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Synthesis and properties of nonlinear optical polymers based on poly(ether imides) for electrooptical devices

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Summary: Nonlinear optical poly(ether imides) with an adequate thermal stability has been synthesized by direct coupling of hydroxy poly(ether imides) and NLO chromophores with a quantitative yield. The resultant amorphous NLO poly(ether imides) exhibited good solubility in common organic solvents, providing optical-quality thin films by spin coating. The glass transition temperatures of the polymers are at around 180 °C. The electrooptic coefficients (r_{33}, @1.3µm) of PEI-DR1 was 12.3 pm/V with an electrical poling field of 100 V/µm and it decayed about 10 % over 10 months at 90 °C under atmospheric conditions.

Introduction

Due to their low dielectric constants and potentially large electrooptic coefficients suitable for high-speed devices, nonlinear optical (NLO) polymers are promising materials for electrooptic (EO) modulators, switches, and wavelength converter (1,2,3). To develop practical devices, however, the polymeric materials should have large EO coefficients for low operating voltages, thermal, chemical, and photochemical stability, low optical propagation losses at 1.3 or 1.55 µm wavelength and mechanical properties for multilayed films processing. As leading materials, aromatic polyimides appending NLO chromophores have shown a great potential because of their high temporal alignment stability, excellent mechanical properties, and low optical propagation losses over other aliphatic side chain NLO polymers (4,5).

In previous work, we reported on the synthesis of aromatic soluble polyimides containing pendant chromophores prepared by direct polycondensation of diaminophenol dihydrochloride salt and aromatic dianhydride followed by chromophore coupling (6). This system possesses the advantage of a wide variety for selecting the chromophores, a facility of synthesis, flexibility for the adjustment of the polymer backbone rigidity, as well as an oxidation stability of diamine monomers and insensitivity to imidization environment. The resulting polyimides have an excellent temporal dipole alignment stability due to their high glass transition temperature above 220 °C. Using a similar synthetic method, we newly prepared the poly(ether imides) bearing two pendant NLO chromophore in the repeat unit. Also, it has a flexible ether

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linkage into the polymer backbone. This polymeric system has a higher chromophore loading density and a lower processing temperature than that of EO polyimides previously reported (6). In this article, we present our results on the synthesis of nonlinear optical poly(ether imides) and their characterization for electrooptical devices.

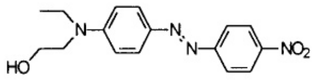
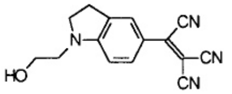
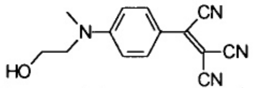
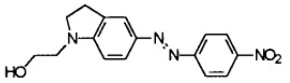
Experimental

Materials. A 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (AHHFP) and 3,3',4,4'-oxydiphthalic anhydride (ODPA) were obtained from Central glass Co. and TCI, respectively. These monomer-grade materials were used without further purification. Disperse red 1 (DR1) was obtained from Aldrich Chem. Co. (2-Hydroxyethyl) indolinoazo nitrobenzene (IANB) was synthesized by the azo coupling reaction of (2-hydroxyethyl) indoline with p-nitroaniline (7). TCVA and TCVI were synthesized by reaction of (2-hydroxyethyl)-methylaniline and (2-hydroxyethyl)indoline with tetracyanoethylene in DMF under nitrogen at 0 °C to room temperature for 4 h, respectively. **TCVA**; ^{1}H-NMR ($CDCl_3$), δ: 3.26 (s, 3H), 3.71 (t, 2H), 3.80 (t, 2H), 4.71 (t, 1H), 6.90 (d, 2H), 8.04 (d, 2H). **TCVI**: ^{1}H-NMR ($CDCl_3$), δ: 3.16 (t, 2H, ring), 3.54 (t, 2H), 3.92 (m, 4H, N-CH_2), 6.51 (d, 2H), 7.91 (d, 2H). All solvents were used after conventional purification methods. The chemical structures of the chromophores used in this study are summarized in Table I.

Synthesis of hydroxy poly(ether imide) (hydroxy-PEI). A solution of equimolar amount of AHHFP (5.903 g, 16.1176 mmol) and ODPA (5.0 g, 16.1176 mmol) in 44 mL of m-xylene and DMAc [20/80 (v/v)] were introduced to a three-neck flask equipped with a magnetic stirrer, a Dean-Stark trap, and a reflux condenser. The reaction mixture was stirred at room temperature for 22 h followed by stirred at 60 °C for 6 h. The mixture was heated in an oil bath to 150 °C for 3 h under the nitrogen atmosphere. Then the polymer solution was diluted with 20 mL of DMAc and precipitated by slowly dropping the polymer solution into water in a high-speed blender. The product was collected by filtration, then redissolved in DMF and then reprecipitated into methanol/water. The polymer was filtered and dried at 80 °C under vacuum for 24 h. Yield = 98 %, ^{1}H-NMR ($CDCl_3$), δ: 7.09 (d, 2H), 7.20 (d, 2H), 7.40 (s, 2H), 7.59 (m, 4H), 8.02 (d, 2H), 10.51 (s, 2H, -OH). Mw = 23,800 g/mol, Mw/Mn = 2.29.

