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Chain-Growth Polycondensation of Potassium 3-Cyano-4-fluorophenolate Derivatives for Well-Defined Poly(arylene ether)s

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Summary: Polycondensation normally proceeds in a step-growth reaction manner to give polymers with a wide range of molecular weights. However, the polycondensation of potassium 2-alkyl-5-cyano-4-fluorophenolate (**1**) proceeded at 150 °C in a chain polymerization manner from initiator, 4-fluoro-4'-trifluoromethyl benzophenone (**2**), to give aromatic polyethers having controlled molecular weights and low polydispersities ($M_w/M_n \leq 1.2$). 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. Sulfolane was a better solvent for chain-growth polycondensation of **1** than other aprotic solvents. The polyether from **1** with a low polydispersity showed higher crystallinity than that with a broad molecular weight distribution, obtained by the conventional polycondensation of **1** without **2**.

Keyword: chain-growth polycondensation, crystallinity, living polymerization, MALDI-TOF mass, polyethers

Introduction

The nature of polycondensation that proceeds in a step-growth reaction manner results in polymers with broad molecular weight distributions, which generally contain not only linear polymers but also macrocyclic oligomers and polymers.[1] We have been recently successful in the production of only linear polycondensation polymers with defined molecular weights and low polydispersities by chain-growth polycondensation for polyamides,[2] where the monomer reacts with the polymer end group selectively, not with other monomers by virtue of different subsituent effects of the nucleophilic site on the electrophilic site between the monomer and polymer.[3] We now apply this chain-growth polycondensation to the synthesis of poly(arylene ether)s with low polydispersities and then have designed monomer **1**.[4]

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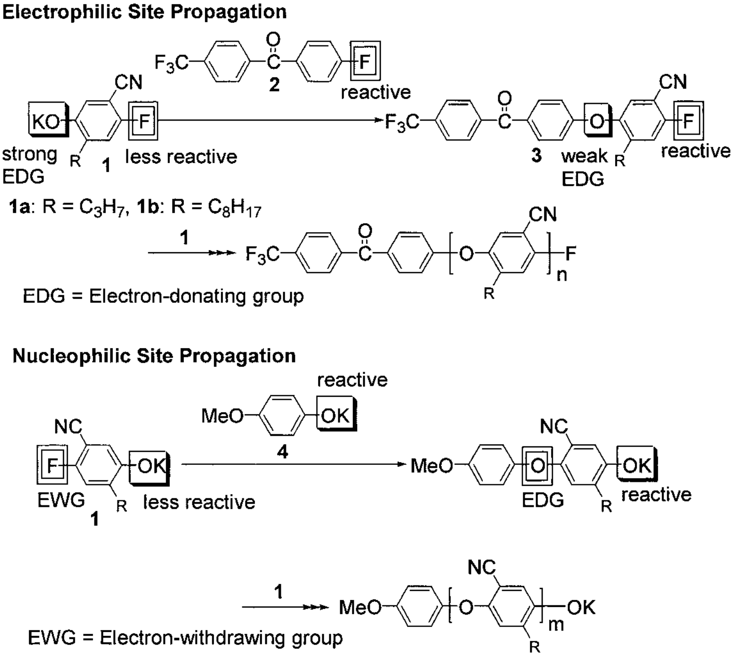
We expect two approaches to the chain-growth polycondensation of **1**: electrophilic site propagation and nucleophilic site propagation (Scheme 1). In the electrophilic site propagation by using reactive initiator **2** bearing an electron-withdrawing group, **1** would react with **2** to yield ether **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 a stronger electron-donating character than fluorine. Both approaches depend on whether there is enough difference of substituent effects between monomer and polymer.



Scheme 1

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. 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. Sulfolane is a suitable solvent for the chain-growth polycondensation of **1**. Furthermore, poly**1** with a low polydispersity from chain-growth polycondensation posesses higher crystallinity than that with a broad molecular weight distribution from conventional polycondensation.

