Investigation of Aromatic Polyester Synthesis by the Chain-Growth Polycondensation Method

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ABSTRACT: Synthesis of aromatic polyesters by chain-growth polycondensation of activated 4-hydroxybenzoic acid derivatives (**1**) was investigated. Model reactions of ester formation between active compounds (**6** and **7**) and phenolic nucleophile (**8**) gave the best result when 3-arylcarbonyl-2-benzothiazolone derivatives were used with tertiary amines in CH_2Cl_2. Therefore, we designed and synthesized 3-(4-hydroxy-3-octylbenzoyl)-2-benzothiazolone (**1h**) as a monomer. The M_n− and M_w/M_n−conversion curves of the polymerization of **1h** with initiator suggested that transesterification between polymer and monomer occurred in the late stage of polymerization. Investigation of the effects of bases and initiators revealed that the transesterification at the initiator end was minimized by using 3-(4-benzoyloxybenzoyl)-2-benzothiazolone (**7h**) and diisopropylethylamine as an initiator and a base, respectively. When the ratio of initiator **7h** to monomer **1h** was 20 mol %, the polycondensation proceeded in a chain-growth manner to give aromatic polyester having a controlled molecular weight and a low polydispersity. However, the polymerization of **1h** with 10 mol % or less of **7h** could not be controlled and gave step-growth polymer as well as chain-growth polymer. The model reaction demonstrated that transesterification would occur at the polymer main chain even by use of weak tertiary amines as a base.

Introduction

A variety of methodologies have been developed for the synthesis of poly(4-hydroxybenzoate) and its derivatives because their unique properties such as liquid crystallinity and morphology depend on the chemical structure of monomers and the manner of polymerization. The polyesters have been frequently synthesized by molten polymerization of 4-acetoxybenzoic acid derivatives.[1] "Single-crystal" type poly(4-hydroxybenzoate) was prepared by Economy using a solvent of high boiling point, and the mechanism of polymerization and the structure of polyester were discussed.[2] Kricheldorf investigated the condensations of various monomers for polyesters and proposed a different mechanism and structure.[3] He also investigated the synthesis, structure, and application of whisker of poly(4-hydroxybenzoate).[4] It was also prepared by direct polycondensation of 4-hydroxybenzoic acid using a variety of condensing reagents.[4,5] Several substituted aromatic polyesters have been synthesized in order to increase their solubility and exploit new characters such as liquid crystallinity.[6]

The M_n values of the polyesters were determined by the ^{1}H NMR analysis of the hydrolyzed compounds because of very poor solubility of the polyesters,[2,3] and the M_n value of poly(4-hydroxybenzoate) prepared by Kricheldorf was estimated to be 200 000 by this ^{1}H NMR method.[3] On the other hand, the polydispersity of poly(4-hydroxybenzoate) derivatives has rarely been reported. Since all of the polycondensation mentioned above were step-growth polymerization, the synthesized polyesters would have broad molecular weight distributions. Recently, we have developed chain-growth polycondensation methodology and synthesized aromatic polyamides[7] and polyethers[8] with controlled molecular weights and low polydispersities like living polymerization. In their syntheses, we took advantage of different electron-donating abilities between the nucleophilic site of monomer and the amide or ether linkage of polymer propagating end. In this paper, we tried to apply our chain-growth polycondensation to the synthesis of poly(4-hydroxy-3-octylbenzoate) with a strategy shown in Scheme 1. The aryl hydroxyl group of monomer **1** having the leaving group X is deprotonated by a base to afford **2**. A strong electron-donating nature of the phenoxide group of **2** reduces electrophilicity of the active acyl moiety at the para position, and the reaction between **2**'s would be suppressed. If there is initiator **3** having the reactive acyl group in the reaction mixture, the phenoxide group of **2** would react with **3** to give ester **4**. Because this reaction changes the strong electron-donating phenoxide group into the weak electron-donating ester linkage, the electrophilicity of the acyl group of **4** is much higher than that of **2**. This change of substituent effect will allow the phenoxide of **2** to react with the acyl moiety of **4**. In this way, the deactivated acyl group in monomer is converted to the reactive one by the reaction of monomer with the polymer end group, which leads to chain-growth polycondensation.

