Articles

Two Novel Fluorinated Poly(arylene ether)s with Pendant Chromophores for Second-Order Nonlinear Optical Application

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ABSTRACT: Two fluorinated poly(arylene ether)s, **P1** and **P2**, containing perfluorophenyl moieties in the main chains and second-order nonlinear optical (NLO) chromophores in the side chains have been conveniently prepared by Knoevenagel condensation reaction between perfluorophenyl-containing poly(arylene ether) **P** and cyanoacetylated NLO chromophores **2** and **3** for the first time. The molar percentages of the pendant chromophores were estimated to be 162% and 138% for **P1** and **P2**, respectively, and their weight percentages were both 42.3%. Both of the two polymers are thermally stable and readily soluble in common organic solvents. The glass transition temperatures (T_g's) of **P1** and **P2** were determined to be 186 and 192 °C, respectively. The in-situ second harmonic generation (SHG) measurement revealed the resonant NLO coefficient (d_{33}) values of 60 and 31 pm/V for the poled films of **P1** and **P2**, respectively. The thermal stability of the SHG signals of the polymer films was studied by the depoling experiment in air using **P1** as the typical polymer, in which the decay onset of the SHG signal occurred at around 160 °C.

Introduction

Considerable effort has been devoted to the development of organic nonlinear optical (NLO) polymeric materials since two decades ago due to their potential photonics applications and many advantages over single crystals.[1−3] Recently, the new discoveries by Dalton[4] and Jen[5] of the enhancement of NLO activities of the polymers and the minimization of the halfwave voltage of electrooptic (E-O) modulators reattracted much new attention to them. For practical applications, the device-quality NLO polymers must retain high optical quality thin films, high optical damage thresholds, low optical propagation loss, and feasibility of device fabrication, besides the sufficiently large and stable NLO susceptibilities.[3,6] Although it is extremely difficult to solve all the problems, they have been ameliorated by different research groups.[7−10] Fluorinated polymers are of growing interest in the investigation of NLO materials in recent years.[11−15] Their unique properties[16−21] including low dielectric constant, refractive index, optical loss and moisture absorption, high thermal and chemical stability, and good processability are all necessary for NLO applications. Furthermore, the fluorinated moieties can improve the properties of the NLO polymeric materials without weakening their NLO activities.[10−15,21,22] Thus, many fluorinated polymers, especially those with high glass transition temperatures (T_g's), such as polyimides[22] and polyquinolines,[23] have been employed as excellent NLO polymers. Lately, Jen et al. also introduced fluorinated moieties into NLO active dendrimers[24,25] and dendronized polymers,[5,26,27] and they found that the fluorinated moieties could also bring many outstanding properties, such as low optical loss, low birefringence, good processability, and high thermal stability to these materials, and retain their extraordinarily large macroscopic NLO activities simultaneously. All of the above studies have demonstrated that the fluorinated polymeric materials may fulfill many of the requirements of the NLO materials.

On the other hand, fluorinated poly(arylene ether)s containing perfluorophenyl moieties in the polymer backbones have been evaluated for optical waveguide components in recent years because they enable the balance of the properties such as birefringence, T_g, and adhesion by adjusting the structures and fluorine contents.[16,28−31] In addition, the perfluorophenyl moieties give the polymers good thermal stability and mechanical properties similar to those of polyimides, while the flexibilizing ether groups make them exhibit better solubility than polyimides.[29,32,33] So they are more accessible for optical utilization.

In this paper, two fluorinated poly(arylene ether)s **P1** and **P2** containing perfluorophenyl moieties in the backbones and NLO chromophores in the side chains were successfully prepared for NLO application. Thus, a fluorinated poly(arylene ether) **P** with aldehyde groups in the side chains was first prepared by the nucleophilic aromatic substitution polycondensation

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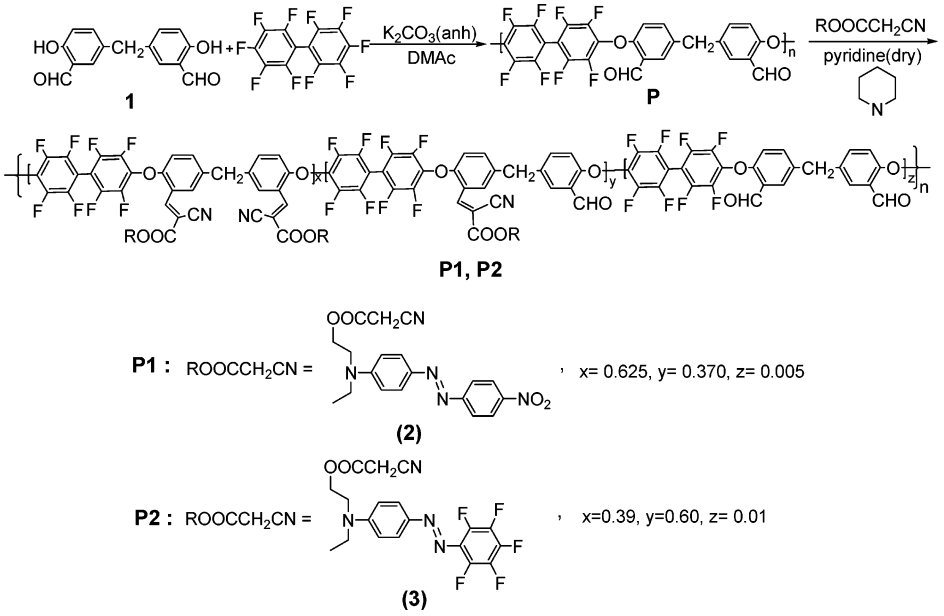
Scheme 1. Synthetic Route to P, P1, and P2



