Chain-Growth Polycondensation for Aromatic Polyethers with Low Polydispersities: Living Polymerization Nature in Polycondensation

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ABSTRACT: Polycondensation normally proceeds in a step-growth reaction manner to give polymers with a wide range of molecular weights. However, the polycondensation of potassium 5-cyano-4-fluoro-2-propylphenolate (**1**) proceeded at 150 °C in a chain polymerization manner from an initiator, 4-fluoro-4′-trifluoromethylbenzophenone (**2a**), to give aromatic polyethers having controlled molecular weights and low polydispersities ($M_w/M_n \leq 1.1$). The resulting polycondensation of **1** had all of the characteristics of living polymerization and displayed a linear correlation between molecular weight and monomer conversion, maintaining low polydispersities. The MALDI−TOF mass spectrum of poly**1** revealed that this polycondensation did not include conventional step-growth polycondensation which gave the polymer without initiation unit and macrocycles. The poly**1** with low polydispersity showed higher crystallinity than that with broad molecular weight distribution, obtained by the conventional polycondensation of **1** without **2a**.

Introduction

Poly(arylene ether)s are one of the important classes of high-performance engineering plastics and possess excellent chemical and thermal stabilities as well as good mechanical properties.[1] These polymers are generally produced by polycondensation such as oxidation of phenol derivatives[2] and aromatic nucleophilic substitution,[3] and the nature of polycondensation that proceeds in a step-growth reaction manner results in polymers with broad molecular weight distributions. If poly(arylene ether)s with low polydispersities were produced, further novel physical properties could be added to these high-performance functional polymers. Percec conducted the oxidative poymerization of 4-bromo-2,6-dimethylphenol in the presence of chain initiators to obtain poly(arylene ether)s with low polydispersities.[4] The polymers, however, were obtained after precipitation, and the crude polymerization mixture had a broad molecular weight distribution.

We have been recently successful in the synthesis of polyamides with defined molecular weights and low polydispersities[5] by chain-growth polycondensation,[6] where the monomers react with the polymer end group selectively, not with other monomers. The principle of this polycondensation is different substituent effects between monomer and polymer; strong electron-donating ability of the aminyl anion in the monomer deactivates the phenyl ester moiety in the monomer, whereas the amide linkage in the polymer activates the polymer end phenyl ester moiety in comparison with that of the monomer. Therefore, the monomer is prevented from the reaction with other monomers and reacts with only the polymer end group, resulting in chain-growth polymerization like living polymerization. We now apply this chain-growth polycondensation to the synthesis of poly(arylene ether)s with low polydispersities and then have designed monomer **1**.[7]

We expect two approaches to the chain-growth polycondensation of **1**: electrophilic site propagation and nucleophilic site propagation (Scheme 1). In the electrophilic site propagation by using reactive initiator **2a** bearing an electron-withdrawing group, **1** would react with **2a** to yield ether **3** faster than with the aromatic fluorine of another **1** having the strong electron-donating phenoxide group. Monomer **1** would now react with **3** to yield a dimeric ether faster than with another **1** because the ether linkage of **3** is a weaker electron-donating group than the phenoxide group of **1**, and the aromatic fluorine of **3** would be more reactive than that of the monomer. Growth would continue in a chain polymerization manner with the conversion of the strong electron-donating phenoxide group of **1** to the weak electron-donating ether linkage in polymer. In the nucleophilic site propagation, phenoxide is the propagating end group instead of fluorine. Thus, when potassium 4-methoxyphenoxide (**4**) having an electron-donating group is used as an initiator, **4** would react with **1**, and the ether linkage formed would make the polymer terminal phenoxide more reactive than the phenoxide of monomer because ether linkage has stronger electron-donating character than fluorine. Both approaches depend on whether there are enough difference of substituent effects between monomer and polymer. It is not easy to predict which approaches could achieve chain-growth polycondensation, but it seems that the electrophilic site propagation of **1** would be at least more difficult to be achieved than the successful electrophilic site propagation for polyamides.[5] This is because the substituent effects on the electrophilic site are not expected to change much between the phenoxide in monomer and the ether linkage in polymer in the polycondensation of **1**, in comparison with the change of substituent effects between the aminyl anion in monomer and the amide linkage in polymer in the chain-growth polycondensation for polyamides.[5]

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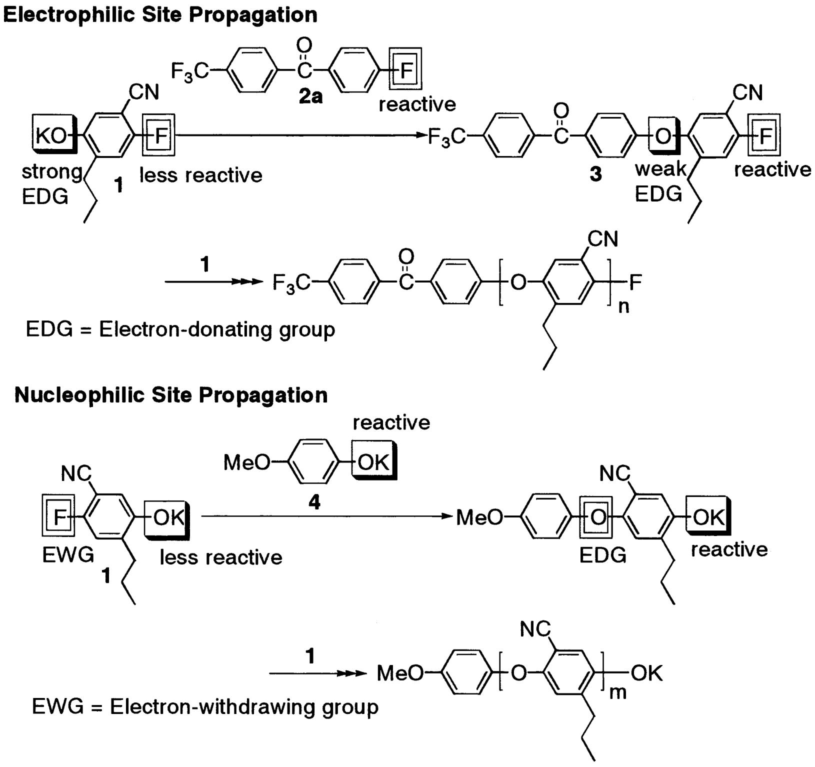
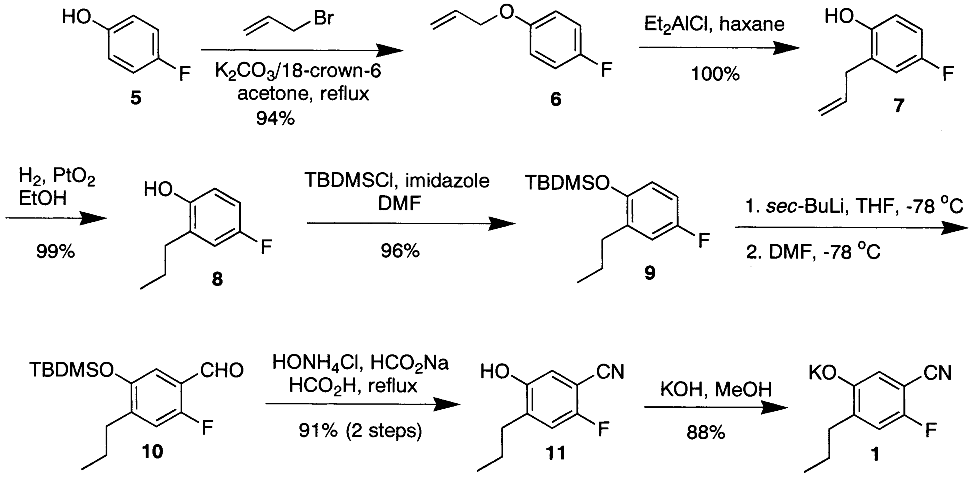
Scheme 1



Scheme 2



In this paper, we report the chain-growth polycondensation of **1** for well-defined poly(arylene ether)s through the electrophilic site propagation. The polymerization behavior has all of the characteristics of living polymerization and displays a linear correlation between molecular weight and monomer conversion, maintaining low polydispersities. Furthermore, the ^{1}H NMR spectrum of poly**1** is studied in detail by comparing with the spectra of unimer and dimer connected with initiator **2** unit, indicating that the polymer without **2** unit is not produced from conventional step-growth polycondensation. The MALDI−TOF mass spectrum of poly**1** also reveals that this polycondensation does not include conventional polycondensation which gives macrocycles and the polymer without **2** unit. On the basis of all of the results, it has proved that the polycondensation of **1** possesses a real living polymerization nature.