In the previous paper, we investigated the reaction conditions for the chain-growth polycondensation of 4-trimethylsilyloxybenzoyl chloride using model reactions.[9] We attempted the chain-growth polycondensation of this monomer under the optimized conditions, but polymerization could not proceed in a chain-growth manner because of unstable and highly reactive nature of the monomer and of poor solubility of the polymer obtained. Therefore, we first examined the leaving group

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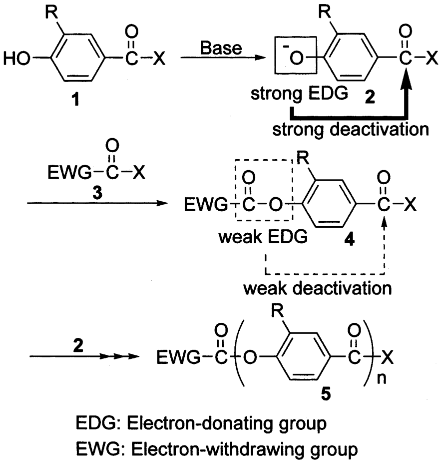
Scheme 1. Mechanism of Chain-Growth Polycondensation of 1



(X) of monomer **1** by model reactions. Then we synthesized a monomer having an appropriate leaving group and a linear alkyl chain on the aryl moiety and investigated its chain-growth polycondensation.

Results and Discussion

Model Reactions. To carry out the polymerization of **1** in a chain-growth manner, the activated acyl group (−COX) in **1** must have an adequate reactivity not only to prevent the reaction between **2**'s (resulting in step-growth polymerization) but also to undergo the reaction between **2** and **4** or **5** (resulting in chain-growth polymerization). As mentioned above, acid chloride as an active acyl group was too reactive to prevent step-growth polymerization. Furthermore, electrophilicity of the active acyl group of **1** should be higher than that of the aryl ester linkage of polymer formed. Considering these factors, we chose eight leaving groups and studied their abilities for chain-growth polycondensation by model reactions (Scheme 2). We used **6a**−**h** as models of the electrophilic site of monomer, **7a**−**h** as those of the electrophilic site of the propagating end of polymer, and **8** as a model of the nucleophilic site of monomer. This reaction will give two products. Product **9** is formed by the reaction between monomer electrophilic model **6** and its nucleophilic model **8** and corresponds to a "step-growth polymerization" product. On the other hand, the reaction of **8** with propagating end model **7** gives **10**, which corresponds to a "chain-growth polymerization" product. Therefore, the leaving group X which gives **10** most selectively should be the best one for chain-growth polycondensation. A mixture of equimolar amounts of **6**, **7**, and **8** was treated with Et_3N in CH_2Cl_2 at room temperature for 48 h, and the chemoselectivity of **8** toward **6** or **7** was evaluated (Table 1). Trichloroethyl (**a**) and 2,4,6-trichlorophenyl esters (**b**) did not react under this condition at all, but 2,4-dinitrophenyl ester (**c**) gave **10** selectively (**9**/**10** = 17/83) in high yield. The reaction of thiolester (**d**) proceeded much slower, but introduction of the nitro group at the para position (**e**) accelerated the reaction. When X's were benzothiazole derivatives and benzothiazolone (**f**, **g**, and **h**),[10] 3-acyl-2-benzothiazolone (**h**) gave the ester products quantitatively and most selectively of all the eight leaving groups we examined.

According to the above results, we decided 2-benzothiazolone (**h**) as a leaving group of monomer and optimized reaction conditions. The effects of solvents on the reaction of **6h**, **7h**, and **8** are shown in Table 2. When THF was used as a solvent, the reaction resulted in low yield and moderate chemoselectivity. The reaction in DMF, NMP, and CH_2Cl_2 gave quantitative yields of the products. Since the selectivity in CH_2Cl_2 (**9**/**10** = 14/86) was the highest of the three solvents, we next studied the effect of base in CH_2Cl_2 (Table 3). The reaction with pyridine resulted in low conversion of **8**. When 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 4-(dimethylamino)pyridine (DMAP) was used, yields of the products were very high but chemoselectivities were low. Et_3N, *i*-Pr_2NEt, and K_2CO_3 gave products in high yields and high selectivities. Of the three bases, the reaction with *i*-Pr_2NEt was the most selective. According to these results, we concluded tentatively that a suitable solvent and base for the chain-growth polycondensation of **1** was CH_2Cl_2 and *i*-Pr_2NEt, respectively.