reaction between perfluorobiphenyl and double aldehyde groups containing bisphenol **1**, and then the cyanoacetylated NLO chromophores **2** and **3** were attached to **P** as pendant groups by Knoevenagel condensation reaction under mild conditions (Scheme 1). To the best of our knowledge, **P1** and **P2** are the first two examples of fluorinated poly(arylene ether)s for NLO applications. In addition, the postfunctionalization reaction condition in this study is mild enough to tolerate other sensitive high $\mu\beta$ chromophores, which can also be conveniently introduced into **P** as pendant groups by this synthetic route. We hope that this study can promote much research interest to the fluorinated poly(arylene ether)s for NLO applications.

Results and Discussion

Synthesis. The synthetic route to **P**, **P1**, and **P2** is shown in Scheme 1. To introduce the perfluorophenyl moieties and the NLO chromophores, a very active monomer, perfluorobiphenyl, first reacted with a double aldehyde group containing bisphenol **1** under the nucleophilic aromatic substitution polycondensation condition to afford fluorinated poly(arylene ether) **P** with pendant aldehyde groups. Knoevenagel condensation reaction was chosen as the postfunctionalization reaction to synthesize **P1** and **P2** due to its mild synthetic conditions and the high reactivity of the aldehyde groups toward this reaction, and the cyanoacetates were selected as the active hydrogen species because of their high reactivity and minimized byproduct in this reaction.[34] In this study, pyridine was utilized as the solvent instead of dimethylformamide (DMF) which had ever been used by our group in Knoevenagel condensation reaction to prepare a NLO chromophore functionalized poly(*N*-vinylcarbazole) (PVK).[35] As a result, we found that in this reaction pyridine was more favorable than DMF, in which the reaction time was shortened from 48 h (in DMF[35]) to only 6 h. Furthermore, the high molar percentages of the chromophores of **P1** and **P2** also demonstrated that this synthetic method was very effective.

Structural Characterization of P, P1, and P2. The IR spectra of **P**, **P1** and **P2** are shown in Figure 1. In the IR spectrum of **P**, the absorption bands at 1225 and 1693 cm^{-1} were attributed to the stretching vibration of the aromatic ether group and the carbonyl of the aromatic aldehyde group, respectively, which confirmed the formation of **P**. In the IR spectra of **P1** and **P2**, the absorption band at 1225 cm^{-1} exhibited no significant change, while the absorption band at 1693 cm^{-1} was weakened significantly, and two new absorption bands at 1734 and 2220 cm^{-1} appeared, contributed by the carbonyl stretching vibration of the conjugated carboxylic esters and the nitrile stretching vibration. In addi-

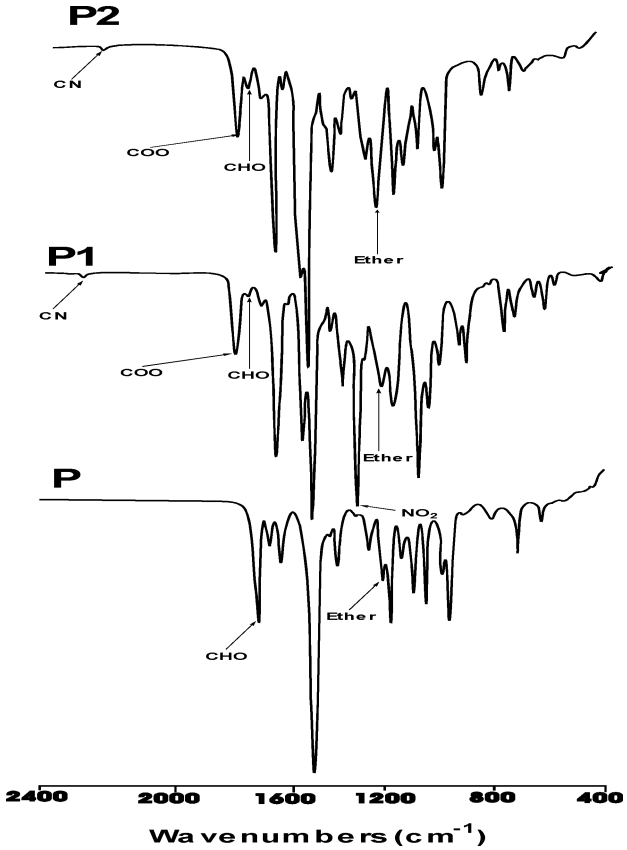


Figure 1. IR spectra of **P**, **P1**, and **P2**.