Results and Discussion

Synthesis and Conventional Polycondensation of 1. Monomer **1**, potassium 5-cyano-4-fluoro-2-propylphenolate, was prepared as shown in Scheme 2. Fluorophenol **5** was reacted with allyl bromide to give allyl ether **6**, which was then subjected to Claisen rearrangement with Et_2AlCl to yield **7**. After hydrogenation of **7** the hydroxy group of **8** was protected with *tert*-butyldimethylsilyl (TBDMS) group. Regioselective lithiation of **9** was carried out with *sec*-butyllithium at −78 °C, followed by the reaction with *N*,*N*-dimethylfolmamide (DMF) to give aldehyde **10**.[8] The formyl group of **10** was converted to the cyano group with hydroxylamine hydrochoride and sodium formate in formic acid.[9] Phenol **11** obtained was then treated with potassium hydroxide in methanol to yield monomer **1**.

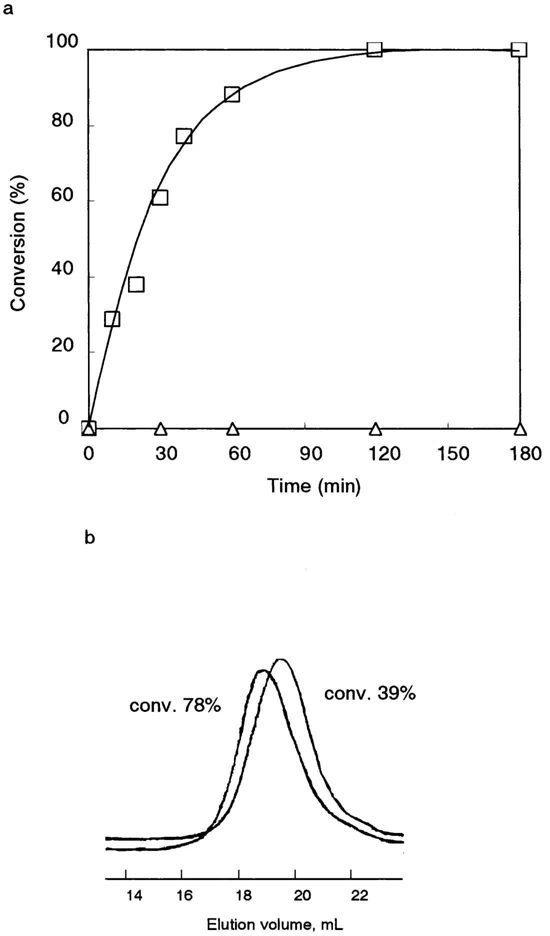


Figure 1. (a) Monomer conversion as a function of time for the polymerization of **1** in the presence of initiator (open squares) **2a** and (open triangles) **4** in sulfolane at 150 °C: $[\mathbf{1}]_0 = 0.17$ M; $[\text{initiator}]_0 = 11.7$ mM. (b) GPC profile of poly**1** obtained in the polymerization of **1** with **2a** for 40 min and for 120 min.

Before study of chain-growth polycondensation of **1**, conventional polycondensation of **1** was carried out in the absence of initiator **2a** or **4** in sulfolane at 220 °C for 4 h to see the polymerizability of **1** and the solubility of poly**1** in organic solvents. The reaction mixture was poured into 3% hydrochloric acid, and precipitate was washed with water and then dried in vacuo to give poly**1** in 93% yield. The M_n and M_w/M_n of the polymer, estimated by gel permeation chromatography (GPC) with polystyrene standards, were 15 500 and 3.03, respectively, indicating that **1** possesses sufficient polymerizability. The polymer obtained was soluble in DMF, dichloromethane, and chloroform at room temperature. Monomer without the propyl group was also attempted to polymerize, but the polymer obtained was not soluble in any organic solvents.

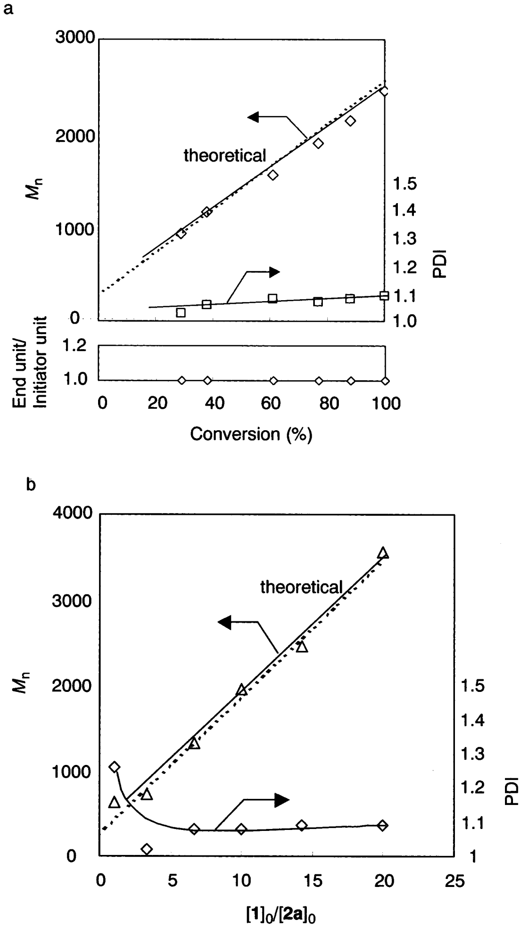


Figure 2. (a) Poly**1** molecular weight and molecular weight distribution (PDI) and the ratios of end group to initiator unit in poly**1** as a function of monomer conversion in the polymerization of **1** with **2a** (sulfolane, 150 °C, $[\mathbf{1}]_0 = 0.17$ M; $[\mathbf{2a}]_0 = 11.7$ mM). (b) Poly**1** molecular weight and as a function of the feed ratio of **1** to **2a** (sulfolane, 150 °C, $[\mathbf{1}]_0 = 0.17$ M; $[\mathbf{2a}]_0 = 8.3-167$ mM; conversion = 100%).

Chain-Growth Polycondensation of 1. According to the two approaches to chain-growth polycondensation of **1** mentioned in the Introduction, the polymerizations of **1** with 7 mol % of initiator **2a** for electrophilic site propagation and with 7 mol % of initiator **4** for nucleophilic site propagation were carried out at 150 °C in sulfolane. Surprisingly, the polymerization of **1** with **4** did not proceed at all, whereas the polymerization with **2a** took place and the GPC chromatogram of polymer shifted toward the higher molecular weight region with increase of monomer conversion (Figure 1). This result implies that not only the reaction of **4** with **1** but also the reaction of monomers **1** with each other did not take place under this condition and that the polymerization of **1** in the presence of **2a** did not involve step polymerization but was initiated with **2a**.