Synthesis of 1h. It was reported that unsubstituted poly(4-hydroxybenzoate) had a poor solubility for organic solvents, but introduction of the alkyl substituents to the aromatic ring increased its solubility.[6] As polyamide synthesis we reported previously,[7] we designed a monomer having the octyl chain in order to gain high solubility of polymer. Ballauf has synthesized 3-alkyl-4-hydroxybenzoic acids by Fries rearrangement of ethyl 4-alkanoyloxybenzoate and subsequent Clemmensen reduction.[6a] However, yields of Fries rearrangement were not high, and harmful mercury was used in the Clemmensen reduction. Therefore, we synthesized **1h** in another way (Scheme 3). 4-Hydroxybenzoic acid (**11**) was brominated at the 3-position selectively,[11] and then the carboxylic acid **12** was converted to methyl ester **13**. We first protected the aryl hydroxyl group of **13** as the benzyl ether, but this ether was not able to be cleaved under standard hydrogenolysis conditions after introduction of the octyl and 2-benzothiazolyl groups, and deprotection under more vigorous conditions accompanied hydrolysis of the 2-benzothiazolyl active amide moiety. Therefore, we chose the *p*-methoxybenzyl (PMB) ether as a protective group because this ether can be easily removed by treatment with acids. PMB ether **14** was synthesized in acetone with PMB-Cl, K_2CO_3, and 18-crown-6. The octynyl group was introduced by the Sonogashira reaction[12] to afford **15**, and subsequent hydrolysis of the methyl ester gave carboxylic acid **16**. We first attempted to convert **16** into the acid chloride with $SOCl_2$ in order to introduce the 2-benzothiazolyl group,[10c] but treatment of **16** with $SOCl_2$ resulted in deprotection of the PMB ether. The 2-benzothiazolyl group was then introduced by condensation of **16** and 2-hydroxybenzothiazole at room temperature in the presence of 1,3-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP). This reaction gave the *N*-acyl product **17** in high yield without formation of the *O*-acyl product. The triple bond was reduced by catalytic hydrogenation in ethyl acetate−ethanol using Pd/C under a H_2 atmosphere, but the PMB ether could not be cleaved under this condition, and addition of aqueous acetic acid to the reaction mixture was ineffective, too. Treatment of **18** with ammonium cerium(IV) nitrate (CAN) in CH_3CN-H_2O[13] resulted in cleavage of not only the PMB ether but also the 2-benzothiazoyl moiety, and treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[14] gave a complex mixture. At last, we found that trifluoroacetic acid (TFA) in CH_2Cl_2[15] could cleave the PMB ether of **18** to give **1h** in 66% yield.

Scheme 2. Model Reaction for Leaving Group

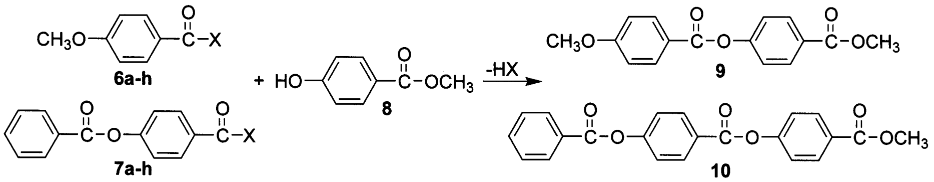
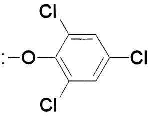
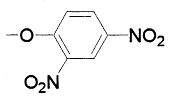
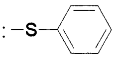
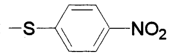
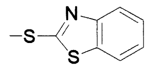
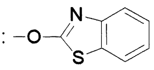
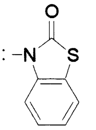


Table 1. Effect of Leaving Group in the Reaction of 6, 7, and 8[a]

Entry	Leaving Group (X)	Conv. of **8** (%)[b]	Yield of **9**+**10** (%)[b]	**9**/**10**[b]
1	**a**: $-OCH_2CCl_3$	0	0	—
2	**b**: 	0	0	—
3	**c**: 	100	98	17/83
4	**d**: 	23	18	28/72
5	**e**: 	91	91	21/79
6	**f**: 	100	91	23/77
7	**g**: 	100	98	18/82
8	**h**: 	100	100	14/86

[a] The reaction was carried out in CH_2Cl_2 ([**6**]$_0$ = [**7**]$_0$ = [**8**]$_0$ = 0.02 M) with Et_3N at room temperature for 48 h. [b] Determined by GC.