Chain-growth Polycondensation of 1a

According to the two approaches to the chain-growth polycondendensation of **1** mentioned in Introduction, the polymerizations of **1a** with 7 mol% of initiator **2** for electrophilic site propagation and with 7 mol% of initiator **4** for nucleophilic site propagation were carried out at 150 °C in sulfolane, respectively. Surprisingly, the polymerization of **1a** with **4** did not proceed at all, whereas the polymerization with **2** took place to yield a polymer with a low polydispersity. This result implies that not only the reaction of **4** with **1a** but also the reaction of monomers **1a** with each other did not take place under this condition, and that the polymerization of **1a** in the presence of **2** did not involve step polymerization but was initiated with **2**. To elucidate whether chain-growth polymerization takes place from **2** in this polycondensation, the M_n values,[5] the M_w/M_n ratios, and the ratios of initiator unit to end group in polymer were plotted against monomer conversion in the polymerization of **1a** with 7 mol% of **2** (Figure 1(a)). 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 initiator unit to end group would be less than 1.0, because monomers react with not only an initiator but also other monomers. As shown in Figure 1(a), 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 initiator unit to end group, which were easily determined by the ^{19}F NMR spectra of polymer, were constantly about 1.0 irrespective of conversion. Consequently, Figure 1(a) shows that the polycondensation of **1a** proceeds in a chain-growth polymerization manner like living polymerization. In another series of experiments, **1a** was polymerized with varying feed ratio ($[\mathbf{1a}]_0/[\mathbf{2}]_0$). As shown in Figure 1(b), 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 $[\mathbf{1a}]_0/[\mathbf{2}]_0$ ratios were more than 1.0.[6] This also agrees with the features of chain-growth polymerization.

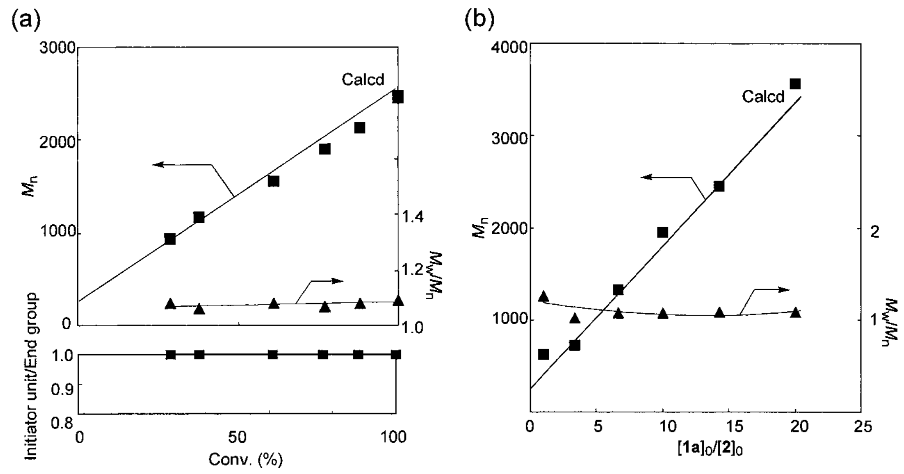


Fig. 1. (a) M_n and M_w/M_n values of poly**1a** and the ratios of initiator unit to end group in poly**1a**, obtained in the presence of **2** in sulfolane at 150 °C, as a function of monomer conversion: $[\mathbf{1a}]_0$ = 0.17 M; $[\mathbf{2}]_0$ = 11.7 mM. (b) M_n and M_w/M_n values of poly**1a**, obtained in the presence **2** in sulfolane at 150 °C, as a function of the feed ratio of **1a** to **2**: $[\mathbf{1a}]_0$ = 0.17 M; $[\mathbf{2}]_0$ = 8.3 –167 mM; conversion = 100%.

Solvent Effect on Chain-growth Polycondensation of 1b with 2

Solvent effect on the chain-growth polycondensation was studied by using potassium 5-cyano-4-fluoro-2-octylphenolate (**1b**), which was more soluble than **1a** in a variety of solvents. Thus, the polymerization of **1b** was carried out in the presence of **2** ($[\mathbf{1b}]_0/[\mathbf{2}]_0$ = 50) at 150 °C for 24 h in various solvents that dissolve **1b** and poly**1b** at the polycondensation temperature. When **1b** polymerized in THF, monomer conversion was low and polymer with a high polydispersity was obtained. In quinoline the polymerization proceeded very slowly but polymer with M_n of 6940 and a low polydispersity ($M_w/M_n < 1.3$) was afforded in spite of low conversion, which was not a step polymerization nature but a chain polymerization nature. In *N,N*-dimethylimidazolidinone (DMI) and tetraglyme, **1b** was converted in more than 80%.

