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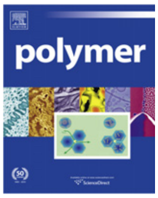

Poly(arylene ether)s with trifluoromethyl groups via meta-activated nitro displacement reaction

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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

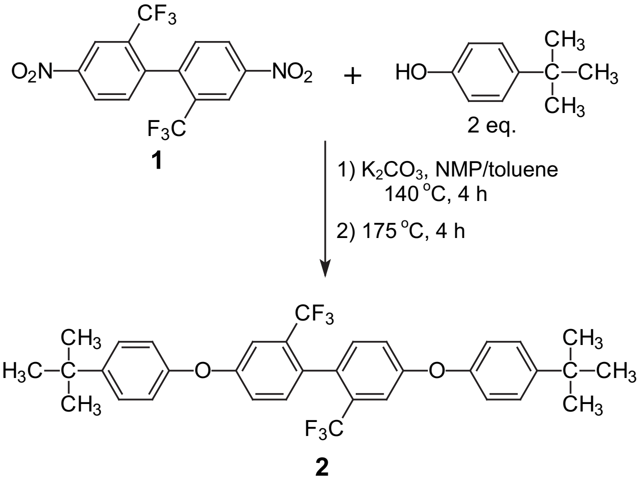
5-Bromo-2-nitrobenzotrifluoride (Marshallton) was used as received. 4-*tert*-Butylphenol was sublimed at 90 °C in vacuum. 2,2-Bis(4′-hydroxyphenyl)propane (Bisphenol A, Aldrich) was recrystallized from toluene, 2,2-bis(4′-hydroxyphenyl)hexafluoropropane (Bisphenol AF, Aldrich) was recrystallized from 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)

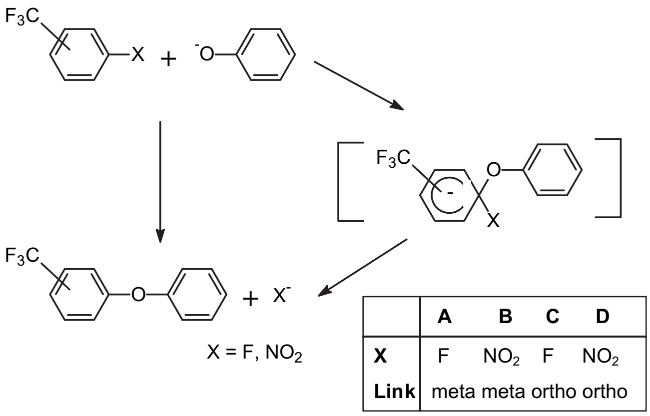
Activated copper (94.0 g, 1.48 mol) was added to a solution of 2-bromo-5-nitrobenzotrifluoride (100 g, 0.37 mol) in 200 mL of DMF. The reaction mixture was stirred mechanically at 150 °C for 6 h, then cooled and poured into vigorously stirred water. The yellow precipitate was filtered, washed with water 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):



	A	B	C	D
X	F	NO$_2$	F	NO$_2$
Link	meta	meta	ortho	ortho

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