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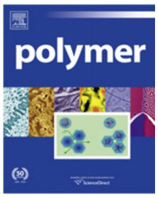

Poly(arylene ether)s with trifluoromethyl groups via meta-activated nitro displacement reaction

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ABSTRACT

New poly(arylene ether)s with pendent trifluoromethyl groups were synthesized from 2,2′-bis(trifluoromethyl)-4,4′-dinitro-1,1′-biphenyl with several bisphenols. The nitro leaving group activated by the trifluoromethyl group at meta position was quantitatively displaced with phenolate ions, resulting in high molecular weight polymers. The quantum mechanical calculation of the energy state suggested that the nitro displacement reaction activated by the trifluoromethyl group at meta position is an energetically favorable process. The polymers having weight average molecular weight of 42,100–95,000 g/mol and molecular weight distribution of 2.65–2.95 were obtained. The polymers were amorphous and dissolved in a wide range of organic solvents. Transparent and flexible films were obtained by solution casting. The resulting polymers are thermally stable, and T_gs of the polymers are in the range of 176–199 °C depending on their molecular structure. All of the synthesized polymers show refractive indices in the range of 1.592–1.624 with low birefringence below 0.006.

1. Introduction

Nucleophilic aromatic substitution (S_NAr) reaction has been utilized in commercial production of poly(arylene ether)s, one of high-performance engineering plastics with excellent hydrolytic, thermal and dimensional stability along with good mechanical properties [1]. The S_NAr reaction requires a leaving group activated with an electron withdrawing group [2], and sulfone, ketone, and imide groups are used as activating groups for S_NAr reaction to make poly(ether sulfone)s, poly(ether ketone)s, and poly(ether imide)s respectively [3–5]. Various heterocyclic rings have been also used as an activating group to produce high molecular weight poly(arylene ether)s [6].

The activating groups in S_NAr reaction are generally electron withdrawing groups, and they stabilize the negative charge developed during the transition state largely through conjugation [7–9]. So, the electron withdrawing group at meta position of the leaving group is less effective than the same group at ortho or para position, and therefore activating groups at ortho or para position are generally required to obtain high molecular weight polymers. Even though there are a few examples of meta-activated S_NAr reaction [10–16], most of them are not suitable for the synthesis of linear high molecular weight polymers through polycondensation [17,18].

It has been reported that the trifluoromethyl group at ortho or para position activates fluoro or nitro groups for displacement by phenoxides [19–26]. The steric congestion caused by bulky trifluoromethyl group at ortho position of the nitro leaving group significantly affects the formation of a Meisenheimer complex with release of steric strain [27–32]. The perfluoroalkyl activation in S_NAr reaction provides an effective way to incorporate fluorines into the polymer chains, which may improve many physical properties of polymers such as dielectric constant, moisture absorption, and solubility [33–38].

In the previous work [39], we have found that trifluoromethyl groups and ether linkages are stable in the nitro displacement reaction even at 190 °C, and the displacement reaction occurs quantitatively without any side reactions which are frequently observed during the nitro displacement reaction at high temperature due to the reactive nitrite ion by-product [40–46]. Furthermore, the nitro group activated by trifluoromethyl group at meta position undergoes the displacement reaction quantitatively at high temperature, and the trifluoromethylated poly(biphenylene oxide)s were successfully synthesized through meta-activated nucleophilic nitro displacement reaction [47].

In this study, new poly(arylene ether)s with pendent trifluoromethyl groups were prepared from 2,2′-bis(trifluoromethyl)-

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4,4′-dinitro-1,1′-biphenyl through meta-activated nucleophilic nitro displacement reaction, and their properties were investigated.

2. Experimental section

2.1. Materials

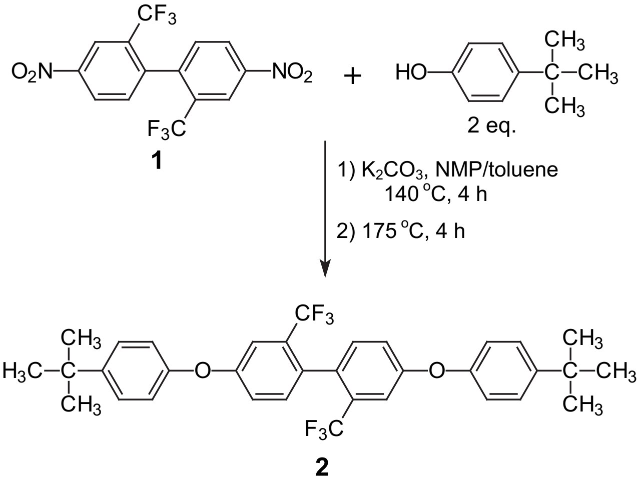
5-Bromo-2-nitrobenzotrifluoride (Marshallton) was used as received. 4-*tert*-Butylphenol was sublimed at 90 °C in vacuum. 2,2-Bis(4′-hydroxyphenyl)propane (Bisphenol A, Aldrich) was recrystallized from toluene, 2,2-bis(4′-hydroxyphenyl)hexafluoropropane (Bisphenol AF, Aldrich) was recrystallized from toluene/ethyl acetate ($v/v = 95/5$), and 4,4′-biphenol (Aldrich) was recrystallized from ethanol/water ($v/v = 60/40$). Potassium carbonate (K_2CO_3) was dried in vacuo at 150 °C for 24 h prior to use. *N*-Methyl pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), and *N,N*-dimethyl formamide (DMF) were stirred in the presence of P_2O_5 overnight and then distilled under reduced pressure. Toluene was stirred in the presence of CaH_2 overnight and then distilled under nitrogen. Other commercially available reagent grade chemicals were used without further purification.