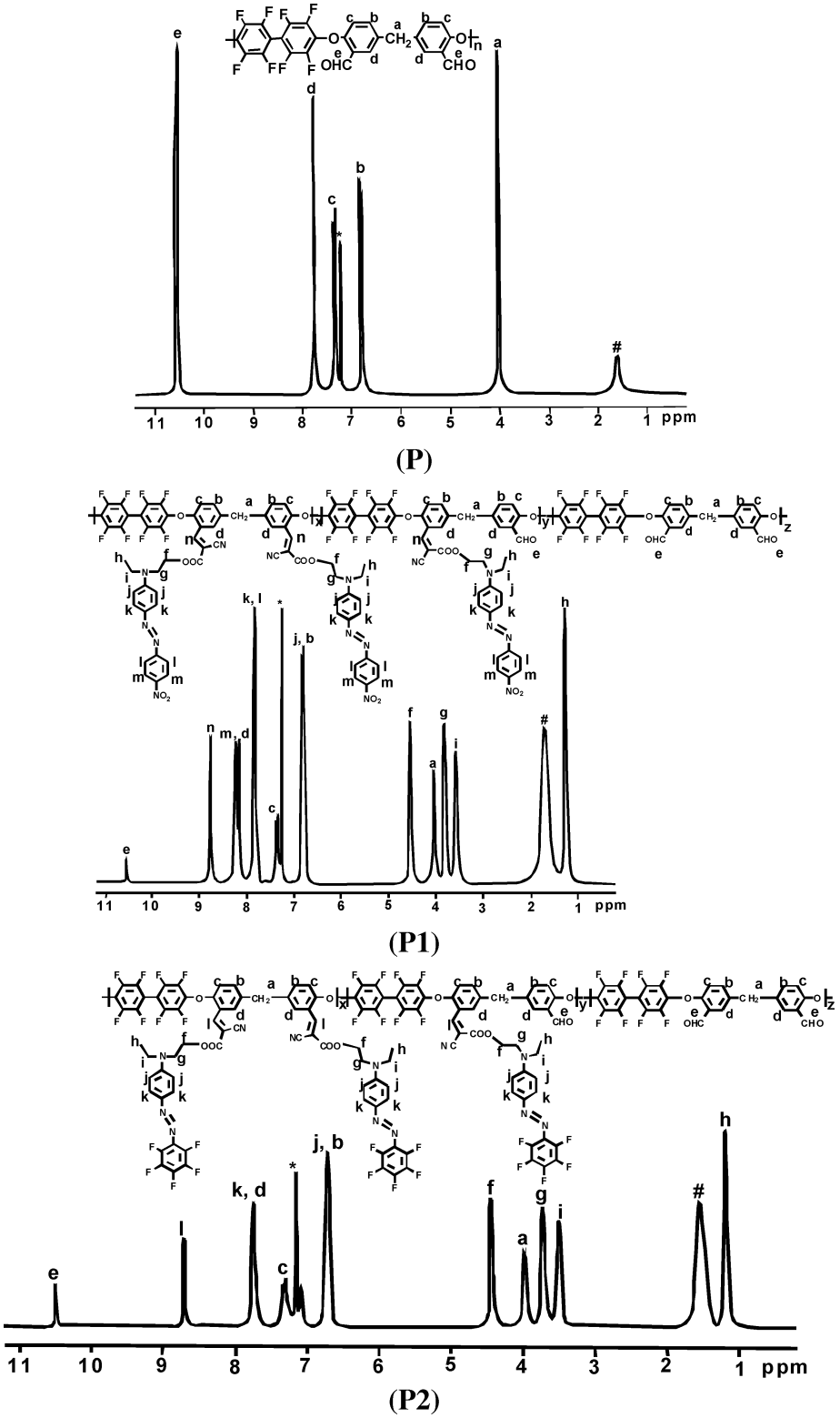


Figure 2. ^{1}H NMR spectra of **P**, **P1**, and **P2** (in $CDCl_3$, with TMS as a reference; *, solvent; #, water).

tion, a new absorption band at 1339 cm^{-1} emerged in the IR spectrum of **P1**, contributed by the nitro stretching vibration of chromophore **2**. The above results confirmed that cyanoacetylated chromophores **2** and **3** were successfully introduced into the side chains of the polymers.

Figure 2 exhibits the ^{1}H NMR spectra of **P**, **P1**, and **P2**. In the ^{1}H NMR spectrum of **P**, all of the peaks accorded with the chemical shifts of the protons of bisphenol **1**. While in the ^{1}H NMR spectra of **P1** and **P2**, some new peaks appeared distinctly. These new peaks were in good agreement with the chemical shifts of the protons of the chromophores **2** and **3**, respectively. From the comparison of the integration of the methylene in the backbones and the aldehyde groups in the side chains in the ^{1}H NMR spectra of **P1** and **P2**, the molar ratios of the double-substituted, monosubstituted, and nonsubstituted aldehyde groups were estimated to be