Synthesis of chromophore-contained poly(ether imide)s (PEI-chromophore). A general procedure for the synthesis is as follows. Diethyl azodicarboxylate (DEAD) (1.63 g, 9.37 mmol) was added dropwise into a solution of hydroxy-PEI (2 g, 3.12 mmol), triphenylphosphine (2.45 g, 9.37 mmol), and DR 1 (2.45 g, 7.81 mmol) in THF (50 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 48 h. The resulting reaction mixture was precipitated into an agitated solution of methanol with acid. The collected precipitate was dissolved in THF and reprecipitated into the solution of methanol in a high-speed blender. The precipitate was filtered and washed with methanol. The polymer was further purified by Soxhlet extraction with methanol and dried at 80 °C under vacuum for 24 h.

Table I. Chemical structures of the chromophores used in this study

Code	Chromophores	λ_{max} (nm)[a]	Code	Chromophores	λ_{max} (nm)[a]
DR1		489	TCVI		530
TCVA		513	IANB		498

[a]UV-visible spectra were measured using a Hitachi U-3501 spectrophotometer in a methylene chloride solution.

Instruments for Characterization. ^{1}H NMR spectra were recorded with the use of a Bruker AM-300 spectrometer, and chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. IR spectra were measured with the coated polymer film on a NaCl window in a Nicolet Magna 560 spectrometer, and frequencies were given in reciprocal centimeters (cm^{-1}). A Hitachi U-3501 spectrophotometer was used for UV-visible spectral data. The molecular weight and polydispersity were determined in a THF solvent with a Waters GPC-150C calibrated with polystyrene standards. A DuPont 9900 thermal analyzer was used to obtain the DSC thermograms with heating rates of 10 °C/min.

Measurement. Refractive index, *n*, of the polymer film was measured by prism coupling method. Thickness of the polymer film was confirmed with α-step surface profiler (Tencor instruments, α-step 200). The electrooptic coefficients, r_{33}, of the poled films were measured at the wavelength of 1.3 μm using a reflection method.

Results and Discussion

Synthesis and structural characterization. Our approach to the synthesis of poly(ether imides)-based side chain NLO polymers began with the synthesis of hydroxy-PEI using AHHFP and ODPA as the monomers. A polycondensation and imidization was carried out in the DMAc/m-xylene solution (8). Scheme 1 shows the synthetic route and the chemical structure of the hydroxy-PEI. The molecular weight (M_w) and the polydispersity value of the resulting hydroxy-PEI estimated by GPC were 23,800 g/mol and 2.29, respectively. As shown in Scheme 1, the precursor hydroxy-PEI has the two hydroxy phenolic groups in the repeat unit for attaching NLO chromophores and the flexible ether linkage in the polymer backbone. These structural features are anticipated the large EO coefficients and mild processing temperatures due to the high chromophore loading density and the adequate glass transition temperature below 200 °C, respectively. To investigate the electrooptical properties and the thermal stability of this polymer system, commercially available or synthesized chromophores were introduced in the poly(ether imides) backbone. Table I summarized the chemical structure and absorption maximum of the chromophores.

Scheme 1. Synthetic route of the nonlinear optical poly(ether imides)