2.2. General measurements

Fourier-transform infrared (FTIR) spectra of the compounds were obtained with a Bruker EQUINOX-55 Spectrophotometer using a KBr pellet or film. Nuclear magnetic resonance (NMR) spectra of synthesized compounds were recorded on Bruker Fourier Transform AVANCE400 spectrometers (400 MHz for ^{1}H and 100 MHz for ^{13}C). Chemical shift of NMR was reported in part per million (ppm) using tetramethylsilane as an internal reference. Splitting patterns designated as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublets of doublet), m (multiplet), and br (broaden). High-resolution mass spectra (HRMS) of the synthesized compounds were obtained with a Jeol JMS-SX-102 mass spectrometer. Intrinsic viscosity data were obtained in *N,N*-dimethylacetamide (DMAc) with a Canon-Ubbelohde type viscometer at 30 °C. Size exclusion chromatography (SEC) diagrams were obtained with Senshu SSC-7100 equipped with RI detector and high temperature packing column (SUS-316) using *o*-dichlorobenzene as an eluent at 85 °C. Number and weight average molecular weight of the polymers were calculated on the basis of polystyrene standards. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) and were performed on a TA 2200 thermal analyzer system. Melting points (m.p.) of the synthesized compounds and T_gs of the polymers were obtained with DSC instrument at a heating rate of 10 °C/min in N_2. TGA measurements were conducted at a heating rate of 10 °C/min in N_2 and air. The refractive indices of the synthesized polymers were measured with a Metricon 2010 prism coupler. The light source was a He–Ne laser of 632.8 nm wavelength, i.e., 474.08 THz frequency. The refractive index (n) of films was measured in transverse electric (TE) and transverse magnetic (TM) modes by choosing the appropriate polarization of the incident laser beam, giving the in-plane refractive index ($n_{TE} = n_{xy}$) and the out-of-plane refractive index ($n_{TM} = n_z$), respectively.

2.3. 2,2′-Bis(trifluoromethyl)-4,4′-dinitro-1,1′-biphenyl (**1**)

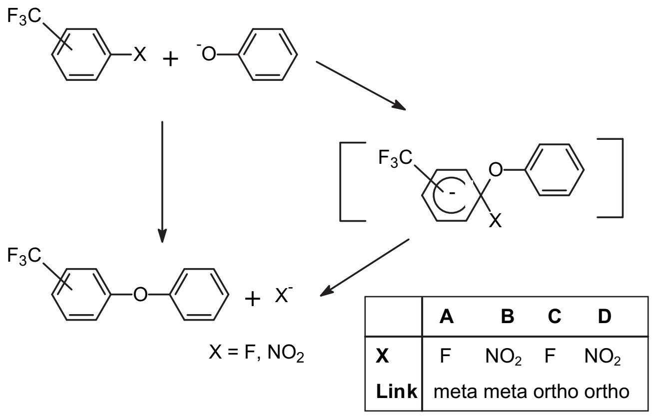
Activated copper (94.0 g, 1.48 mol) was added to a solution of 2-bromo-5-nitrobenzotrifluoride (100 g, 0.37 mol) in 200 mL of DMF. The reaction mixture was stirred mechanically at 150 °C for 6 h, then cooled and poured into vigorously stirred water. The yellow precipitate was filtered, washed with water and 1N HCl solution, and dried in vacuo. The crude product was recrystallized from benzene/diethyl ether ($v/v = 1/2$), and then sublimed at 120 °C in vacuo to give pale yellow solid (52.3 g, 0.138 mol, 74.6% yield).: m.p. 140–141 °C (lit [48]. m.p. 138–140 °C). IR (KBr, cm^{-1}): 3071 (aromatic C–H); 1593 (aromatic C=C); 1529, 1351 (NO_2); 1190–1120 (C–F). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 8.61 (dd, 2H, $J = 8.32$ Hz, $J = 2.32$ Hz), 8.59 (d, 2H, $J = 2.18$ Hz), 7.81 (d, 2H, $J = 8.35$ Hz). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): 147.90, 140.90, 133.30, 128.54 (q, $J = 32.1$ Hz), 126.67, 122.44 (q, $J = 273.6$ Hz), 121.37 (q, $J = 5.82$ Hz). HRMS (m/e): calc. for $C_{14}H_6N_2O_4F_6$, 328.0232; found, 380.0257.



