parameter Φ by measuring the absorbance A_0 of an unpoled system and A_p of a poled sample with light polarized perpendicular to the poling direction.[2b] Owing to the absorbance change, the order parameter Φ of the poled film, which is related to the poling efficiency, was estimated to be 0.27 ($\Phi = 1 - A_p/A_0$) for PEI 2-DANS. The optical measurements were taken after the removal of residual charges caused by the electronic poling field, by leaving it at room temperature overnight. The second harmonic generation (SHG) measurements were performed at a fundamental wavelength of 1064 nm using the mode-locked Nd : YAG laser. In order to determine the microscopic second-order susceptibility of the material, the angular SHG dependence was recorded and then compared with the values obtained from a 4.65 mm thick, Y-cut quartz plate (Fig. 3). The SHG coefficient, d_{33}, was calculated using a model for the fitting derived from that of Herman and Hayden,[11a] including corrections of the absorption and birefringence of the film sample with reflections. The SHG measurement showed large d_{33} values of 76 pm V^{-1} for PEI 1-DANS and 54 pm V^{-1} for PEI 2-DANS. As the polymer films showed non-negligible absorption at 532 nm, we calculated the non-resonant values ($d_{33}(\infty)$) of these polymers by the approximation of two level model.[15] The $d_{33}(\infty)$ values of PEI 1-DANS and PEI 2-DANS were 21 pm V^{-1} and 14 pm V^{-1}, respectively. As compared with our previous study through a different synthetic approach, these order parameter values were lower than those, but these non-resonant values were higher than those.[13c]

Our polymer films had lower d_{33} values than that of $LiNbO_3$ (98 pm V^{-1} in d_{33} value) used in practical devices.[16] The study in temperature ranges and conditions for the stability of the poled polymers is needed to satisfy the conditions required in real applications.[2a]

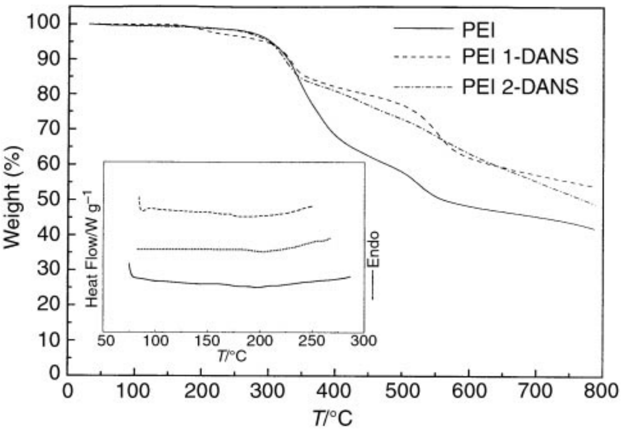


Fig. 2 TGA and DSC (inset) thermograms of PEI, PEI 1-DANS and PEI 2-DANS (at a heating rate of 10 °C min^{-1} under nitrogen atmosphere).

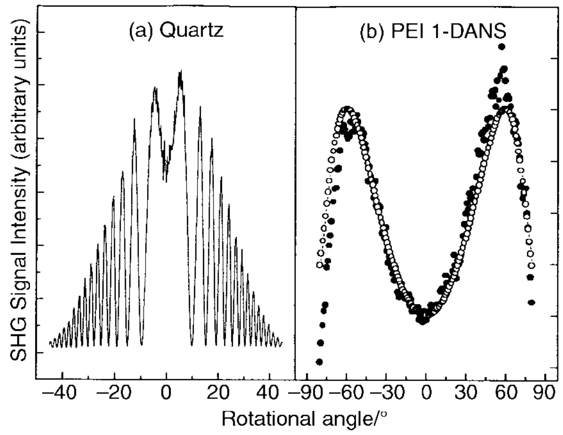


Fig. 3 Maker fringe patterns of (a) a reference, Y-cut quartz plate, (b) PEI 1-DANS (●), the fitting curve (○).

Conclusions

We have directly prepared PEI and two NLO-functionalized PEIs through a simple synthetic route using the nitro-displacement reaction between an alkanediol and a dinitro-imide monomer without any side reaction such as the breaking of the imide ring. The resulting polymers showed good second-order NLO activity with d_{33} values of 76 pm V^{-1} (PEI 1-DANS) and 54 pm V^{-1} (PEI 2-DANS). We are working on the preparation of a series of poly(etherimide)s with various substituents and a further study of the thermal and temporal stability of a second-order NLO activity will be carried out.

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