Table 2. Solvent Effect in the Reaction of 6h, 7h, and 8[a]

entry	solvent	conv of **8** (%)[b]	yield of **9** + **10** (%)[b]	**9**/**10**[b]
1	THF	26	21	24/76
2	DMF	100	100	15/85
3	NMP	100	97	17/83
4	CH_2Cl_2	100	100	14/86

[a] The reaction was carried out with Et_3N ([**6h**]$_0$ = [**7h**]$_0$ = [**8**]$_0$ = 0.02 M) at room temperature for 48 h. [b] Determined by GC.

Table 3. Effect of Base in the Reaction of 6h, 7h and 8[a]

entry	base	conv of **8** (%)[b]	yield of **9** + **10** (%)[b]	**9**/**10**[b]
1	pyridine	20	17	30/70
2	DBU	100	98	51/49
3	DMAP	100	91	23/77
4	Et_3N	100	100	14/86
5	*i*-Pr_2NEt	100	96	12/88
6	K_2CO_3	100	90	17/83

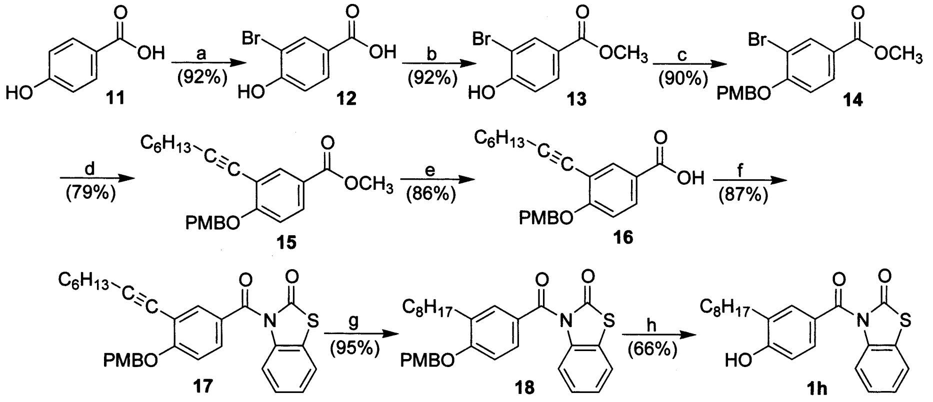
[a] The reaction was carried out in CH_2Cl_2 ([**6h**]$_0$ = [**7h**]$_0$ = [**8**]$_0$ = 0.02 M) at room temperature for 48 h. [b] Determined by GC.

Step-Growth Polycondensation of 1h. To examine the ability of polymerization of **1h** and the solubility of the polyester formed, the polymerization of **1h** was carried out with Et_3N or *i*-Pr_2NEt as a base in CH_2Cl_2 for 72 h at room temperature (conversion = 97−100%). Conversion−M_n and −M_w/M_n curves shown in Figure 1 indicate that these polymerizations proceeded in a typical step-growth polycondensation manner; the increase of M_n and M_w/M_n was slow up to the middle stage of polymerization but accelerated in the last stage. The two bases gave similar polyesters, whose M_n and M_w/M_n were 1.7×10^4 and 2.5−2.7, respectively. The obtained polyester was easily soluble in $CHCl_3$ and CH_2Cl_2, modestly in THF and CCl_4, and insoluble in hydrocarbons (hexane, cyclohexane, and toluene), aprotic polar solvents (DMF, DMSO, and NMP), alcohols (MeOH and EtOH), and other solvents such as CH_3CN, acetone, and diethyl ether.

Chain-Growth Polycondensation of 1h from 19. We then investigated the chain-growth polycondensation of **1h** with 5 mol % of 3-(4-nitrobenzoyl)-2-benzothiazolone (**19**) as an initiator (Scheme 4). **19** has the strong electron-withdrawing nitro group at the para position to the active acyl group, whose electrophilicity would be much higher than that of monomer **1h**. The effect of bases on the polymerization are shown in Table 4. CH_2Cl_2 was used as a solvent in the polymerization with amines (entries 1−4) because of the results of the model reactions and of dissolving freely the polyester formed. The reaction was continued until monomer was consumed completely. The polymerization with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and DBU gave polyesters with higher M_n than the calculated one (M_n(calcd) = 4900) and with high polydispersity. However, Et_3N or *i*-Pr_2NEt showed better results: the M_n was close to the calculated one, and the M_w/M_n was narrower than others. These results were consistent with those of model reactions shown in Table 3. Considering the basicity of tertiary amines such as Et_3N and *i*-Pr_2NEt, the phenol moiety of **1h** would not be deprotonated completely by these bases. As shown in Scheme 1, it seemed that the acyl group of nondeprotonated **1h** was not deactivated so strongly as that of deprotonated **1h** (that is, **2** in Scheme 1) and that the reaction between **1h**'s each other might occur, resulting in rather broad molecular weight distributions. We then used stronger bases such as Et_3SiH/CsF/18-crown-6 and *t*-BuOK/18-crown-6. THF was used as a solvent despite a modest solubility of the polymer in THF, because CH_2Cl_2 was not thought to be inert for such strong bases. The polymerization with these stronger bases proceeded faster than those with the amines but gave poor results like the polymerization with DBN and DBU; the obtained polymer had high polydispersities and much higher M_n values than the calculated one.