Scheme 1. Model reaction.

2.4. Model reaction of 1 with 4-tert-butylphenol (**2**)

A 25 mL three-necked flask equipped with an argon inlet, Dean–Stark trap, and condenser was charged with **1** (0.7212 g, 1.897 mmol), 4-*tert*-butylphenol (0.5700 g, 3.794 mmol), K_2CO_3 (0.7865 g, 5.691 mmol), 6 mL of NMP, and 5 mL of toluene. The reaction mixture was heated to 140 °C for 4 h at which the toluene was brought to reflux. The toluene was periodically removed from the Dean–Stark trap, and fresh dry toluene was added to the reaction mixture to ensure dehydration of the system. The temperature was raised to 175 °C and the reaction mixture was stirred for 4 h. The product was precipitated into water and then filtered. Further purification was carried out by short-path silica gel column chromatography using ethyl acetate/*n*-hexane ($v/v = 1/2$) as an eluent to give colorless **2** (1.062 g, 1.810 mmol, 95.4% yield):



Scheme 2. 4 Sets of the reaction for quantum mechanical calculation.

Table 1
Reaction energy in gas phase (values in kcal/mol).[a]

No.	A	B	C	D
HF/6-31G*	45.4(13.1)	−13.6(9.8)	43.6	−26.6
HF/6-311G*//HF/6-31G*	37.1(13.4)	−11.4(9.7)	34.9	−26.1
HF/6-311G(2d)//HF/6-31G*	38.0(14.2)	−9.72(11.7)	35.9	−24.4
HF/6-311G(2df)//HF/6-31G*	39.6(38.2)	−9.73(34.2)	37.5	−25.0

[a] The values in parenthesis are the energy difference of reactants and intermediate.

FTIR (KBr, cm^{-1}): 3092, 2887 (aromatic and aliphatic C–H); 1590, 1478 (aromatic C=C); 1251 (C–O–C); 1170–1110 (C–F). ^1H NMR ($CDCl_3$, 400 MHz, ppm): 7.42 (d, 2H, J = 2.62 Hz), 7.25 (d, 2H, J = 8.32 Hz), 7.13 (d, 2H, J = 8.47 Hz); 7.44 (d, 4H, J = 7.57 Hz), 7.04 (d, 4H, J = 7.51 Hz); 1.37 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 157.63, 153.32, 147.31, 133.36, 130.87, 130.40 (q, J = 32.7 Hz), 126.23, 123.42 (q, J = 273.0 Hz), 119.52, 119.10, 115.63 (q, J = 5.41 Hz); 34.33, 31.37. HRMS (m/e): calc. for $C_{34}H_{32}O_2F_6$, 586.2306; found, 586.2321.