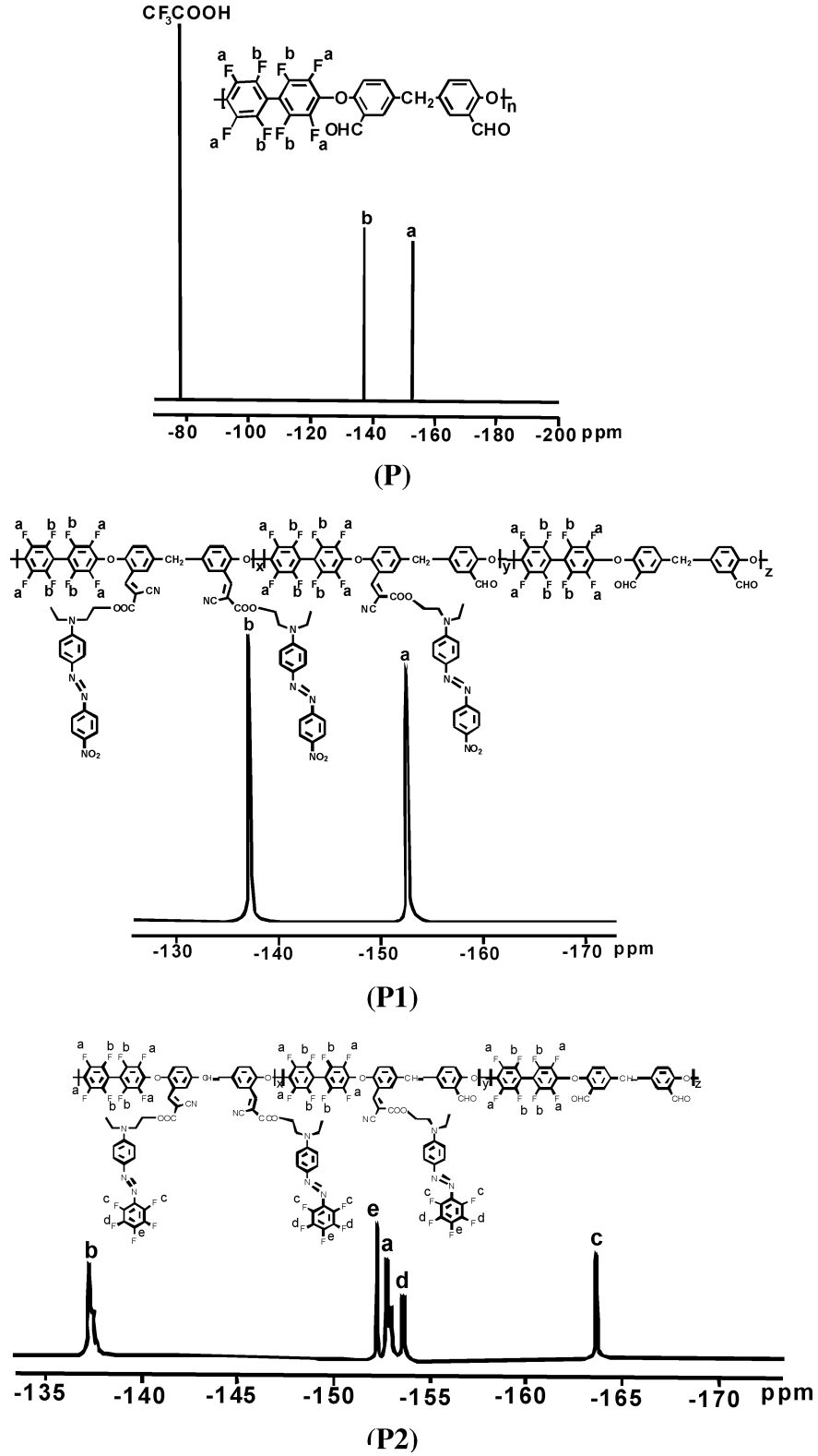


Figure 3. ^{19}F NMR spectra of **P**, **P1**, and **P2** (in $CDCl_3$, with CF_3COOH as a reference).

0.625:0.370:0.005 and 0.39:0.60:0.01 for **P1** and **P2**, respectively. Thus, the molar percentages of the chromophores were calculated to be 162% and 138% for **P1** and **P2**, respectively, and the weight percentages of the chromophores were calculated to be 42.3% for both **P1** and **P2**. These percentages of the chromophores were consistent with the results of elemental analysis.

^{19}F NMR study was also conducted using trifluoroacetic acid (CF_3COOH) as a reference to confirm the structures of **P**, **P1**, and **P2**, which are presented in Figure 3. In the nucleophilic substitution reactions, perfluorobiphenyl is very active, and the reactions usually take place at 4,4′-sites of perfluorobiphenyl first; however, the fluorines at other sites will also react under appropriate conditions and produce cross-linking products.[36] In the ^{19}F NMR spectrum of **P**, only two peaks at the chemical shifts of −137.34 and −152.87 ppm appeared, attributed to the fluorines meta and

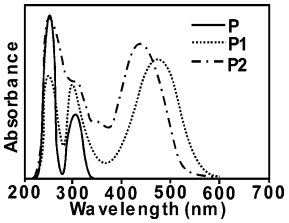


Figure 4. UV−vis spectra of **P**, **P1**, and **P2** (in THF).

ortho to the ether linkage, respectively. This result demonstrated that the nucleophilic substitution reaction only took place at 4,4′-sites of perfluorobiphenyl under our polymerization conditions. After being functionalized with cyanoacetylated chromophores **2** and **3**, these two peaks exhibited no significant changes in the ^{19}F NMR spectra of **P1** and **P2**, which indicated that there were no changes of the perfluorophenyl moiety in the polymer backbones in Knoevenagel condensation reaction. In addition, three new peaks at the chemical shifts of −152.23, −153.70, and −163.67 ppm emerged distinctively in the ^{19}F NMR spectrum of **P2**. These new peaks were in good agreement with the chemical shifts of the fluorines in chromophore **3**, which confirmed the successful attachment of the chromophores to **P** as the pendent groups.