To elucidate whether chain-growth polymerization takes place in this polycondensation, the M_n values,[10] the M_w/M_n ratios (PDI), and the ratios of end group to initiator unit in polymer were plotted against monomer conversion in the polymerization of **1** with 7 mol % of **2a** (Figure 2a). In general polycondensations that proceed in a step polymerization manner, the molecular weight does not increase much in low conversion of monomer and is accelerated in high conversion, and the M_w/M_n ratios increase up to 2.0. The ratios of end group to initiator unit would be larger than 1.00 because monomers react with not only an initiator but also other monomers. As shown in Figure 2a, the M_n values increased in proportion to conversion, and the M_w/M_n ratios were less than 1.1 over the whole conversion range. The ratios of end group to initiator unit, which were easily determined by the ^{19}F NMR spectra of polymer, were constantly about 1.00 irrespective of conversion. Consequently, Figure 2a shows that the polycondensation of **1** proceeds in a chain-growth polymerization manner like living polymerization. In another series of experiments, **1** was polymerized with varying feed ratio ($[\mathbf{1}]_0/[\mathbf{2a}]_0$). As shown in Figure 2b,

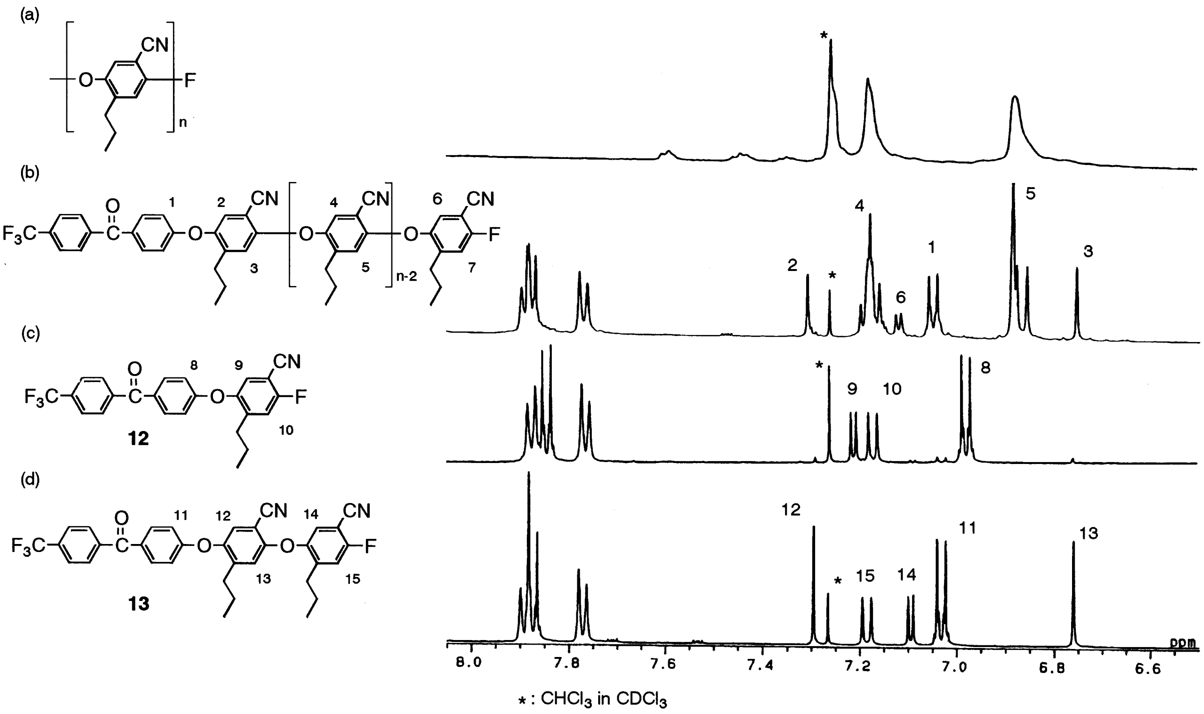
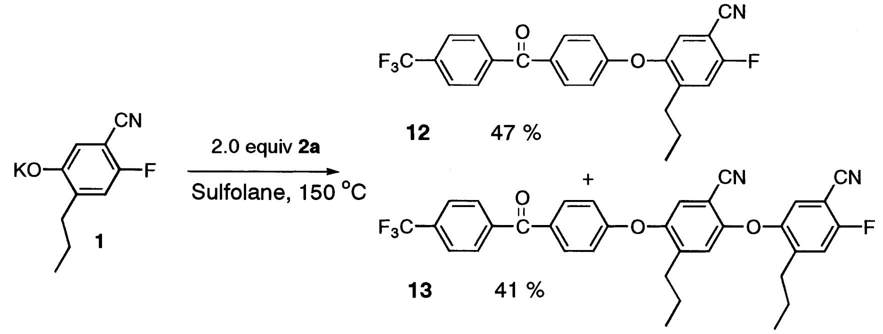


Figure 3. ^{1}H NMR spectra of (a) poly**1** from conventional polycondensation, (b) poly**1** from chain-growth polycondensation with **2a** ($[\mathbf{1}]_0/[\mathbf{2a}]_0 = 7.5$), (c) unimer **12**, and (d) dimer **13**.

Scheme 3



the observed M_n values of polymers were in good agreement with those calculated with the assumption that one initiator molecule forms one polymer chain. The M_w/M_n ratios were less than 1.1 when the $[\mathbf{1}]_0/[\mathbf{2a}]_0$ ratios were more than 1.0.[11] This also agrees with the features of chain-growth polymerization.

^{1}H NMR Spectra of Poly1. The ^{1}H NMR spectrum of poly**1** from conventional polycondensation was simple, as shown in Figure 3a: two singlets of the polymer repeating unit at δ 7.18 and 6.88 ppm as aromatic proton signals. In the ^{1}H NMR spectrum of poly**1** obtained by chain-growth polycondensation from **2a**, however, several signals other than those of the repeating unit were obtained (Figure 3b). To assign those signals, model compounds were prepared. Thus, **1** reacted with 2 equiv of **2a** in sulfolane at 150 °C to give 1:1 reactant **12** (unimer) and dimer **13** bonded to **2a** residue in 47% and 41% yields, respectively (Scheme 3).

The ^{19}F NMR spectrum of **12** showed two signals: a singlet corresponding to the trifluoromethyl group at δ 99.3 and a doubled doublet corresponding to the aromatic fluorine at δ 50.9 ($J_{H9-F} = 5.4$ Hz and $J_{H10-F} = 9.2$ Hz). The ^{1}H NMR spectrum of **12** is shown in Figure 3c. The signals of initiator **2a** unit were observed as a multiplet between 7.90 and 7.83 and two doublets at δ 7.76 and 6.99 (H_8). The signal of **1** unit was assigned on the basis of the ^{1}H−^{19}F coupling: the doublet of H_9 at δ 7.22 ($J_{H9-F} = 5.5$ Hz) and the doublet of H_{10} at δ 7.18 ($J_{H10-F} = 9.2$ Hz).

The ^{19}F NMR spectrum of **13** also showed the signals of the trifluoromethyl group as a singlet at δ 99.3 and the signal of the aromatic fluorine as a doubled doublet at δ 50.9 ($J_{H14-F} = 5.4$ Hz and $J_{H15-F} = 9.2$ Hz). In the ^{1}H NMR spectrum of **13** (Figure 3d), the signals of initiator **2a** unit appeared as a multiplet between 7.91 and 7.85 and two doublets at δ 7.77 and 7.03 (H_{11}). The signals of the internal aromatic ether unit were observed as two singlets at δ 7.30 (H_{12}) and 6.78 (H_{13}). The signals of the chain end group appeared as two doublets at δ 7.19 ($J_{H15-F} = 9.2$ Hz) and 7.10 ($J_{H14-F} = 5.5$ Hz).