However, the ratios of initiator unit to fluorine end group were more than 1.0, indicating that termination took place by the substitution of the polymer terminal fluorine in the side reaction.[7] The ratios of initiator unit to fluorine end group of the polymer obtained in DMI were almost 1.0 for 1 h but less than 1.0 for 5 h. Since this ratio of less than 1.0 means that there are more end groups than the initiator units, both step-growth polymerization and chain-growth polymerization took place for 5 h. In sulfolane, the conversion of monomer was 100% and high moleclure weight polymer (M_n = 5900) was obtained, but the molecular weght distribution was rather broad ($M_w/M_n \geq 2.0$). This may be because poly**1b** was precipitated during polymerization. The polymerization of **1b** was then carried out at the feed ratios of [**1b**]$_0$/[**2**]$_0$ of less than 30. The polymerizaton proceeded homogeneously to yield polyethers with low polydispersities. The M_n values of polymers were in good agreement with those calculated M_n. The ratios of initiator unit to end group was constantly 1.0. Sulfolane was the best solvent for the chain-growth polycondensation of **1b** in all of the solvents we examined.

Table 1. Polymerization of **1b** with **2**.

Solv.	[**1b**]$_0$/[**2**]$_0$	Time (h)	Conv. (%)$^{a)}$	M_n (Calcd)	$M_n$$^{b)}$	$M_w/M_n$$^{b)}$	Initiator unit /End group
Quinoline	50	24	6	956	6940	1.22	c)
THF/18-crown-6	50	24	65	7716	3600	1.88	c)
Tetraglyme	50	24	82	10218	5160	2.11	1.18
DMI	50	1	29	3400	2150	2.15	0.98
	50	5	88	10318	3250	3.13	0.76
	50	24	87	10088	5090	1.92	2.44
Sulfolane	50	24	100	11725	5900	2.01	1.02
	10.2	24	95	2648	2240	1.13	1.01
	14.9	24	85	3560	2750	1.14	1.00
	26.8	24	85	5070	4550	1.17	1.02

The polymerization of **1b** was carried out in the presence of initiator **2** at 150 °C; [**1b**]$_0$ = 0.17 M; [**2**]$_0$ = 3.4 mM.

a) Determined by HPLC (eluent: MeOH/H_2O = 70/30).

b) Determined by GPC based on polystyrene standards (eluent: THF).

c) Not determined.

MALDI-TOF Mass Spectra of Poly1b

MALDI-TOF mass spectrometry is an ideal technique for the detection of small quantities of side reaction products and could analyze chain-growth polycondensation polymer having the initiator unit and conventional polycondensation polymer bearing no initiator unit. Thus, the polymers obtained in DMI and in sulfolane, mentioned in the above section, were analyzed by the MALDI-TOF mass spectra, respectively.

Under the MALDI-TOF mass conditions used, poly**1b** is ionized to $[M + Ag]^+$ ion. The mass spectrum obtained from the product of the polymerization in DMI (conversion = 29%; the ratio of initiator unit to end group = 0.98) is shown in Figure 2. It contains two distributions. The distribution in the lower mass range corresponds to the Ag^+ adducts of poly**1b** without **2** unit from conventional polycondensation. For example, the 6-mer of this distribution is expected to produce a signal at *m/z* 6 × 229.14 (repeat unit) + 20.01 (HF) + 106.90 ($^{107}Ag^+$) = 1501.75, as indeed is observed at 1503.53. The distribution in the higer mass range is due to the Ag^+ adducts of poly**1b** with initiator **2** from chain-growth polycondensation. For example, *m/z* 3585.71 detected in Figure 2 is in good agreement with the expected signal of the 14-mer at *m/z* 14 × 229.14 (repeat unit) + 268.06 (**2**) + 106.90 ($^{107}Ag^+$) = 3582.92. Therefore, the polymerization of **1b** in DMI involves both chain-growth polycondensation and conventional polycondensation even in low conversion.