2.5. Poly(arylene ether) from 1 and Bisphenol A (*P1*)

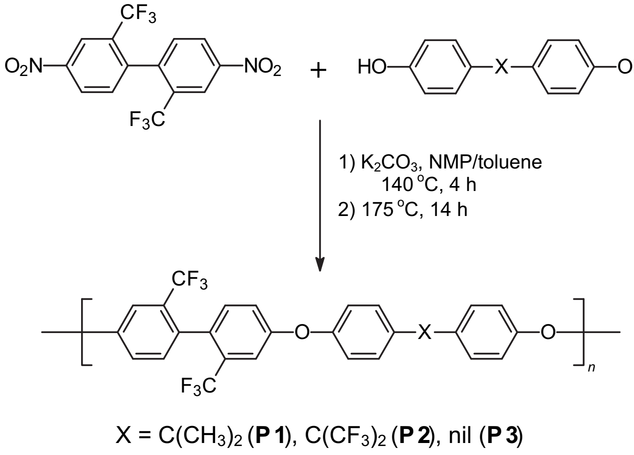
A 25 mL three-necked flask equipped with an argon inlet, mechanical stirrer, Dean–Stark trap, and condenser was charged with 1.212 g (3.188 mmol) of **1**, 0.7278 g (3.188 mmol) of Bisphenol A, 1.322 g (9.565 mmol) of K_2CO_3, 8 mL of NMP, and 5 mL of toluene. The reaction mixture was heated to 140 °C for 4 h at which the toluene was brought to reflux. The toluene was periodically removed from the Dean–Stark trap, and fresh dry toluene was added to the reaction mixture to ensure dehydration of the system. The temperature was raised to 175 °C and the reaction mixture was stirred for 14 h. The polymer was precipitated into a 400 mL of vigorously stirred methanol/water (v/v = 1/1) mixture and then filtered. The precipitated polymer was washed with hot water and methanol repeatedly, and dried in vacuo at 100 °C for 24 h (1.682 g, 96.6% yield). Further purification was carried out by dissolving the polymers in *N,N*-dimethylacetamide, filtering the polymer solution, and then precipitating it into methanol.: FTIR (Thin film, cm^{-1}): 3070–2880 (aromatic and aliphatic C–H); 1592, 1491 (aromatic C=C); 1248 (C–O–C); 1170–1100 (C–F). ^1H NMR (DMSO-d_6, 400 MHz, 100 °C, ppm): 7.45–7.32 (br, 8H), 7.30 (br, 2H), 7.05–7.03 (br, 4H); 1.71 (s, 6H). ^{13}C NMR (DMSO-d_6, 100 MHz, 100 °C, ppm): 157.26, 153.01, 146.43, 133.86, 130.47, 129.14 (q, J = 30.2 Hz), 128.34, 123.24 (q, J = 271.8 Hz), 120.11, 119.06, 115.16 (br); 41.83, 30.43.

2.6. Poly(arylene ether) from 1 and bisphenol AF (*P2*)

The same procedure used for **P1** was repeated with 1.012 g (2.662 mmol) of **1**, 0.8950 g (2.662 mmol) of Bisphenol AF, 1.1048 g (7.988 mmol) of K_2CO_3, 8 mL of NMP (1.701 g, 97.7% yield).: FTIR (Thin film, cm^{-1}): 3031 (aromatic C–H); 1592, 1468 (aromatic C=C); 1250 (C–O–C); 118–1090 (C–F). ^1H NMR (DMSO-d_6, 400 MHz, 100 °C, ppm): 7.49 (br, 8H), 7.40 (br, 2H), 7.20 (br, 4H). ^{13}C NMR (DMSO-d_6, 100 MHz, 100 °C, ppm): 158.20, 155.80, 134.00, 131.79, 131.76, 130.93, 129.57 (q, J = 30.2 Hz), 123.22 (q, J = 271.8 Hz), 122.166, 118.55, 116.67 (br); 123.90 (q, J = 282.4 Hz), 63.40 (m).

Table 2
Reaction energy using SCRF calculation (values in kcal/mol).

No.	A	B	C	D
HF/6-31G*	4.27	−10.2	1.14	−23.3
HF/6-311G*//HF/6-31G*	−6.57	−10.8	−9.67	−25.9
HF/6-311G(2d)//HF/6-31G*	−2.05	−6.24	−5.13	−21.2
HF/6-311G(2df)//HF/6-31G*	−6.62	−12.8	−11.1	−29.5



Scheme 3. Polymerization.

2.7. Poly(arylene ether) from 1 and 4,4′-biphenol (*P3*)

The same procedure used for **P1** was repeated with 1.393 g (3.644 mmol) of **1**, 0.6823 g (3.664 mmol) of 4,4′-biphenol, 1.519 g (10.99 mmol) of K_2CO_3, 8 mL of NMP (1.796 g, 97.2% yield).: FTIR (Thin film, cm^{-1}): 3011 (aromatic C–H); 1591, 1492 (aromatic C=C); 1251 (C–O–C); 1170–1100 (C–F). ^1H NMR (DMSO-d_6, 400 MHz, 100 °C, ppm): 7.74 (d, 4H, J = 7.76 Hz), 7.22 (d, 4H, J = 7.94 Hz); 7.48 (s, 2H), 7.40 (d, 4H, J = 8.21 Hz), 7.34 (d, 4H, J = 8.17 Hz). ^{13}C NMR (DMSO-d_6, 100 MHz, 100 °C, ppm): 157.34, 154.84, 135.72, 133.97, 130.79, 128.96 (q, J = 30.1 Hz), 128.22, 123.33 (q, J = 272.5 Hz), 120.51, 120.04, 115.38 (br).