Perfluorophenyl moieties make **P**, **P1**, and **P2** exhibit excellent solubility. At room temperature, they are readily soluble in common organic solvents, such as chloroform, methylene dichloride, tetrahydrofuran (THF), pyridine, *m*-cresol, cyclopentanone, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), etc. Figure 4 shows the UV−vis spectra of **P**, **P1**, and **P2** in the solution of THF. After Knoevenagel condensation reaction, a new strong absorption maxima (λ_{max}) corresponding to the intramolecular charge transfer of chromophore **2** at about 473 nm appeared in the UV−vis spectrum of **P1**, while that of chromophore **3** at about 432 nm emerged in the UV−vis spectrum of **P2**. Compared with the λ_{max} of **P1**, the λ_{max} of **P2** was blue-shifted about 41 nm due to the enhancement of the transparency of chromophore **3** by the perfluorophenyl moiety.

Gel permeation chromatography with multiangle static light scattering (GPC-MASLS) measurement in THF indicated that the absolute weight-average molecular weights (M_w) of **P**, **P1**, and **P2** were 48 700, 212 700, and 248 500, respectively, with the polydispersities (M_w/M_n) of 2.31, 3.22, and 2.68, respectively. Perfluorophenyl moieties also give excellent thermal properties to **P**, **P1**, and **P2**. Observed from DSC experiments, the T_g's of **P**, **P1**, and **P2** were 198, 186, and 192 °C, respectively. The TGA thermograms of **P**, **P1**, and **P2** indicated that their 5% weight loss temperatures were all above 260 °C in both air and argon.

NLO Properties of P1 and P2. To evaluate the NLO activities of **P1** and **P2**, uniform and transparent thin films of these two polymers were prepared by spin-coating their cyclopentanone solution onto ITO substrates for second harmonic generation (SHG) measurements. The noncentrosymmetric alignment of the chromophores, which was essential for second-order optical nonlinearity, was achieved by corona poling, and the optimum poling temperatures for the films of **P1** and **P2** in the SHG measurements were 170−180 and 150−160 °C, respectively. Figure 5 shows the UV−vis spectra of the polymer films before and after poling. It

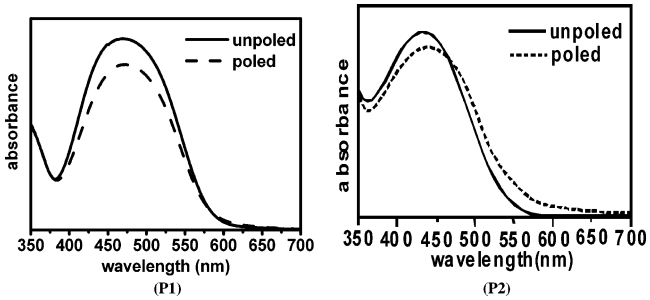


Figure 5. UV−vis spectra of the films of **P1** and **P2** before and after poling.

could be seen from the spectra that, after poling, the absorbance bands with the λ_{max} at about 473 and 445 nm for **P1** and **P2**, corresponding to the intramolecular charge transfer of chromophore **2** and **3**, decreased significantly. The order parameters (Φ)[37] of the poled films ($\Phi = 1 - A_1/A_0$, where A_0 and A_1 are the maximum absorbance before and after poling, respectively) were calculated to be 0.14 and 0.18 for **P1** and **P2**, respectively. Calculation of the resonant NLO coefficient (d_{33}) values for the poled films of **P1** and **P2** was based upon the following equation:[38]

$$\frac{d_{33,s}}{d_{11,q}} = \sqrt{\frac{I_s}{I_q}} \frac{I_{c,q}}{I_s} F$$

where the $d_{11,q}$ was d_{11} of the quartz crystals, which was 0.45 pm/V, I_s and I_q were the SHG intensities of the sample and the quartz, respectively, $l_{c,q}$ was the coherent length of the quartz, l_s was the thickness of the polymer films, and F was the correction factor of the apparatus and equaled 1.2 when $l_c \gg l_s$. The d_{33} values of the poled films of **P1** and **P2** were calculated to be 60 and 31 pm/V, respectively, at 1064 nm fundamental wavelength, and the nonresonant NLO coefficient ($d_{33}(\infty)$) values were estimated to be 10 and 8 pm/V for **P1** and **P2**, respectively, by using the approximate two-level model.[39] Yu et al.[40] have reported a series of polyimides containing chromophore **2** with very high d_{33} values of 59, 69, and 169 pm/V (the relevant $d_{33}(\infty)$ values were 7, 9, and 18 pm/V). To the best our knowledge, the d_{33} value of 169 pm/V is the highest one so far among the d_{33} values of the polymers containing **2** as the NLO chromophore. On the other hand, until now, there is only one paper[41] reporting the d_{33} value of 11.5 pm/V for the polymer containing **3** as the NLO chromophore. Compared with the above results, the d_{33} and $d_{33}(\infty)$ values of **P1** and **P2** were relatively high.