The detailed behavior in polymerization with Et_3N and *i*-Pr_2NEt is shown in Figures 2 and 3. The time−conversion curves (Figure 2) show that the polymerization with *i*-Pr_2NEt is faster than that with Et_3N. The conversion−M_n and −M_w/M_n relationships (Figure 3) indicate that, in contrast to polycondensation in a step-growth manner shown in Figure 1, the M_n increased in proportion to conversion despite a slight difference from the calculated value and the M_w/M_n ratios kept less than

Scheme 3. Synthesis of 1h[a]



[a] Reagents and conditions: (a) Br_2, 1,4-dioxane, rt, 1 day; (b) H_2SO_4, MeOH, reflux, 2.5 h; (c) PMB−Cl, 18-crown-6, K_2CO_3, acetone, reflux, 12 h; (d) 1-octyne, $Pd_2(dba)_3$, CuI, PPh_3, Et_3N, THF, 80 °C in a sealed tube, 37 h; (e) KOH, EtOH−H_2O, reflux, 0.5 h; (f) 2-hydroxybenzothiazole, DCC, DMAP, CH_2Cl_2, rt, 1 h; (g) H_2, Pd−C, EtOH−AcOEt, rt, 3 days; (h) CF_3CO_2H, CH_2Cl_2, rt, 3 h.

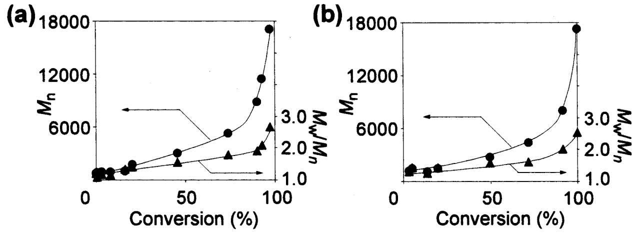


Figure 1. M_n (circle) and M_w/M_n (triangle) values of poly**1h**, obtained with (a) Et_3N and (b) *i*-Pr_2NEt in CH_2Cl_2 at room temperature, as a function of monomer conversion: $[\mathbf{1h}]_0 = [Et_3N]_0 = [i\text{-}Pr_2NEt]_0 = 0.10$ M.

1.3 up to 50% conversion in polymerization with both bases. These results suggest that chain-growth polycondensation is a dominant reaction in the low conversion stage. However, in the higher conversion stage, increase of the M_n was once retarded and then both the M_n and M_w/M_n were accelerated, implying that some side reactions occurred in this stage.

The efficiency of initiator was checked by the model reaction using initiator **19** and nucleophilic monomer model **8** in the presence of Et_3N or *i*-Pr_2NEt as a base (Scheme 5). The reaction proceeded rapidly at the same rate irrespective of the kind of bases (Figure 4). The yield of **20** was about 80% only in 5 min and quantitative in 2 h. Therefore, we concluded that acceleration of the M_n and increase of the polydispersity in the late stage were caused not by the initiation step but by other factor concerning polymerization process.

Transesterification at Initiator End. We assumed tentatively that the curious behavior observed in Figure 3 might be caused by transesterification among monomer, oligomer, and polymer. Because the ester linkage formed in polymerization is a kind of aryl ester, this linkage has a moderate reactivity for nucleophiles. Especially, because of the strong electron-withdrawing nature of the nitro group of initiator **19**, electrophilicity of the ester carbonyl carbon at the initiator unit in polymer would be enhanced, and transesterification would take place at this position, which might cause deviations from the chain-growth polycondensation manner we designed. Therefore, we examined the possibility of the transesterification at the initiator unit by a model reaction (Scheme 6). We used **21** as a polymer initiator unit model and **8** as a nucleophilic monomer model, and the reaction was carried out under the same conditions as polymerization. Results are shown in Table 5. Transesterification proceeded quickly in the case of DBN, DBU, Et_3SiH/CsF/18-crown-6, and *t*-BuOK/18-crown-6 but did slowly in the case of Et_3N and *i*-Pr_2NEt. These results agree with the effect of bases on polymerization shown in Table 4; that is, polymerization with Et_3N or *i*-Pr_2NEt gave better results than those with other bases.