3. Results and discussion

3.1. Model reaction

The monomer, 2,2′-bis(trifluoromethyl)-4,4′-dinitro-1,1′-biphenyl (**1**), was synthesized by the Ullmann reaction of 5-bromo-2-nitrobenzotrifluoride with copper in DMF [48]. The crude product was recrystallized from benzene/diethyl ether. In order to study the reactivity of the monomer, model reaction was conducted with **1** and 4-*tert*-butylphenol (Scheme 1). **1** and two equivalents of 4-*tert*-butylphenol were reacted in the presence of K_2CO_3 as a base in NMP as a solvent at 20 w/v % of solid content. Toluene as an azeotrope was used during the initial stage of polymerization to remove water by the phenoxide generation. During the initial stage of model reaction, the reaction temperature was maintained at 140 °C, and the water generated by deprotonation of the 4-*tert*-butylphenol was removed through Dean–Stark trap. The reaction mixture was heated to 175 °C to complete the displacement

Table 3
Physical properties of the synthesized polymers.

Polymer	[η][a] (dL/g)	M_n[b]/10^3	M_w[b]/10^3	PDI[c]	T_{d5}[d] (°C)		T_g[e] (°C)
					In N_2	In Air	
P1	0.63	33.7	95.0	2.82	493	451	176
P2	0.42	14.3	42.1	2.95	481	428	181
P3	0.60	30.8	81.6	2.65	502	463	199

[a] Intrinsic viscosity, measured at a concentration of 0.5 g/dL in DMAc at 30 °C.
[b] Determined by GPC using *o*-dichlorobenzene as eluent at 85 °C with polystyrene standards.
[c] Polydispersity Index = M_w/M_n.
[d] 5% weight loss temperature measured by TGA with a heating rate of 10 °C/min.
[e] Measured by DSC with a heating rate of 10 °C/min.

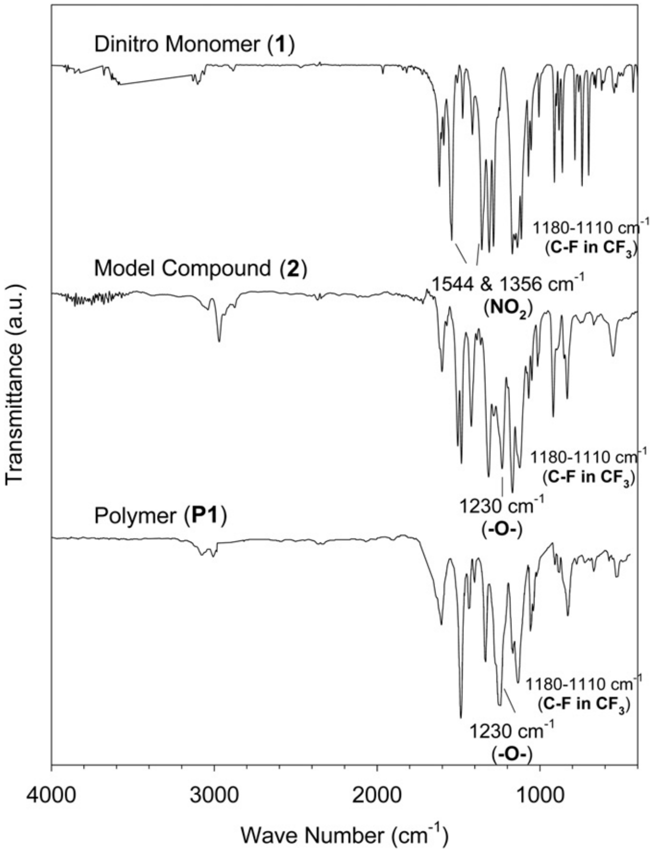


Fig. 1. FTIR spectra of monomer **1**, model compound **2**, and polymer **P1**.

reaction. Conversion was complete within 4 h at 175 °C, and the isolation yield was 95%. The spectroscopic analyses of the model compound **2** showed the successful formation of the ether linkages without any degradation of trifluoromethyl groups. In our previous report [47], the model meta-activated S_NAr reaction, which is the reaction of 4-nitro-2-trifluoromethylbiphenyl with 4-*tert*-butylphenol, is complete at 175 °C for 12 h. It seems that the higher reactivity of the compound **1** compared to 4-nitro-2-trifluoromethylbiphenyl is caused by the strong electron withdrawing character of the nitro leaving group and trifluoromethyl group attached to the other aromatic ring of the biphenyl structure.

3.2. Quantum mechanical calculation

In order to understand the unusual reaction behavior of a nitro leaving group, quantum mechanical calculation for the energy state of 4 sets of the reaction (Scheme 2) in gas and solution phase was carried out at Hartree-Fock level using the HF/6-31G(d) and 3 more models as a basis set and initial molecular geometries optimized in vacuo with GAUSSIAN98 program. SCRF (Self Consistent Reaction Field) calculations for solution phase were also performed by the PCM (Polarizable Continuum Model) [49]. The solvent was NMP at 298 K (dielectric constant $\varepsilon = 32.2$). The results of calculations in gas and solution phase are summarized in Tables 1 and 2, respectively.