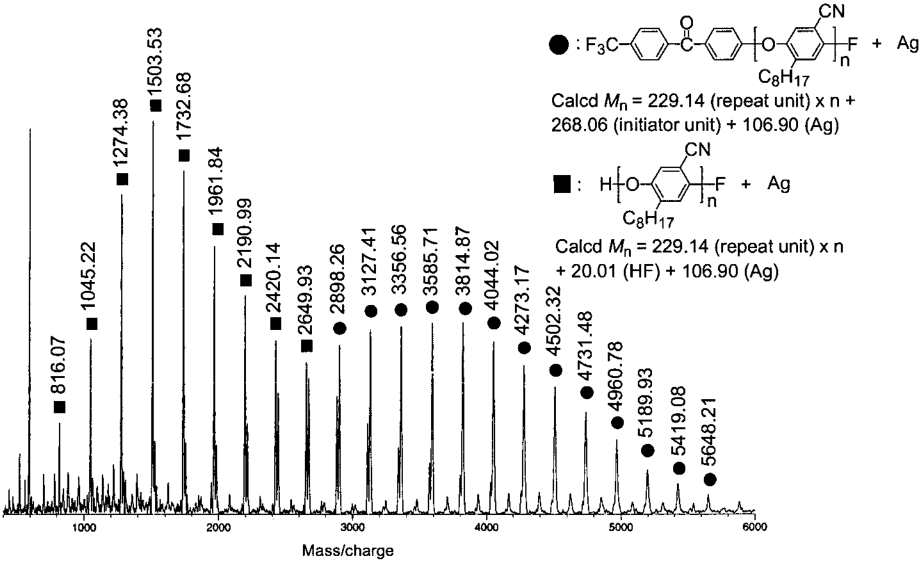


Fig. 2. MALDI-TOF mass spectrum of poly**1b** obtained in the presence of **2** ($[\mathbf{1b}]_0/[\mathbf{2}]_0$ = 50) in DMI at 150 °C (conversion = 29%; the ratio of initiator unit to end group = 0.98).

On the other hand, the mass spectrum obtained from the product of the polymerization in sulfolane (conversion = 85%; the ratio of initiator unit to end group = 1.00) contains only the one series of peaks, whose *m*/*z* values correspond to the Ag$^+$ adducts of the poly**1b** with **2** (Figure 3). For example, the 11-mer of this distribution is expected to produce a signal at *m*/*z* 11 × 229.14 (repeat unit) + 268.06 (**2**) + 106.90 (^{107}Ag$^+$) = 2895.50, as indeed is observed at 2896.15 as the highest signal. The linear polymer without **2** unit from conventional polycondensation (-268.06 Da + 20.01 Da (HF)) and macrocycles with no **2** unit (-268.06 Da) are absent (no *m*/*z* 2647 and 2627 detected in Figure 3). This mass spectrum indicates that the polymerization of **1b** in sulfolane proceeded in a chain polymerization manner from initiator **2** without accompanying conventional polycondensation.

Conseqauently, it turns out that the chain-growth polycondensation of **1b** for poly(arylene ether) is strongly depend on the reaction solvent; sulfolane is a specific solvent for the chain-growth polycondensation of **1b**.

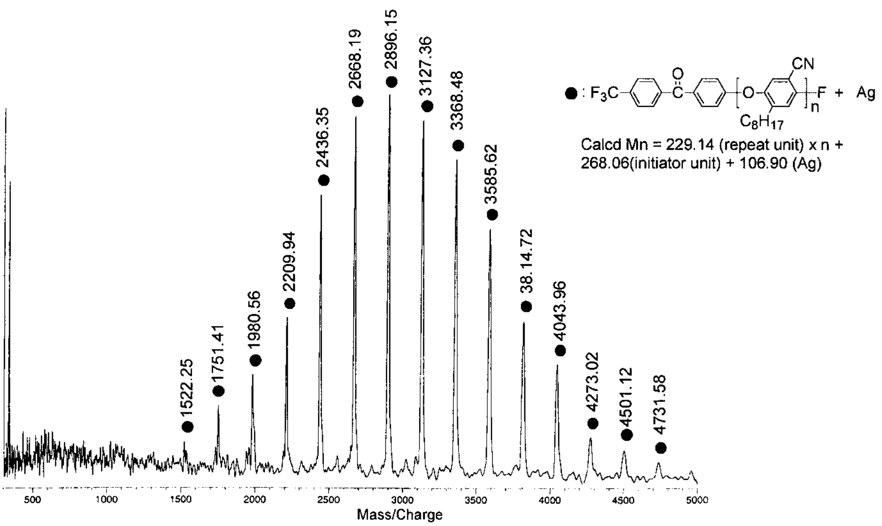


Fig. 3. MALDI-TOF Mass spectrum of poly**1b** obtained in the presence of **2** ([**1b**]$_0$/[**2**]$_0$ = 14.9) in sulfolane at 150 °C (conversion = 89%; the ratio of initiator unit to end group = 1.00).

Crystallinity of Polymers Effected by Polydispersity

We found that poly**1a** having initiator **2** unit with low polydispersity was less soluble in organic solvents than the polyether obtained by conventional polycondensation without **2**. The powder X-ray diffraction (XRD) pattern of both polymers with similar molecular weight.