On the basis of the spectra of **12** and **13**, the signals of poly**1** obtained by chain-growth polycondensation at the feed ratio $[\mathbf{1}]_0/[\mathbf{2a}]_0 = 7.5$ could be assigned as shown in Figure 3b. Thus, a doublet at δ 7.07 is H_1 of the initiator unit. Two singlets at δ 7.30 and 6.76 are H_2 and H_3 of the **1** unit adjacent to the initiator unit **2a**, respectively. The doublet at δ 7.13 is H_6 of the polymer end group. The intensity ratio of signals of the end group

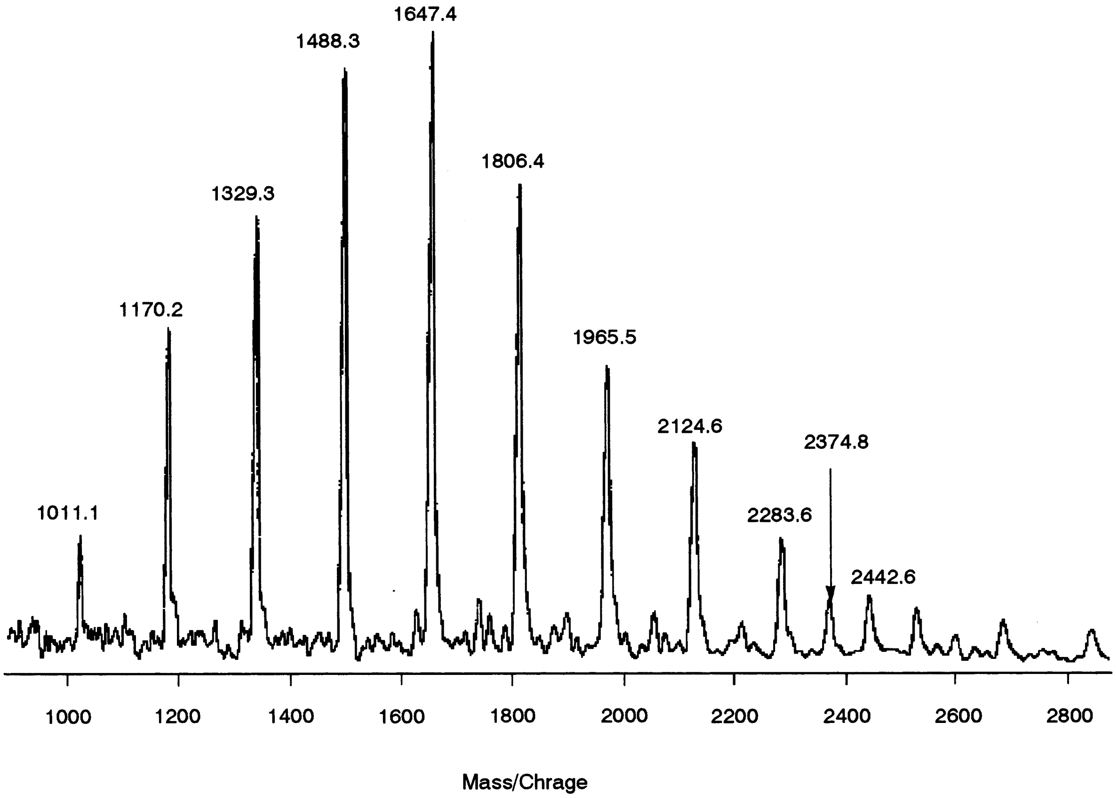


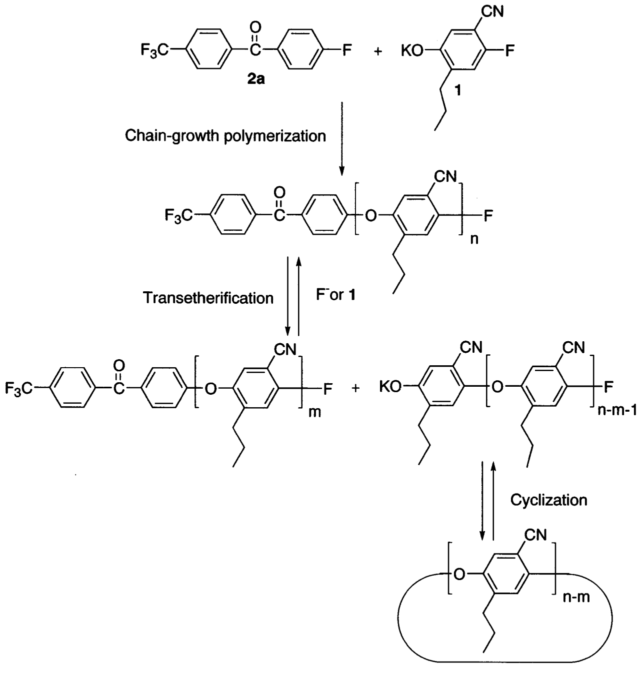
Figure 4. MALDI−TOF mass spectrum of poly**1** obtained in the presence of **2a** ($[\mathbf{1}]_0/[\mathbf{2a}]_0 = 7.5$) in sulfolane at 150 °C.

proton H_6 to the initiator unit proton H_1 was 1:2, indicating that there was no polymer without initiator **2a** unit from conventional polycondensation. In addition, the ^{19}F NMR spectrum of the polymer also showed that one initiator molecule forms one polymer chain.

MALDI−TOF Mass Spectrum of Poly1. It is well-known that some polycondensations for poly(arylene ether)s are equilibrium polymerization. At high temperatures, and in the presence of fluoride or phenolate ions, transetherification can take place and is greatly facilitated by the presence of an electron-withdrawing group in either the ortho or para positions relative to the electrophilic site of monomers.[12,13] Since the polycondensation of **1**, which has the electron-withdrawing cyano group at the ortho position of fluorine, forms potassium fluoride as a byproduct, one might think that the reversible transetherfication takes place also in the polycondensation of **1** as shown in Scheme 4. If a linear polymer bearing phenoxide and fluorine at each end was formed, the ratios of end group to initiator unit would be more than 1.0, which is not consistent with the results of Figure 2. However, if macrocycles were formed, it would not affect the ratios of end group to initiator unit of linear polymer, and the ^{1}H NMR spectra of polymer could not rule out the possibility of the formation of macrocycles.

For this reason, we have examined the MALDI−TOF mass spectrum of poly**1**. MALDI−TOF mass spectrometry is an ideal technique for the detection of small quantities of side reaction products. Under the MALDI conditions used, poly**1** is ionized to $[M + Ag]^+$ ions. The mass spectrum obtained from the product of the polymerization of **1** with **2a** at feed ratio $[\mathbf{1}]_0/[\mathbf{2a}]_0 = 7.5$ is shown in Figure 4. It contains a major distribution whose *m/z* values correspond to the Ag^+ adducts of poly**1** with initiator **2a**. For example, the 8-mer of this distribution is expected to produce a signal at *m/z* 8 × 159.06 (repeat unit) + 268.06 (**2a**) + 106.90 ($^{107}Ag^+$) = 1647.44, as indeed is observed as the highest signal and in good agreement with the feed ratio $[\mathbf{1}]_0/[\mathbf{2a}]_0 = 7.5$. Macrocycles with no **2a** unit (−268.06 Da) is absent (no *m/z* 1379 detected in Figure 4). The linear polymer without **2a** unit from conventional polycondensation (−268.06 Da + 20.01 Da (HF)) is also absent (no *m/z* 1399 detected in Figure 4). The minor distribution between signals of the Ag^+ adducts of poly**1** with initiator **2a** is due to the K^+ adducts of the same polymer. For example, *m/z* 2374.8 detected in Figure 4

Scheme 4



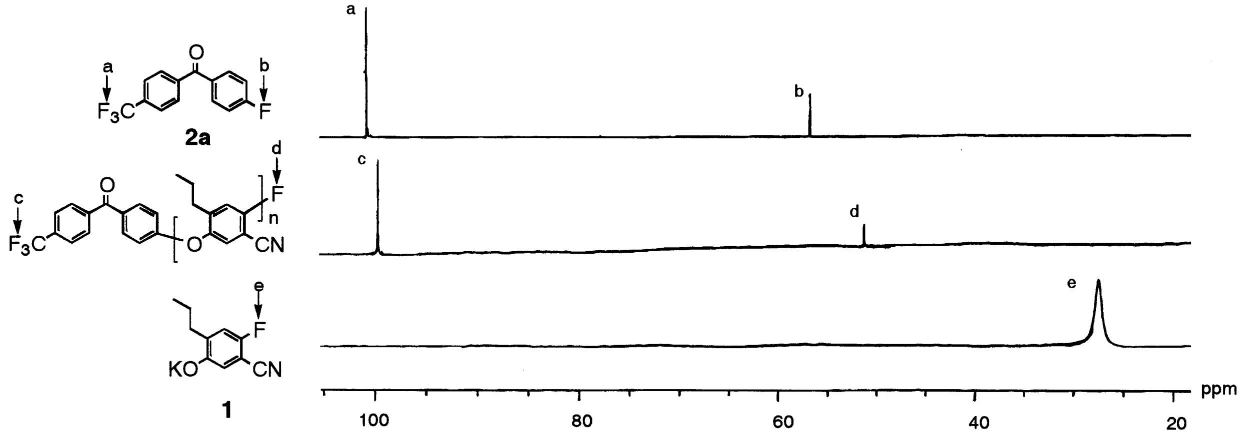
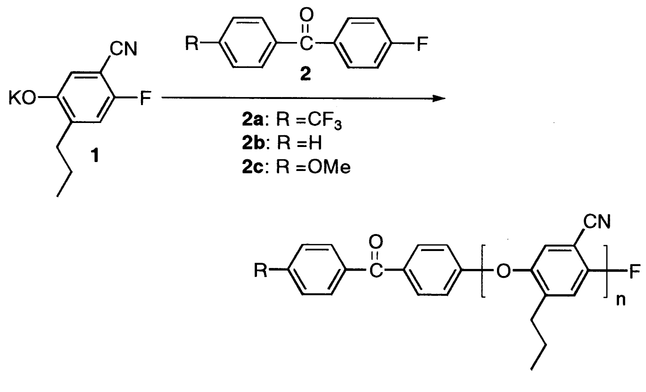