In the case of meta-activated aryl moiety **A** and **B**, the energy differences of reactants and intermediate in gas phase were calculated, but the calculation for **C** and **D** which contain ortho activated aryl moieties were unsuccessful due to the difficulty of obtaining optimized molecular geometry of the intermediate. **A** showed higher energy difference (3–4 kcal/mol) between the reactant and the intermediate than **B**, which implies that the nitro leaving group is more susceptible to the displacement reaction than the fluorine when they are activated by trifluoromethyl group at meta position. However, the energy differences between the reactant and the product in gas phase were not reasonable because of the uncertainty caused by the fluoride anions in the products.

SCRF calculations were also carried out by following the PCM/DIR procedure using NMP (dielectric constant $\varepsilon = 32.2$) as a solvent. In the case of **D** known as the most reactive one, the products are more stable (over 20 kcal/mol) than the reactants, but in the case of **A**, the products and the reactants had similar energy state, indicating that **A** procedure is not energetically favorable. In the case of **B**, the products are more stable (*c.a.* 10 kcal/mol) than the reactants. The calculated energy values of **B** and **C** shows that the reaction of **B** is slightly more favorable than that of **C** which is also known to occur rapidly [21–26]. These calculation results suggest that **B** procedure, nitro displacement reaction activated by the trifluoromethyl group at meta position, is an energetically favorable process.

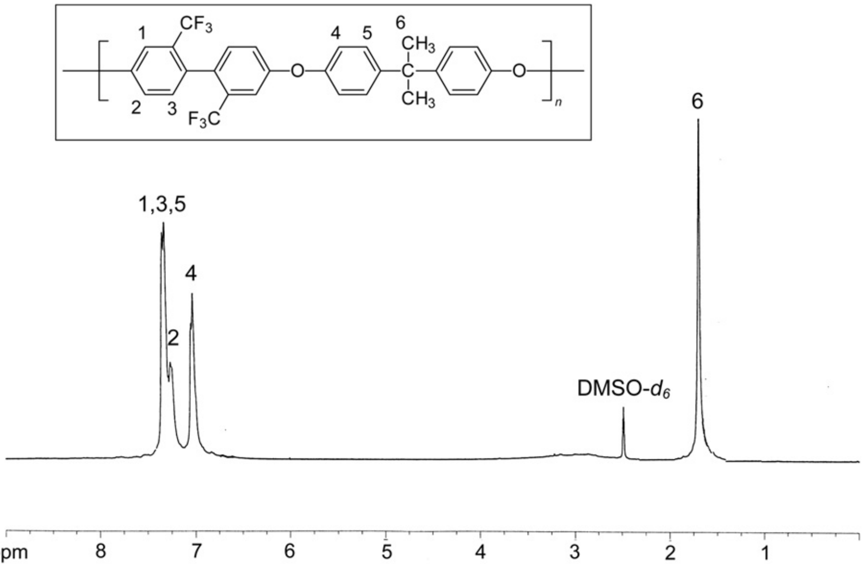


Fig. 2. ^{1}H NMR Spectra of polymer **P1** (DMSO-d_6, 400 MHz, 100 °C, ppm).

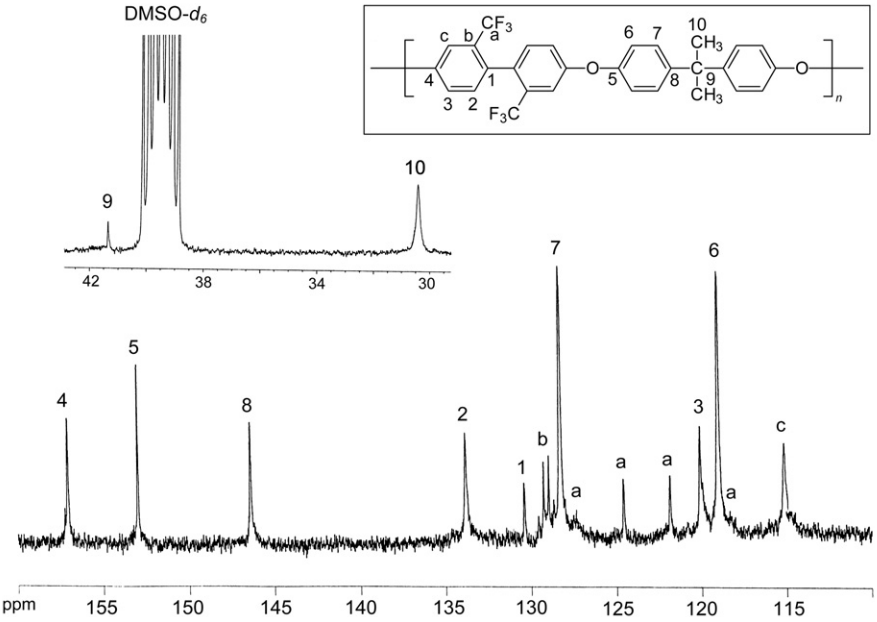


Fig. 3. ^{13}C NMR Spectra of polymer **P1** (DMSO-d_6, 100 MHz, 100 °C, ppm).