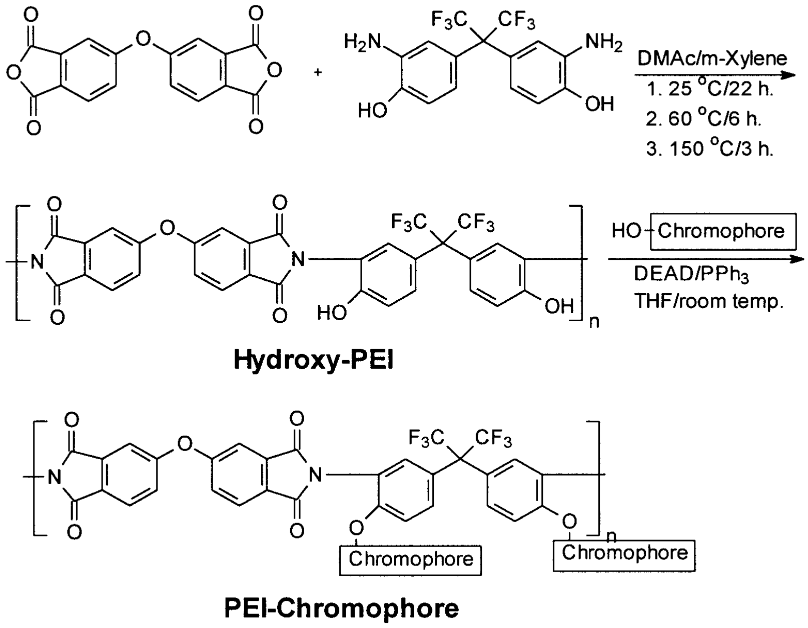


Table II. Synthetic data of the NLO polymers

polymer	CLL (%)[a]	M_w (g/mol)[b]	M_w/M_n[b]	CY (%)[c]	T_g (°C)
PI-DR1	32.5	25,000	2.17	98.9	223
PI-TCVA	27.0	34,900	2.70	98.0	219
PEI-DR1	43.7	27,200	1.89	> 99	173
PEI-TCVA	37.4	36,000	2.02	99	185
[d]PEI-TCVI	38.7	-	-	95	-
[d]PEI-IANB	43.5	-	-	94	-

[a]Chromophore loading level (CLL); (chromophore fw/repeated polymer unit fw) x 100. [b]Determined by GPC analysis with polystyrene standards. [c]Coupling yield (CY) of attached chromophores at the polymer backbone estimated by ^{1}H-NMR. [d]The polymers gradually turned to an intractable material.

Side chain NLO PEI was synthesized from hydroxy-PEI and NLO chromophores with the terminal hydroxy group. The hydroxy-PEI was reacted with 2.5 equiv (relative to the equivalent of the repeat units of the polymer) of the terminal hydroxy group on the chromophores in the presence of triphenyl phosphine and diethyl azodicarboxylate in THF solvent at room temperature. The results of chromophore-contained PEI synthesis are listed in Table II. The coupling of precursor polymers with NLO chromophores gave almost a quantitative yield. It seems that the coupling reaction is very effective in this polymer system. As shown in Table II, EO PEIs have the higher chromophore loading level (CLL) calculated chromophore formula weight per repeated polymer backbone unit formula weight than that of EO polyimides. It means that larger EO coefficients of the EO PEI will be obtains due to the higher chromophore density. All of the polymers except PEI-TCNI and PEI-IANB were soluble in organic solvents such as THF, diglyme, cyclohexanone, and γ-butyrolactone. However, PEI-TCNI and PEI-IANB bearing an indoline ring as a donor group gradually turned to an intractable material due to the photosensitivity of the indoline ring.

FT-IR, 1H NMR and the UV-visible spectrophotometer characterized the polymer structures. The ^{1}H NMR spectrum of the hydroxy-PEI shows a completely imidized structure with the phenolic hydroxy proton peak at 10.5 ppm. As the coupling reaction proceeds, a phenolic proton peak completely disappears and new azobenzene peaks appear at the range of 6.7 - 8.3 ppm together with aromatic imide peaks. The percentage of introduced chromophore to the polymer backbone (coupling yield) was determined by a ^{1}H NMR integration of the disappearance of the hydroxy proton on the polymer backbone vs. the appearance of the azobenzene proton at 6.75 ppm on the side chain chromophore. The FT-IR spectrum of hydroxy-PEI clearly showed the characteristic imide absorbencies at 1787, 1730.9, 1369, and 721 cm^{-1} as well as the broad absorbance at 3380 cm^{-1} due to the phenolic hydroxy groups. After the Mitsunobu reaction for covalent bonding of the chromophores onto the polymer backbone, new band appear at the 1338.7 and 1514 cm^{-1} due to the nitro group in the chromophore. The band of phenolic hydroxy groups in the hydroxy-PEI at 3380 cm^{-1} almost disappears.

Table III. Physical and optical properties of the polymers

polymer	λ_{max} (nm)[a]	refractive index[b] n_{TE}	refractive index[b] n_{TM}	T_p (°C)[c]	r_{33} (pm/V)[b]
PI-DR1	481	1.6396	1.6271	230	7.6
PI-TCVA	512	1.6237	1.6106	220	6.2
PEI-DR1	478	1.6272	1.6179	173	12.3
PEI-TCVA	510	1.6567	1.6523	180	8.7

[a]Measured the polymer films on fused silica windows. [b]Refractive index and EO coefficient are measured at the 1.3 μm wavelength. [c]Poling temperature.