Figure 5. ^{19}F NMR spectra of **2a** and **1** (470 MHz DMSO-d_6 at 25 °C) and of the end group of poly**1** prepared with **2a** ($[\mathbf{1}]_0/[\mathbf{2a}]_0 = 7.5$) in sulfolane at 150 °C (470 MHz, $CDCl_3$ at 25 °C).

is identical with the expected signal of the 13-mer at m/z 13×159.06 (repeat unit) + 268.06 (**2a**) + 38.96 (K^+) = 2374.8. Consequently, this polycondensation does not contain conventional step-growth polycondensation giving the linear polymer having no initiator unit and macrocycles.

Reactivity of Aromatic Fluorines. This successful chain-growth polycondensation would be based on the different reactivity of aromatic fluorines between the polymer end group and monomer **1**; initiator **2a** and the polymer end group are more reactive than **1**. It has been reported that more reactive aromatic fluorines show the signals in lower field in the ^{19}F NMR spectra,[14] so the ^{19}F NMR spectra of **1**, **2a**, and the polymer end group were measured to estimate their reactivities (Figure 5).[15] The signal of **2a** appeared in the lowest field, and the signal of the polymer end group and that of **1** appeared in higher field in this order. Especially, the signal of **1** was about 24 ppm upfield for that of the polymer end group, which was only 5 ppm upfield for the signal of **2a**. This result indicates that the negative charge of phenoxide in **1** effectively deactivates the fluorine of **1** and that there is the difference of reactivity between the monomer and the polymer end group enough to attain chain-growth polycondensation, contrary to our first expectation described in the Introduction. Consequently, an approach to successful chain-growth polycondensation will be to use monomers having negative charged nucleophilic site.

Scheme 5



Effect of Initiator 2. Monomer **1** was polymerized with 7 mol % of some 4-X-4′-fluorobenzophenone (X = CF_3, H, MeO) initiators **2** in sulfolane at 150 °C (Scheme 5). All the polymerizations were completed in 2−4 h (Figure 6), implying that the polymerization proceeded in a chain-growth polymerization manner because the step polymerization of **1** did not proceed in this time as shown in Figure 1. Linear increase of the M_n against conversion also showed chain-growth polymerization, and the M_n values were in good agreement with those calculated ones (Figure 6b). The polymerization behaviors of **1** with **2a** and **2b** were almost the same: similar polymerization rate and similar M_w/M_n ratios. In the polymerization of **1** with **2c** having an electron-donating group, however, the initiation was slower than the polymerization with **2a** and **2b**, and the M_n values were slightly higher than the calculated ones in the initial stage and became closer to them as the polymerization proceeded. The M_w/M_n ratios were a little broader than the polymerization with **2a** and **2b**. All these observed differences in the polymerization with **2c** can be accounted for by slow initiation relative to propagation. Ridd and co-workers have reported the rates of the reactions of substituted 4-halogenobenzophenones with the potassium salts of substituted 4-hydroxybenzophenones.[16] These reactions obey the Hammett equation using normal σ values for substitution; the order of the reactivities of aromatic fluorines of 4-X-4′-fluorobenzophenone is X = CF_3 > H > MeO. Consequently, slower initiation in the polymerization of **1** with **2c** is identical with the reported substituent effects. It should be also noted that 4-fluorobenzophenone **2b** is a sufficient initiator for the chain-growth polycondensations of **1** as well as **2a**. This means that an electron-withdrawing group such as the CF_3 group at the 4′-position of 4-fluorobenzophenone is not necessary for the initiator of this polymerization and that bifunctional modified fluorobenzophenone could be used for applications to block copolymerization.

Crystallinity of Polymers Effected by Polydispersity. We found that the polyether having initiator **2a** unit with low polydispersity was less soluble in organic solvent than the polyether obtained by conventional polycondensation without **2a**. Furthermore, the powder X-ray diffraction (XRD) pattern of both polymers with similar molecular weights showed that the crystallinity of the polymer obtained by chain-growth polycondensation ($M_n = 2450$, $M_w/M_n = 1.13$) was higher than that of the polymer obtained by conventional polycondensation ($M_n = 2240$, $M_w/M_n = 1.36$) (Figure 7). The differential scanning calorimetry (DSC) profile of the polymer obtained by conventional polycondensation showed no peak of both the first run and second run

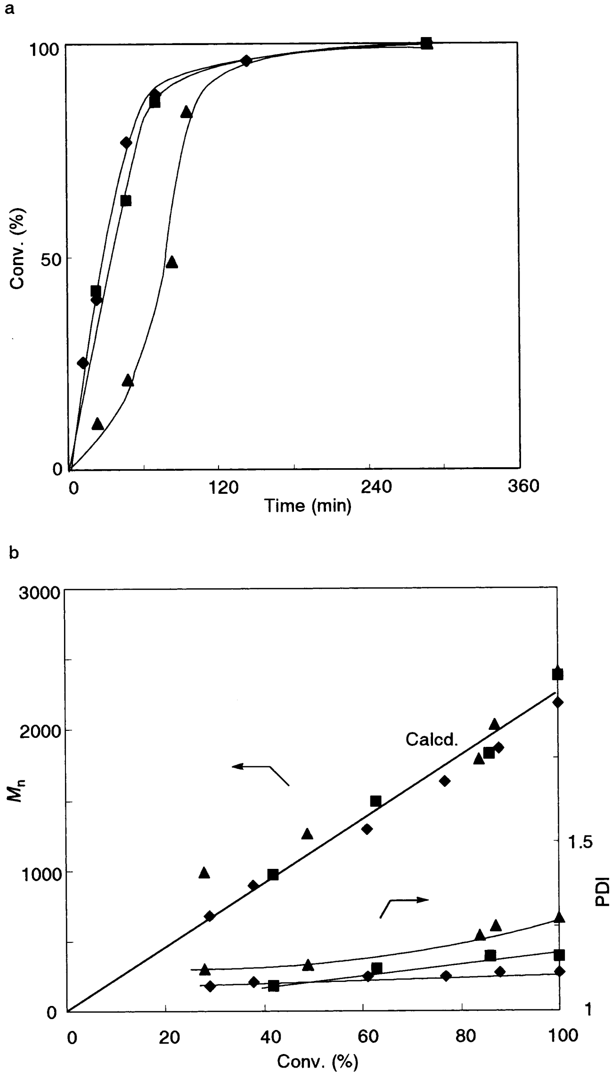


Figure 6. (a) Monomer conversion as a function of time for the polymerization of **1** in the presence of initiator (filled diamonds) **2a**, (filled squares) **2b**, and (filled triangles) **2c** in sulfolane at 150 °C: $[\mathbf{1}]_0 = 0.17$ M; $[\mathbf{2}]_0 = 11.7$ mM. (b) Poly**1** molecular weight and PDI as a function of monomer conversion: (filled diamonds) **2a**, (filled squares) **2b**, and (filled triangles) **2c** (sulfolane, 150 °C, $[\mathbf{1}]_0 = 0.17$ M; $[\mathbf{2}]_0 = 11.7$ mM).