The dynamic thermal stability of the SHG signals of the poled polymer films was investigated through depoling experiment in which the real-time decay of the SHG signals was monitored when the poled films were heated at a rate of 4−5 °C/min in the range 20−200 °C in air. **P1** was selected as the typical polymer, and its plot of $d_{33}(t)/d_{33}(0)$ vs temperature is shown in Figure 6. It can be seen that the decay onset of the SHG signal occurred at around 160 °C, and its half-decay temperature of the SHG signals was at about 180 °C. Progresses in identifying the NLO chromophores with large hyperpolarizabilities, high thermal stability, and low optical loss have already taken place.[1,42−47] These chromophores could be exploited with the fluorinated poly(arylene ether)s considered here to prepare more excellent

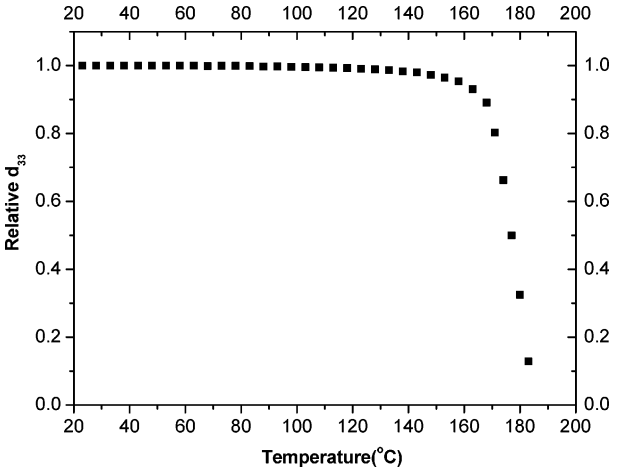


Figure 6. Decay of the SHG coefficient signals as a function of temperature for **P1**.

candidates for electrooptic (E-O) applications in the future.

Conclusions

The first two examples of NLO active fluorinated poly(arylene ether)s **P1** and **P2** have been conveniently prepared under mild postfunctionalization reaction condition in this study. The molar percentages of the chromophores are 162% and 138% for **P1** and **P2**, respectively, and their weight percentages are both 42.3%. The introduction of the perfluorophenyl moieties provides the polymers with excellent solubility and good thermal properties. SHG measurement indicated that the resonant NLO coefficient (d_{33}) values of **P1** and **P2** were 60 and 31 pm/V, respectively, and the nonresonant NLO coefficient ($d_{33}(\infty)$) values were respectively estimated to be 10 and 8 pm/V for **P1** and **P2**. **P1** and **P2** exhibit high T_g's (186 °C for **P1** and 192 °C for **P2**), and the SHG signal of the typical polymer **P1** was thermally stable below 160 °C after poling. These two polymers represent a promising NLO polymeric system.

Experimental Section

Materials. Perfluorobiphenyl, pentafluoroaniline, and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) were purchased from Acros and used as received. Cyanoacetic acid and 1,3,5-trioxane were purchased from Fluka and used as received. 1,3-Dicyclohexylcarbodiimide (DCC) and 2-hydroxybenzaldehyde were distilled under reduced pressure before use. Pyridine, piperidine, tetrahydrofuran (THF), and cyclopentanone were dried and distilled over potassium hydroxide (KOH), calcium hydride (CaH_2), sodium, and pentaphosphine oxide (P_2O_5), respectively, before use. 5,5′-Methylenebis(salicylaldehyde) (**1**) was prepared from 1,3,5-trioxane and 2-hydroxybenzaldehyde according to the method of the literature[48] and recrystallized twice from acetone before use. Cyanoacetylated dispersed red 1 (DR-1) (**2**) was prepared from DR-1 and cyanoacetic acid following the method in the literature.[35] Other chemicals were used as received without further purification.

Measurements. ^{1}H NMR and ^{19}F NMR spectra were recorded on a Varian-Mercury VX300 spectrophotometer using chloroform-*d* ($CDCl_3$) as a solvent and tetramethylsilane (TMS) (^{1}H) or trifluoroacetic acid (CF_3COOH) (^{19}F) as a reference. The IR spectra were recorded on a NICOLET 170SKFT-IR spectrophotometer with KBr pellets in the region 4000−400 cm^{-1}. Elemental analysis (EA) was performed on a Calo-Erba elemental analyzer (model 1106). The FAB-MS spectrum was conducted with a VJ-ZAB-3F mass spectrometer. Differential scanning calorimetry (DSC) was performed with a Pyris 1 DSC instrument under nitrogen at a heating rate of 15 °C/min with gas flow of 20 mL/min. Thermogravimetric analysis (TGA) was performed with a Shimadzu-DT 40 instrument at a heating rate of 20 °C/min under static air and argon with gas flow of 50 mL/min. The molecular weights were determined by gel permeation chromatography with multiangle static light scattering (GPC-MASLS). GPC-MALLS measurements were performed on a DAWN DSP multiangle laser photometer with a pump P100 (Thermo Separation Products, San Jose, CA) equipped with a TSK-GEL G4000 HHR and a differential refractive index detector (RI-150) at 25 °C. The eluent was THF, and its flow rate was 1.00 mL/min. All solutions were filtered with sand filter and 0.45 μm filter (PTFE, Puradisc 13 mm Syringe Filters, Whattman, England). Astra software was utilized for data acquisition and analysis. The thickness of the poled films of the polymers was determined by a Talysurf-S4C surface profiler.