3.3. Synthesis of poly(arylene ether)s

Based on the successful result of the model reaction and the quantum mechanical calculation, we carried out the polymerization at 175 °C. Dinitro monomer **1** was polymerized with Bisphenol A, Bisphenol AF, and 4,4′-Biphenol according to the conventional poly(arylene ether) synthesis, with K_2CO_3 as a base in NMP, to make **P1**, **P2**, and **P3**, respectively (Scheme 3). The solid content was maintained over 20 w/v%, and toluene as an azeotrope was used during the initial stage of polymerization to remove water by the phenoxide generation. After bisphenoxide generation and dehydration for 4 h, the polymerization mixtures were heated to 175 °C, and reacted for 14 h at this temperature. The pale yellow polymers were precipitated in water/methanol ($v/v = 1/1$) mixture.

The polymerization results are summarized in Table 3. The intrinsic viscosity values of **P1**, **P2**, and **P3** are 0.63, 0.42, and 0.60 dL/g, respectively. The SEC data for the polymers indicate formation of high molecular weight polymers. Weight average molecular weight and polydispersity of **P1**, **P2**, and **P3** are 95000, 42100, and 82100 g/mol, and 2.82, 2.95, and 2.65, respectively. The polydispersity values are within the expected range for condensation polymerization.

The structures of the polymers were confirmed by FTIR, ^{1}H NMR, and ^{13}C NMR spectroscopy, which indicated the formation of ether linkages without degradation of trifluoromethyl groups. All of the FTIR spectra of dinitro monomer **1**, model compound **2**, and polymers show the absorption bands at 1140–1060 cm^{-1} corresponding to trifluoromethyl (C–F) stretching (Fig. 1.). While the FTIR spectrum of monomer **1** show the absorption bands at 1529 and 1351 cm^{-1} corresponding to nitro (–NO$_2$) stretching, the FTIR spectra of model compound **2** and the corresponding polymers show the absorption band around 1250 cm^{-1} corresponding to aryl ether (Ph–O–Ph) stretching generated in the polymer-forming reaction without any trace of nitro stretching. ^{1}H and ^{13}C NMR spectra show all expected proton and carbon peaks, respectively, without any signals corresponding to the nitro and hydroxyl end groups. Representative ^{1}H and ^{13}C NMR spectra with the corresponding assignment of **P1** are shown in Figs. 2 and 3, respectively.

3.4. Properties of the polymers

The synthesized polymers exhibit good solubility in common organic solvents. The solubility of the synthesized poly(arylene ether)s is summarized in Table 4. All of the synthesized polymers are well dissolved in polar aprotic solvents such as NMP, DMAc and DMF. **P1** and **P2** are also soluble in dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), chlorobenzene, and 1,1,2,2-tetrachloroethane at room temperature. **P3** shows lower solubility than **P1** and **P2** presumably due to its more rigid structure. It is soluble in DMSO, *o*-dichlorobenzene, and 1,1,2,2-tetrachloroethane at elevate temperature, and partially soluble in THF and chlorobenzene, but insoluble in chloroform and toluene. However, all polymers are insoluble in acetone, ethyl acetate, benzene, cyclohexane, and methanol. Transparent, pale yellow, and flexible films are prepared by solution casting from *N,N*-dimethylacetamide solutions of the polymers.

Table 4
Solubility of the synthesized polymers.[a]

Polymer	NMP	DMAc	DMF	DMSO	THF	CHCl$_3$	TCE	CB	ODCB	Toluene
P1	++	++	++	++	++	±	++	++	++	±
P2	++	++	++	++	++	±	++	++	++	±
P3	++	++	++	+	±	−	+	±	+	−

Abbreviations: NMP (*N*-methyl pyrrolidone), DMAc (*N,N*-dimethylacetamide), DMF (*N,N*-dimethyl formamide), DMSO (dimethyl sulfoxide), THF (tetrahydrofuran), CHCl$_3$ (chloroform), TCE (1,1,2,2-tetrachloroehtane), CB (chlorobenzene), ODCB (*o*-dichlorobenzene).

[a] ++: Soluble at room temperature, +: soluble on heating, ±: partially soluble, −: insoluble.