(Figure 8a). On the other hand, the DSC profile of the polymer obtained by chain-growth polycondensation showed the endothermic peak at 255 °C (T_m), where the heating fusion (ΔH) was evaluated to be 20 J g^{-1} (Figure 8b). The complete melting sample was glassified by rapidly cool quenching to room temperature. The second heating DSC profile of the polymer showed the endothermic peak at 78 °C (T_g) and the exothermic peak at 172 °C (cold crystallization) with ΔH of 28 J g^{-1} and the endothermic peak at 255 °C (T_m) with ΔH of 21 J g^{-1}. These results distinctly also indicate that the polymer with low polydispersity obtained by chain-growth polycondensation possesses higher crystallinity. This implies that the crystallinity of condensation polymers could be controlled by polydispersity.

Conclusion

Our present results demonstrate that potassium fluorophenolate derivative **1** undergoes chain-growth polycondensation via electrophilic site propagation to yield aromatic polyethers having defined molecular weights and low polydispersities. The MALDI−TOF mass spectrum of poly**1** reveals that this polycondensation does not include conventional step-growth polycondensation which gives macrocycles and the polymer without initiation unit. The poly**1** with low polydispersity showed higher crystallinity than that with broad molecular weight distribution, obtained by the conventional polycondensation of **1**. Since not only the previous monomer having the acyl group for polyamides but also the monomer without acyl group for polyethers undergo chain-growth polycondensation like living polymerization, we are confident that deactivation of the electrophilic site in monomers with the negative charged nucleophilic site is an effective approach to chain-growth polycondensation. A lot of condensation polymers with low polydispersities would be produced by chain-growth polycondensation with this approach, and their novel physical properties could be discovered. Experiments along these lines are in progress.

Experimental Section

General. ^{1}H, ^{13}C, and ^{19}F NMR spectra were obtained on a JEOL A-500 and FX-200 operating in the pulsed Fourier transfer (FT) modes, using tetramethylsilane (^{1}H and ^{13}C NMR) as an internal standard and C_6F_6 (^{19}F NMR) as an external standard, respectively. IR spectra were recorded on a JASCO FT/IR-410. The M_n and M_w/M_n of polymers were measured with a TOSOH HLC-8020 gel permeation chromatography (GPC) unit [eluent: *N*,*N*-dimethylformamide (DMF) containing LiBr (1.05 g L^{-1}), calibration: polystyrene standards] using two TSK-gel columns (2 × Multipore H_{XL}-M). MALDI−TOF mass spectra were recorded on a Shimazu/Krotos Kompact MALDI IV tDE in the reflectron mode using laser ($\lambda = 337$ nm). A sample solution of polymer, dithranol as a matrix, and silver trifluoromethanesulfonate as a cationizing salt was made in chloroform. X-ray diffraction was performed on a Rigaku RAD-rA diffractometer using Cu Kα radiation, a diffracted beam monochromator, and counting equipment. Differential scanning calorimertry (DSC) was performed on a Seiko Instruments Inc. DSC 6000 at a heating rate of 10 °C min^{-1}.

p-Fluorobenzophenone was commercially available and used without further purification. Sulfolane was vacuum-distilled over CaH_2.

Synthesis of Monomer 1. Allyl 4-Fluorophenyl Ether (6). A mixture of 4-fluorophenol (22.4 g, 200 mmol), allyl bromide (20.2 g, 220 mmol), potassium carbonate (33.2 g, 220 mmol), and 18-crown-6 (5.28 g, 20 mmol) in dry acetone (200 mL) was heated at reflux and stirred vigorously for 8 h. The mixture was then poured into water and extracted with diethyl ether three times. The combined organic layer was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo, and the residue was distilled under reduced pressure to give 28.6 g of **6** (94%); bp 54−55 °C/4.2 mmHg (lit.[17] 46−50 °C/4.2 mmHg). IR (neat): 3082, 2921, 2862, 1601, 1506, 1245, 1121, 828, 768, 726 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 6.94 (m, 4H), 6.03 (ddt, J = , 9.3, 20.5, and 5.3 Hz, 1H), 5.38 (dd, $J = 1.5$ and 20.5 Hz, 1H), 5.32 (dd, $J = 1.5$ and 9.3 Hz, 1H), 4.48 (d, $J = 5.3$ Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 157.3 (d, $J_{C-F} = 247.2$ Hz), 155.0, 133.3, 121.2, 117.0 (d, $J_{C-F} = 9.3$ Hz), 115.7 (d, $J_{C-F} = 7.6$ Hz), 69.5.

2-Allyl-4-fluorophenol (7). A three-necked flask, equipped with a dropping funnel and a gas inlet tube, was purged with argon. To a solution of **6** (27 g, 178 mmol) in dry hexane (800 mL), 0.94 M diethlyaluminum chloride in hexane (270 mL, 254 mmol) was added dropwise with stirring at ambient temperature under nitrogen. The mixture was stirred at that temperature for 2 h. The solution was poured into ice-cooled 1 M hydrochloric acid (1 L). The organic layer was separated and treated with a solution of 4 M sodium hydroxide. The aqueous layer was acidified with 6 M hydrochloric acid and extracted with diethyl ether three times. The combined organic layer

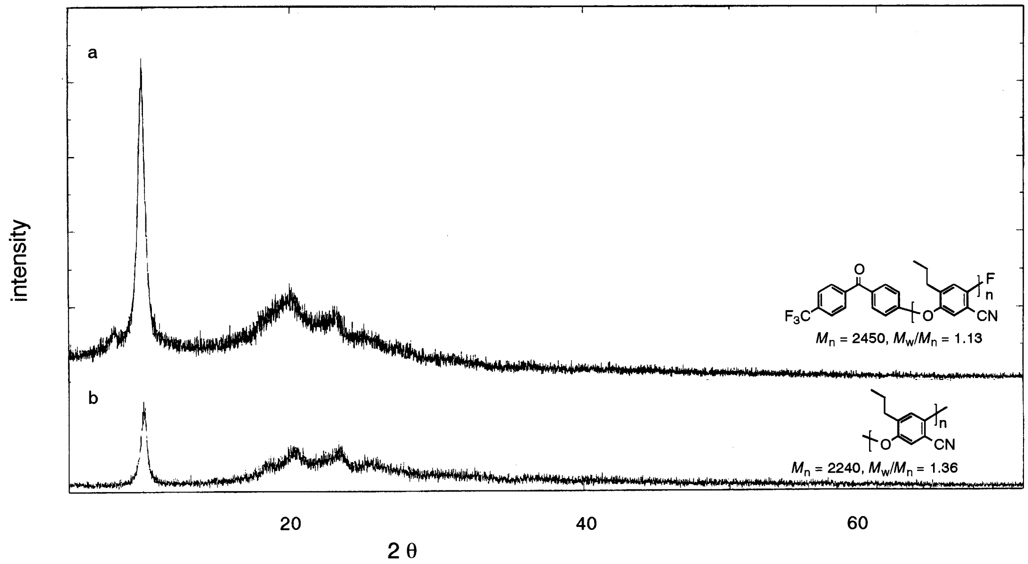


Figure 7. XRD pattern: (a) poly**1** obtained in the presence of **2a** at 150 °C in sulfolane: $[\mathbf{1}]_0 = 0.17$ M; $[\mathbf{2a}]_0 = 11.7$ mM. (b) poly**1** obtained by conventional polycondensation in sulfolane at 150 °C: $[\mathbf{1}]_0 = 0.17$ M.