Chromophore Synthesis. Synthesis of *N*-Ethyl-*N*-(2-hydroxyethyl)-4-(pentafluorophenylazo)aniline. This new chromophore was prepared from *N*-ethyl-*N*-(2-hydroxyethyl)-aniline and pentafluoroaniline in a similar way reported in the literature.[49] After recrystallization from toluene/petroleum (60−90 °C), pure product was obtained as an orange crystalline solid; yield 53%. ^{1}H NMR ($CDCl_3$, TMS int) δ (ppm): 1.23 (t, J = 7.2 Hz, 3H, −CH_3), 3.73 (q, 4H, −NCH_2), 4.41 (t, J = 7.2 Hz, 2H, −CH_2OH), 6.69 (d, J = 9.0 Hz, 2H, ArH), 7.51 (d, J = 9.0, 2H, ArH).

Synthesis of Cyanoacetylated *N*-Ethyl-*N*-(2-hydroxyethyl)-4-(pentafluoro-phenylazo)aniline (3). Chromophore **3** was prepared from the above new chromophore and cyanoacetic acid in a similar way reported in the literature.[35] The crude product was purified by column chromatography using chloroform/ethyl acetate (6/1, v/v), and pure chromophore **3** was obtained as an orange powder; yield 78%, mp 93−94 °C. FT-IR (KBr pellet, cm^{-1}): 2262 (ν_{CN}), 1745 ($\nu_{C=O}$). ^{1}H NMR ($CDCl_3$, TMS int) δ (ppm): 1.25 (t, J = 7.2 Hz, 3H, −CH_3), 3.47 (s, 2H, CNCH_2COO−), 3.75 (q, J = 7.0 Hz, 2H, −NCH_2-CH_3), 4.43 (t, 2H, −COOCH_2−), 6.78 (d, J = 9.0 Hz, 2H, ArH), 7.86 (d, J = 9.0 Hz, 2H, ArH). MS (FAB), m/z [M$^+$]: 426. Calcd for $C_{19}H_{15}N_4O_2F_5$: C, 53.52; H, 3.52; N, 13.14. Found: C, 53.45; H, 3.47; N, 13.15.

Polymer Synthesis. Synthesis of P. A dry, 50 mL three-necked flask equipped with an oil bath, a mechanical stirrer, a Dean−Stark trap, a cold water condenser, an argon inlet/outlet, and a thermometer was charged with **3** (0.2563 g, 1 mmol), anhydrous potassium carbonate (0.1935 g, 1.4 mmol), 5 mL of *N*,*N*-dimethylacetamide (DMAc), and 10 mL of toluene. The reaction mixture was heated under an argon atmosphere at 130−140 °C to remove the water by means of azotropic distillation with toluene. After about 3 h, all the water was removed and toluene was distilled. Then, the solution was cooled to room temperature, and perfluorobiphenyl (0.3341 g, 1 mmol) was added into the flask. The solution was then heated to 165−170 °C and stirred vigorously at this temperature until a very viscous solution was obtained. After cooling to room temperature, 3 mL of DMAc was added into the solution, which was then poured into 200 mL of methanol containing a few drops of glacial acetic acid to precipitate the polymer. The precipitate was collected, dried, and dissolved in chloroform, filtered to remove insoluble solid, and reprecipitated by adding the solution dropwise into methanol. After being dissolved/precipitated from chloroform/methanol twice and dried in vacuo at 60 °C overnight, 0.38 g of white fibrous solid was obtained; yield 69.1%. ^{1}H NMR ($CDCl_3$, TMS int) δ (ppm): 4.04 (s, 2H, −CH_2−), 6.83 (d, 2H, ArH), 7.35 (d, 2H, ArH), 7.77 (s, 2H, ArH), 10.57 (s, 1H, −CHO). ^{19}F NMR ($CDCl_3$, CF_3COOH int) δ (ppm): −137.34, −152.87.