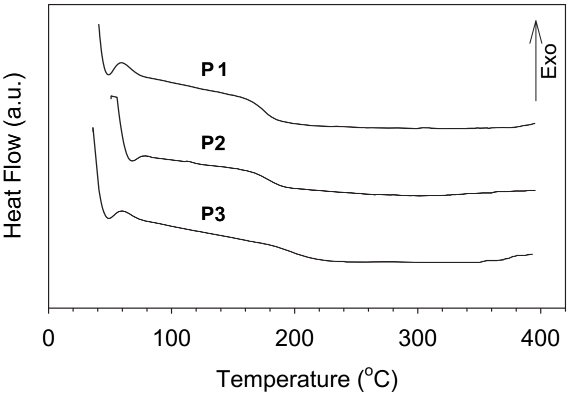


Fig. 4. DSC curves of the polymers (Heating rate: 10 °C/min, in N_2 flow).

Thermal properties of the poly(arylene ether)s were evaluated by TGA and DSC, and the results are summarized in Table 3. Thermal analyses show that the polymers have high thermal stability. Dynamic TGA shows 5% weight loss occurred for **P1**, **P2**, and **P3** at 493, 481, and 502 °C in nitrogen, and 451, 428, and 463 °C in air, respectively. None of the poly(arylene ether)s showed crystallization or melt transition in DSC measurement. The T_gs of the polymers depends on the structure of bisphenol comonomer unit (Fig. 4.). The T_gs of **P1**, **P2**, and **P3** are 176, 181, and 199 °C, respectively. The T_g of **P3** approaches that of PPO™ ($T_g = 210$ °C [50]) even though they do not have any pendent group near the ether linkage. **P1** display a T_g comparable to that of the poly(arylene ether) made from bisphenol A and 4,4′-dibromobiphenyl by Ullmann condensation ($T_g = 166$ °C [51], 175 °C [52]). It seems that the presence of two trifluoromethyl groups appears to have minimal effect on T_g in this case. However, while the T_g of **P3** are comparable to that of the poly(arylene ether) made from 3,3′-bis(trifluoromethyl)-4,4′-dinitrobiphenyl and 4,4′-biphenol, **P1** and **P2** display about 10 °C higher T_gs than those of the poly(arylene ether) from 3,3′-bis(trifluoromethyl)-4,4′-dinitrobiphenyl with bisphenol A or bisphenol AF ($T_g = 167$ °C [27]).

In-plane and out–of plane refractive indices (n_{xy} and n_z) of the polymers were measured using a prism coupling waveguide technique with a laser beam having 632.8 nm wavelength (474.58 THz), and the results are summarized in Table 5. All of the synthesized polymers show refractive indices (n_{av}) in the range of 1.592–1.624 with low birefringence (Δ) below 0.006. A dielectric constant (ε) of a material at optical frequencies can be estimated from the refractive index n according to Maxwell's equation, $\varepsilon \cong n^2$. The ε value at 1 MHz has been evaluated as $\varepsilon \cong 1.10\ n_{av}^2$, including an additional contribution of approximately 10% from the infrared absorption [53]. The ε values estimated from average refractive indices of the resulting polymer films were in the range of 2.81–2.90. The low dielectric constants may be attributed to the existence of the trifluoromethyl groups in the main chain.

Table 5
Refractive indices of the synthesized polymers.[a]

Polymer	n_{xy}[b]	n_z[c]	n_{av}[d]	Δ[e]	ε[f]	d[g] (μm)
P1	1.6210	1.6184	1.6201	0.0026	2.89	5.8
P2	1.6030	1.5917	1.5992	0.0059	2.81	4.3
P3	1.6238	1.6194	1.6223	0.0044	2.90	4.1

[a] Measured at 632.8 nm (474.58 THz).
[b] n_{xy}: In-plane refractive index.
[c] n_z: Out-of plane refractive index.
[d] n_{av}: Average refractive index ($n_{av} = (2\ n_{av} + n_{av})/3$).
[e] Δ: Birefringence ($\Delta = n_{xy} - n_z$).
[f] Dielectric constant estimated from the refractive index: $\varepsilon \cong 1.10\ n_{av}^2$.
[g] Film thickness.

4. Conclusions

The nitro leaving group activated by trifluoromethyl group at meta position undergoes S_NAr reaction quantitatively. The quantum mechanical calculation for the energy state suggests that the nitro displacement reaction is an energetically favorable process. High molecular weight poly(arylene ether)s were prepared from 2,2′-bis(trifluoromethyl)-4,4′-dinitro-1,1′-biphenyl with several bisphenols. The synthesized polymers were amorphous and dissolved well in a wide range of organic solvents regardless of the position of trifluoromethyl pendent groups. They showed good thermal stability as well as low refractive index and birefringence.

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