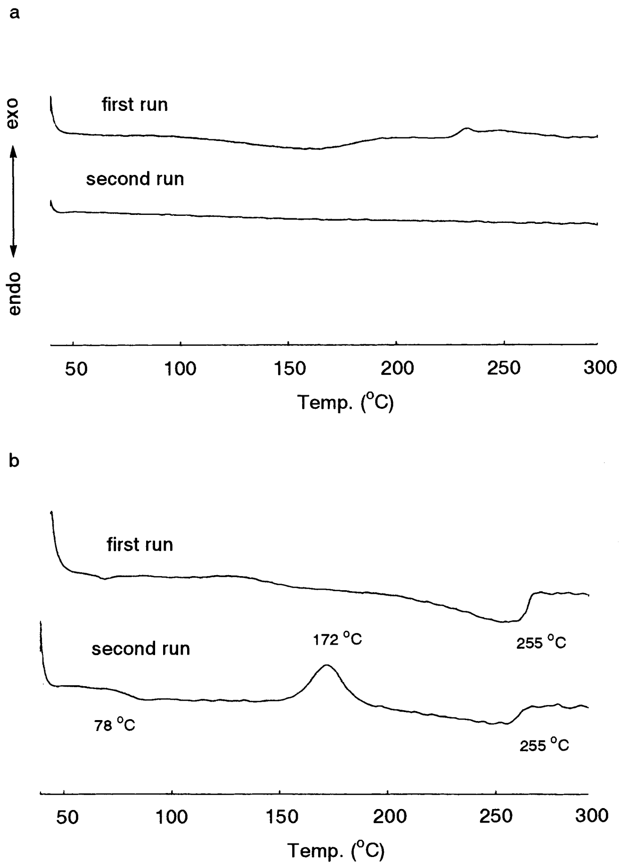


Figure 8. DSC profiles of poly**1**: (a) poly**1** obtained by conventional polycondensation in sulfolane at 150 °C: $[\mathbf{1}]_0 = 0.17$ M ($M_n = 2240$, $M_w/M_n = 1.36$). (b) poly**1** obtained in the presence of **2a** at 150 °C in sulfolane: $[\mathbf{1}]_0 = 0.17$ M; $[\mathbf{2a}]_0 = 11.7$ mM ($M_n = 2450$, $M_w/M_n = 1.13$).

was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo, and the residue was distilled under reduced pressure to give 26.8 g of **7** (100%); bp 97−98 °C/8.4 mmHg. IR (KBr): 3320, 2959, 2859, 1612, 1494, 1254, 1226, 1199, 866, 806, 780 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 6.86−6.70 (m, 3H), 6.09−5.89 (m, 1H), 5.19 (dd, J = 1.5 and 9.8 Hz, 1H), 5.15 (dd, J = 1.5 and 18.7 Hz, 1H), 4.98 (s, 1H), 3.38 (d, J = 6.3 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 157.3 (d, J_{C-F} = 238.8 Hz), 149.9, 135.6, 127.1 (d, J_{C-F} = 6.9 Hz), 117.1, 116.5 (d, J_{C-F} = 13.0 Hz), 116.5 (d, J_{C-F} = 1.5 Hz), 113.9 (d, J_{C-F} = 16.0 Hz), 34.9.

4-Fluoro-2-propylphenol (8). Into a solution of **7** (14.2 g, 93 mmol) in ethanol (450 mL) was added platinum(IV) oxide (0.113 g, 0.5 mmol) with stirring at ambient temperature. The air in the flask was replaced with hydrogen, and the mixture was stirred under a hydrogen atmosphere for 2 h. Platinum(IV) oxide was filtered off, and the solvent was removed in vacuo to give 14.2 g of **8** (99%). IR (neat): 3407, 2963, 2873, 1620, 1506, 1340, 1222, 1181, 865, 709 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 6.86−6.67 (m, 3H), 5.18 (s, 1H), 2.53 (t, J = 7.7 Hz, 2H), 1.62 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 157.2 (d, J_{C-F} = 236.0 Hz), 149.5, 130.3 (d, J_{C-F} = 7.6 Hz), 116.4 (d, J_{C-F} = 22.9 Hz), 115.7 (d, J_{C-F} = 25.0 Hz), 112.9 (d, J_{C-F} = 25.0 Hz), 32.0, 22.7, 13.9.

4-*tert*-Butyldimethylsiloxy-3-propyl-1-fluorobenzene (9). A solution of **8** (13.6 g, 87.6 mmol) in DMF (35 mL) was added to a solution of imidazole (7.15 g, 105 mmol) and *tert*-butyldimethylsilyl chloride (15.8 g, 105 mmol) in DMF (25 mL), and the mixture was stirred at ambient temperature for 6 h. The solution was diluted with water and then extracted with diethyl ether. The organic layer was washed with 10% sodium carbonate and water and then dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel (hexane) to give 22.6 g of **9** (96%). IR (neat): 2959, 2859, 1612, 1494, 1226, 1199, 866, 806, 780 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 6.88−6.78 (m, 3H), 2.55 (t, J = 8.0 Hz, 2H), 1.71−1.51 (m, 2H), 1.03 (s, 9H), 0.96 (t, J = 7.5 Hz, 3H), 0.23 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 157.3 (d, J_{C-F} = 238.0 Hz), 149.6, 134.9 (d, J_{C-F} = 7.6 Hz), 118.9 (d, J_{C-F} = 9.2 Hz), 116.4 (d, J_{C-F} = 22.9 Hz), 112.5 (d, J_{C-F} = 22.9 Hz), 32.7, 25.9, 23.1, 18.3, 14.0, −4.2.

5-Cyano-4-fluoro-2-propylphenol (11).[8,9] A three-necked flask, equipped with a dropping funnel and a gas inlet tube, was purged with argon. To a solution of **9** (16.8 g, 62.6 mmol) in dry THF (300 mL), 0.99 M *sec*-butyllithium in cyclohexane (75 mL, 74 mmol) was added dropwise with stirring at −78 °C under dry nitrogen. The mixture was stirred at that temperature for 1 h. A solution of DMF (15 mL) in dry THF (30 mL) was added dropwise at −78 °C with stirring, and the reaction mixture was stirred at that temperature for 1 h. After 10% aqueous HCl (50 mL) was added at −78 °C, the mixture was warmed to ambient temperature with stirring and then extracted with diethyl ether three times. The combined organic layer was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo to give aldehyde **10**. A mixture of **10**, hydroxylammonium chloride (5.80 g, 66.6 mmol), sodium formate (7.66 g, 111 mmol), and formic acid (80 mL) was heated at reflux for 2 h. The solution was extracted with ethyl acetate three times. The combined organic layer was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo, and the residue was dissolved with diethyl ether again. The etherial layer was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate = 10/1) and then recrystallized from hexane to give 9.04 g of **11** (91%) as a colorless solid; mp 75−76 °C. IR (KBr): 3386, 2961, 2231, 1615, 1189, 911, 798 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 7.04 (d, $J_{H-F} = 5.1$ Hz, 1H), 6.96 (d, $J_{H-F} = 9.3$ Hz, 1H), 6.88 (s, 1H), 3.61 (t, $J = 7.6$ Hz, 2H), 1.68−1.53 (m, 2H), 0.96 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 157.5 (d, $J_{C-F} = 251$ Hz), 150.6 (d, $J_{C-F} = 5.4$ Hz), 139.0 (d, $J_{C-F} = 6.8$ Hz), 117.6 (d, $J_{C-F} = 20.6$ Hz), 117.5 (d, $J_{C-F} = 5.4$ Hz), 114.5, 97.0 (d, $J_{C-F} = 16.5$ Hz), 32.4, 22.1, 13.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ: 41.7. Anal. Calcd for $C_{10}H_{10}FNO$: C, 67.03; H, 5.62; N, 7.82. Found: C, 67.06; H, 5.26; N, 8.05.

Potassium 5-Cyano-4-fluoro-2-propylphenolate (1). Into a solution of **11** (2.00 g, 11.2 mmol) in dry methanol (20 mL) was added a solution of KOH (0.736 g, 10.9 mmol) in dry methanol (50 mL). Following the removal of methanol in vacuo, the residue was washed with dry THF and then dried under reduced pressure to give 2.37 g (88%) of **1** as a colorless solid. IR (KBr): 2922, 2228, 1654, 1189, 850. ^1H NMR (500 MHz, DMSO-d_6) δ: 6.74 (d, $J_{H-F} = 10.5$ Hz, 1H), 6.23 (d, $J_{H-F} = 5.5$ Hz, 1H), 2.40 (t, $J = 7.5$ Hz, 2H), 1.54−1.45 (m, 2H), 0.88 (t, $J = 7.5$ Hz, 3H). ^{19}F NMR (470 MHz, DMSO-d_6) δ: 26.7 (brs, 1F).