Synthesis of P1. A dry, 20 mL two-necked flask equipped with an oil bath, a magnetic stirrer, a cold water condenser, and an argon inlet/outlet was charged with **P** (0.2 g, 0.364 mmol), chromophore **2** (0.28 g, 0.727 mmol), 15 mL of pyridine, and piperidine (10 μL). After the reaction mixture was dissolved, the solution was heated to 55−60 °C for 6 h under an argon atmosphere. Then the solution was cooled to room temperature and poured into 400 mL of methanol to precipitate the polymer. The polymer was collected by filtration and

Table 1. Percentages of Chromophores and Compositions of P1 and P2

						elemental analysis [%]: found (calcd)		
polymer	*x*	*y*	*z*	d_m[a] (%)	d_w[b] (%)	C	H	N
P1	0.625	0.37	0.005	162	42.3	61.26 (60.93)	3.32 (3.33)	9.25 (9.96)
P2	0.39	0.60	0.01	138	42.3	56.89 (57.28)	3.06 (2.72)	6.15 (6.93)

[a] Molar percentages of the chromophores. [b] Weight percentages of the chromophores.

Table 2. Molecular Weights and Thermal Properties of P, P1 and P2

	M_w[a]	polydispersity		T_d (°C)	
polymer	($\times 10^4$)	(M_w/M_n)	T_g[b] (°C)	in air[c]	in argon[d]
P	4.87	2.31	198	347	347
P1	21.27	3.22	186	288	291
P2	24.85	2.68	192	263	269

[a] Molecular weights were determined by GPC-MASLS at 25 °C with THF as the eluent. [b] T_g's were determined by DSC at a heating rate of 15 °C/min under nitrogen with a gas flow of 20 mL/min. [c] 5% weight loss temperatures were detected at a heating rate of 20 °C/min under static air. [d] 5% weight loss temperatures were detected at a heating rate of 20 °C/min under argon with a gas flow of 50 mL/min.

Table 3. NLO Properties of P1 and P2

polymer	T_{opt}[a] (°C)	l_s[b] (μm)	Φ[c]	d_{33}[d] (pm/V)	$d_{33}(\infty)$[e] (pm/V)
P1	170−180	0.44	0.14	60	10
P2	150−160	0.72	0.18	31	8

[a] Optimal poling temperatures of the polymer films. [b] Thickness of the polymer films. [c] Order parameters of the poled films. [d] Resonant NLO coefficient values determined by SHG measurements. [e] Nonresonant NLO coefficient values estimated by the approximate two-level model.

purified by being dissolved/precipitated from chloroform/methanol twice. After being dried in vacuo at 60 °C overnight, 0.29 g of red fibrous solid was obtained; yield 61.7%. ^{1}H NMR ($CDCl_3$, TMS int) δ (ppm): 1.25 (m, 3H, −C*H*$_3$), 3.55 (m, 2H, −NC*H*$_2$CH$_3$), 3.80 (m, 2H, −NC*H*$_2$CH$_2$−), 4.03 (m, 2H, −C*H*$_2$−), 4.53 (m, 2H, −NCH$_2$C*H*$_2$−), 6.79 (m, 4H, ArH), 7.37 (m, 2H, ArH), 7.83 (m, 4H, ArH), 8.23 (m, 4H, ArH), 8.76 (s, 1H, −C*H* = C(CN)−), 10.56 (s, 1H, −C*H*O). ^{19}F NMR ($CDCl_3$, CF_3COOH int) δ (ppm): −137.08, −152.55.

P2 was prepared in the similar way of **P1** and was obtained as an orange fibrous solid; yield 86.3%. ^{1}H NMR ($CDCl_3$, TMS int) δ (ppm): 1.19 (m, 3H, −C*H*$_3$), 3.50 (m, 2H, −NC*H*$_2$CH$_3$), 3.73 (m, 2H, −NC*H*$_2$CH$_2$−), 4.45 (m, 2H, −C*H*$_2$−), 6.72 (m, 4H, ArH), 7.33 (m, 2H, ArH), 7.74 (m, 4H, ArH), 8.70 (s, 1H, −C*H*═C(CN)−), 10.50 (s, 1H, −C*H*O). ^{19}F NMR ($CDCl_3$, CF_3-COOH int) δ (ppm): −137.28, −152.23, −152.78, −153.70, −163.67.

Polymer Film Preparation. P1 and **P2** were dissolved in cyclopentanone, and the solution (10 wt %) was filtered through syringe filters. Polymer films were obtained by spin-coating the polymer solution onto indium tin oxide (ITO)-coated glass substrates (which were cleaned in the ultrasonic bath with DMF, THF, ethanol, and distilled water subsequently). The residual solvent was removed by heating the films in a vacuum oven at 70 °C for 3 days. The thickness of the films of **P1** and **P2** was estimated to be 0.44 and 0.72 μm, respectively, as listed in Table 3.

Characterization of Poled Films. The second-order optical nonlinearities of **P1** and **P2** were determined by the in-situ second-harmonic generation (SHG) measurement technique. Thus, a closed temperature-controlled oven having optical windows and equipped with three needle electrodes was used. The films, which were kept at 45 ° to the incident beam, were poled inside the oven, and the SHG intensity was monitored simultaneously. The poling condition was as follows: voltage, 7.6 kV at the needle point; gap distance, 0.8 cm. The SHG measurements were carried out with a Nd:YAG laser operating with a 10 Hz repetition rate and an 8 ns pulse width at 1064 nm fundemental wavelength. A Y-cut quartz crystal served as a reference. The NLO coefficients d_{33} were deduced by comparing the intensities of the SHG signals of the poled film with those of the quartz crystal.

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