Thermal and optical properties. The thermal characterizations of the polymers were carried out using DSC and TGA. Polyimides based EO polymers have high glass transition temperature (T_g) above 220 °C. During poling around T_g, cladding polymer layers and chromophores were distorted and destroyed to some degree at high temperature. Otherwise, newly synthesized EO poly(ether imides) has the adequate T_g around 180 °C. Therefore, these EO poly(ether imides) are easily poled without the dielectric breakdown of the cladding layers and destroy of NLO chromophores. The results of T_g are summarized in Table II. The TGA curve of PEI-DR1 shows that the initial decomposition temperature are above 295 °C under nitrogen as shown in Figure 1 To measure the optical properties of the polymers, thin films of high optical quality were prepared from the polymer solutions by spin coating on an ITO glass or silicon wafer substrates. The films were baked in an oven at 160 °C for 2 h to ensure the removal of the residual solvent. Table III shows the refractive index, *n*, of unpoled polymer films coated on the silicon wafer measured by a GGG prism coupler at 1.3 μm. The refractive indices of the polymers were found to be in the range of 1.6237 to 1.6567. For the measurement of the EO coefficient (r_{33}), a polymer film was made on ITO glass by spin coating. A gold electrode was deposited on the polymer film by a thermal evaporation. The electrooptic coefficients of the poled films were measured at the wavelength of 1.3 μm using a reflection method (9). A strong DC electric field was applied to the polymer sample on a hot plate. The sample was heated up to the T_g in 15 min, retained for 20 min, and slowly cooled down to room temperature with the DC electric field. It was observed that r_{33} was 12.3 pm/V for PEI-DR1 with a poling field of 100 V/μm at 173 °C as shown in Table III. We found that EO poly(ether imides) gave the larger EO coefficients than those of EO polyimides having the same chromophore. It is due to the high chromophore density and the high poling efficiency of the poly(ether imides).

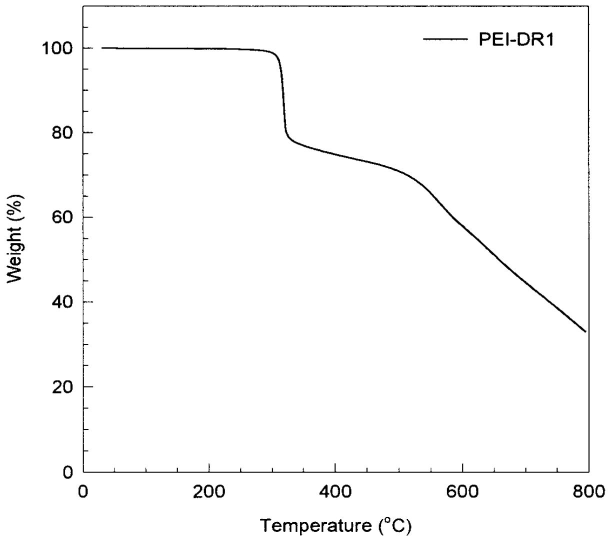


Figure1. TGA curve of the PEI-DR1.

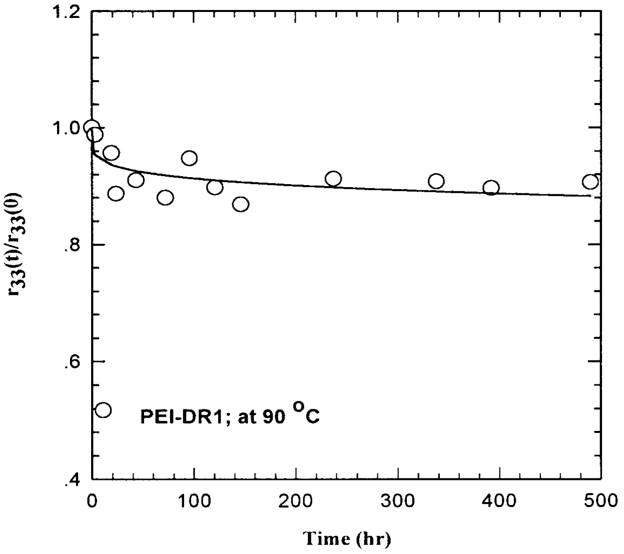


Figure 2. Thermal stability of EO coefficients

EO coefficients of all the polymers remained fairly stable even at longer periods. The initial value of EO coefficient decayed only by ca. 10% at 90 °C after 500 h, as shown in Figure 2. These values retained after 10 months.

Relaxation curves are typically fitted to a stretched exponential function (10, 11).

$$\Phi(t) = e^{-(t/\tau)^{ß}}$$

In this equation, τ is the average relaxation time constant while ß is the stretch parameter, which describes the width of the relaxation time constant distribution. The EO coefficient decay data of the PEI-DR1 were fitted to the stretched exponential represented by above equation. The resulting fitted τ and ß parameter is 1.4526×10^{7} (hr) and 0.2039, respectively. These thermal characteristics are an indication that these polymers may be useful in photonics device applications.

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