Initiator 2a.[16] A solution of 4-trifluoromethylbenzoyl chloride (2.97 mL, 20 mmol), trifluoromethanesulfonic acid (0.02 mL, 0.02 mmol), and fluorobenzene (7.51 mL) was refluxed for 7 days and then concentrated in vacuo. The residual solid was purified by recrystallization from ethanol to give 3.57 g (66%) of **2a** as a colorless solid; mp 97−99 °C. IR (KBr): 1597, 1329, 1172, 1130, 1067, 845 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 7.82−7.70 (m, 4H), 7.24−7.13 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 194.1, 165.1 (d, $J_{C-F} = 256$ Hz), 140.7, 132.8 (d, $J_{C-F} = 9.2$ Hz) 132.0, 130.3 (d, $J_{C-F} = 388$ Hz), 130.0, 125.5, 125.4 (d, $J_{C-F} = 6.8$ Hz), 115.8 (d, $J_{C-F} = 21.3$ Hz). ^{19}F NMR (470 MHz, DMSO-d_6) δ: 98.8 (s, 3F), 57.1 (m, 1F).

Initiator 2c.[16] Into a mixture of 4-fluoro-4′-hydroxybenzophenone (0.216 g, 1.0 mmol) and potassium carbonate (0.166 g, 1.2 mmol) in dry DMF (2 mL) was added a solution of iodomethane (75 μL, 1.2 mmol) in dry DMF (0.5 mL) with stirring at ambient temperature for 6 h. The solution was poured into water and then extracted with ethyl acetate three times. The combined organic layer was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by recrystallization from ethanol to give 0.154 g of **2c** (68%) as a colorless solid; mp 90.3−92.7 °C (lit.[16] 90−92 °C). IR (KBr): 2985, 1641, 1598, 1259, 1151, 858, 765 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.78 (dd, $J_{H-H} = 8.5$ Hz and $J_{H-F} = 5.5$ Hz, 2H), 7.78 (d, $J_{H-H} = 8.5$ Hz, 2H), 7.13 (t, $J_{H-H} = 8.5$ Hz and $J_{H-F} = 8.5$ Hz, 2H), 6.95 (d, $J_{H-H} = 8.5$ Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 194.1, 165.0 (d, $J_{C-F} = 254.3$ Hz), 163.2, 134.4, 132.3, 132.2 (d, $J_{C-F} = 8.7$ Hz) 130.0, 115.3 (d, $J_{C-F} = 21.6$ Hz), 113.6, 55.4.

Conventional Polymerization of 1. In a glass tube was placed **1** (0.217 g, 1.0 mmol) and sulfolane (3 mL). The tube was degassed and sealed in vacuo, followed by heating for 4 h at 220 °C. After the tube was cooled, the solution was added dropwise into vigorously stirred 1 M HCl (50 mL) to afford precipitated polymer. The polymer obtained was dissolved with dichloromethane, and the solution was washed with water and dried over anhydrous $MgSO_4$. After removal of CH_2Cl_2 in vacuo, the residue was again dissolved with a small amount of CH_2Cl_2, followed by pouring into diethyl ether (100 mL) with vigorous stirring. The precipitated polymer was collected and dried in vacuo. IR (KBr): 2925, 2239, 1621, 1223, 889, 864, 749 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.16 (s, 1H), 6.83 (s, 1H), 2.67−2.64 (br, 2H), 1.63−1.59 (br, 2H), 0.99−0.85 (br, 3H).

Chain-Growth Polycondensation of 1 with 2. In a glass tube was placed **1** (0.217 g, 1 mmol), **2** (2−100 mol %), and sulfolane (6 mL). The tube was degassed and sealed in vacuo, followed by heating for 2−5 h at 150 °C. After the tube was cooled, the solution was added dropwise into vigorously stirred 1 M HCl (50 mL) to afford precipitated polymer. The polymer obtained was dissolved with dichloromethane, and the solution was washed with water and dried over anhydrous $MgSO_4$. After removal of CH_2Cl_2 in vacuo, the residue was again dissolved with a small amount of CH_2Cl_2, followed by pouring into diethyl ether (100 mL) with vigorous stirring. The precipitated polymer was collected and dried in vacuo.

Synthesis of Model Compounds 12 and 13. In a glass tube was placed **1** (0.211 g, 0.97 mmol), **2a** (0.638 g, 2.38 mmol), and sulfolane (6 mL). The tube was degassed and sealed in vacuo, followed by heating for 4 h at 150 °C. After the tube was cooled, the solution was added dropwise into vigorously stirred 1 M HCl (50 mL) to afford precipitated oligomer. The oligomer obtained was dissolved with ethyl acetate, and the solution was washed with water and dried over anhydrous $MgSO_4$. After removal of ethyl acetate in vacuo, the residue was purified by high-performance liquid chromatography to give 0.128 g of **12** (47%) as a colorless liquid and 0.087 g of **13** (41%) as a colorless solid; mp 100.4−103.6 °C.

12. IR (KBr): 2964, 2235, 1661, 1598, 1494, 1325, 1277, 1226, 1170, 1130, 1065, 1017, 930, 860, 772 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.90−7.83 (m, 4H), 7.76 (d, $J_{H-H} = 8.2$ Hz, 2H), 7.22 (d, $J_{H-F} = 5.5$ Hz, 1H), 7.18 (d, $J_{H-F} = 9.2$ Hz, 1H), 6.99 (d, $J_{H-F} = 8.8$ Hz, 2H), 2.64 (t, $J = 7.8$ Hz, 2H), 1.68−1.62 (m, 2H), 0.96 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 194.1, 161.3, 160.0 (d, $J_{C-F} = 257.3$ Hz), 149.5, 143.8 (d, $J_{C-F} = 7.3$ Hz), 142.4 (q, $J_{C-F} = 264.9$ Hz), 133.7 (d, $J_{C-F} = 33.2$ Hz), 132.9, 132.0, 130.0, 125.5, 125.4 (d, $J_{C-F} = 4.1$ Hz), 124.4, 116.8 (d, $J_{C-F} = 21.7$ Hz), 116.8, 113.4, 99.7, 32.5, 22.7, 13.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ: 99.3 (s, 3F), 50.9 (dd, $J_{F-H} = 5.4$ and 9.2 Hz, 1F). Anal. Calcd for $C_{10}H_{10}FNO$: C, 69.62; H, 4.47; N, 4.78. Found: C, 69.71; H, 4.39; N, 4.72.

13. IR (KBr): 2963, 2236, 1664, 1598, 1490, 1206, 1190, 1126, 1066, 931, 860 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.91−7.85 (m, 4H), 7.77 (d, $J_{H-H} = 8.2$ Hz, 2H), 7.30 (s, 1H), 7.19 (d, $J_{H-F} = 9.2$ Hz, 1H), 7.10 (d, $J_{H-F} = 5.5$ Hz, 1H), 7.03 (d, $J_{H-F} = 8.9$ Hz, 2H), 6.78 (s, 1H), 2.71 (t, $J = 7.8$ Hz, 2H), 2.58 (t, $J = 7.6$ Hz, 2H), 1.73−1.67 (m, 2H), 1.60−1.54 (m, 2H), 0.99 (t, $J = 7.3$ Hz, 3H), 0.91 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 194.0, 161.1, 159.8 (d, $J_{C-F} = 256.3$ Hz), 154.7, 149.8, 149.3, 143.1 (d, $J_{C-F} = 14.4$ Hz), 141.9 (q, $J_{C-F} = 274.9$ Hz), 132.8, 132.6, 131.9, 130.0, 129.9, 125.3, 125.0, 122.1, 119.6, 118.6 (d, $J_{C-F} = 20.7$ Hz), 117.0, 116.9, 114.5, 113.3, 102.7, 99.7, 32.6, 32.5, 22.8, 22.5, 13.8, 13.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ: 99.3 (s, 3F), 50.9 (dd, $J_{F-H} = 5.4$ and 9.2 Hz, 1F). Anal. Calcd for $C_{24}H_{17}F_4NO_2$: C, 67.45; H, 4.01; N, 3.28. Found: C, 67.32; H, 4.10; N, 2.86.

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