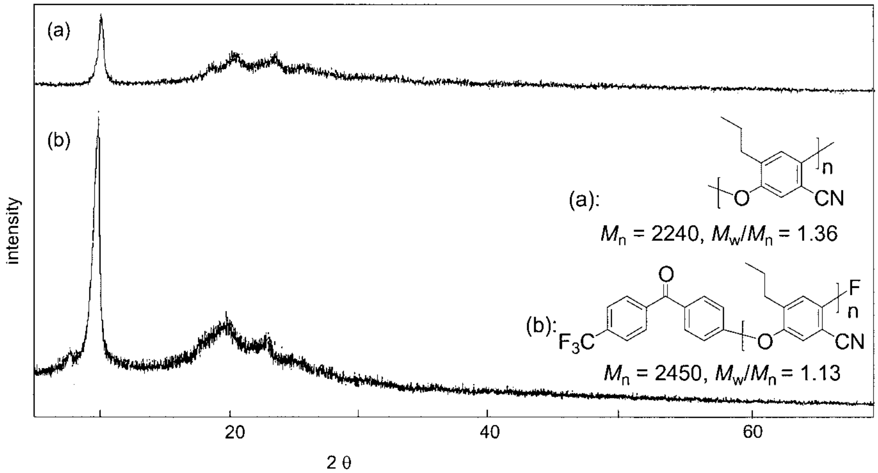


Fig. 4. XRD pattern: (a) poly**1a** obtained by conventional polycondensation without **2** in sulfolane at 150 °C: $[\mathbf{1a}]_0$ = 0.17 M; (b) poly**1a** obtained in the presence of **2** in sulfolane at 150 °C: $[\mathbf{1a}]_0$ = 0.17 M; $[\mathbf{2}]_0$ = 11.7 mM.

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 4). The differential scanning calorimetry (DSC) traces of the above conventional polycondensation polymer did not show any intense peak on both the first and second heatings (Figure 5(a)). On the other hand, the first heating of the polymer obtained by chain-growth polycondensation showed the melting point at 255 °C with a melting enthalpy of 20 J/g. The complete melting polymer was glassified by rapidly quenching to room temperature. On a second heating the glass transition temperture (T_g) appeared at 78 °C, and furthermore the exothermic peak attributed to cold crystallization at 172 °C with ΔH of 28 J/g and the melting point at 255 °C with ΔH of 21 J/g were observed (Figure 5(b)). The DSC analysis of the polymers distinctly also indicates that the polymer with low polydispersity obtained by chain-growth polycondensation possesses higher crystallinity. This result implies that the crystallinity of condensation polymers could be controlled by polydispersity of polymers.

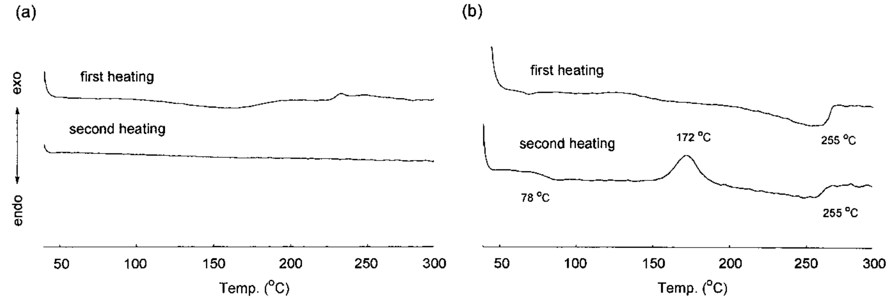


Fig. 5. DSC traces of poly**1a** (heating rate 10 °C/min): (a) poly**1a** obtained by conventional polycondensation in sulfolane ([**1a**]$_0$ = 0.17 M) at 150 °C (M_n = 2240, M_w/M_n = 1.36); (b) poly**1a** obtained in the presence of **2** ([**1a**]$_0$ = 0.17 M; [**2**]$_0$ = 11.7 mM) at 150 °C in sulfolane (M_n = 2450, M_w/M_n = 1.13).

Conclusion

Our present results demonstrate that potassium fluorophenolate derivatives **1** undergo chain-growth polycondensation via electrophilic site propagation to yield aromatic polyethers having defined molecular weights and low polydispersities. The polycondensation of **1b** with **2** was carried out in a variety of solvents to find remarkable solvent effects on this polymerization. The MALDI-TOF mass spectrum of poly**1b** with **2** in sulfolane reveals that this polycondensation does not include conventional step-growth polycondensation which gives macrocycles and the polymer without initiator unit. Poly**1a** with a low polydispersity from chain-growth polycondensation posesses higher crystallinity than that with a broad molecular weight distribution from conventional polycondensation.

Acknowledgments

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[5] The M_n values of polymer were estimated by the ^1H NMR spectra based on the ratios of signal intensities of the repeating units to the initiator unit.

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