Investigation of Initiator. The transesterification at the ester linkage between initiator unit and monomer unit is thought to be reduced by decreasing the electrophilicity of the ester carbonyl carbon at this position. We therefore designed two other initiators **22** and **7h** which have hydrogen and the electron-donating benzoyloxy substituent instead of the nitro group of **19**, respectively. Especially, **7h** is a dimer model of monomer. The effect of these initiators on polymerization of **1h** was evaluated (Scheme 7). The M_n of polymer was estimated by ^{1}H NMR, and the results are shown in Table 6. While the polymerization using **19** or **22** as an initiator resulted in smaller M_n than the calculated one, the initiation by **7h** gave a better result; the M_n of polymer was close to the calculated one, and its polydispersity was the lowest. These results show that **7h**, which has the weak electron-donating benzoyloxy group at the para position to the active ester group, has enough reactivity to initiate polymerization and suggest that such decrease of electrophilicity by a weak electron-donating substituent is necessary in order to prevent the transesterification at the linkage between initiator and monomer units.

Chain-Growth Polycondensation of 1h from 7h. Using **7h** as an initiator, **1h** was polymerized with *i*-Pr_2NEt in CH_2Cl_2 at room temperature. The ratio of chain-growth polymers to total polymers was estimated by the ^{1}H NMR spectrum. Figure 5 shows ^{1}H NMR spectra of (a) step-growth polymer (SP) prepared by the polymerization of **1h** without initiator and (b) polymer obtained by the polymerization of **1h** with initiator **7h**, which was a mixture of SP and chain-growth polymer (CP) propagated from **7h**. The resonance of the aromatic proton H_a placed between the octyl chain and the carbonyl group of the propagating end unit of SP is the same position (7.86 ppm) as that of CP. The phenol end of the step-growth polymer gave unique signals at 8.01 (H_b), 7.98 (H_c), and 6.86 ppm (H_d). The ratio of chain-growth polymerization (designated as “CP/(CP + SP)”)

Scheme 4. Polymerization of 1h with 19

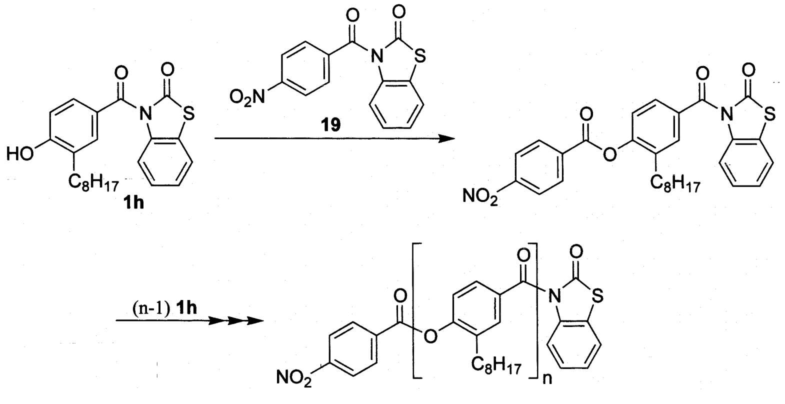


Table 4. Effect of Base in Polymerization of 1h with 19[a]

entry	base	solvent	time (h)[b]	M_n[c,d]	M_w/M_n[c]
1	DBN	CH_2Cl_2	2	9 300	2.69
2	DBU	CH_2Cl_2	48	15 300	2.87
3	Et_3N	CH_2Cl_2	36	5 700	1.54
4	*i*-Pr_2NEt	CH_2Cl_2	6	4 600	1.43
5	Et_3SiH/CsF/18-crown-6	THF	3	15 200	2.67
6	*t*-BuOK/18-crown-6	THF	3	10 900	2.75

[a] The reaction was carried out with base (1.0 equiv) and **19** (5 mol %) in CH_2Cl_2 (entries 1–4, $[\mathbf{1h}]_0 = 0.10$ M) or THF (entries 5 and 6, $[\mathbf{1h}]_0 = 0.17$ M) at room temperature. [b] Conversion = 100%. [c] Determined by GPC based on polystyrene standards. [d] M_n(calcd) = 4900.

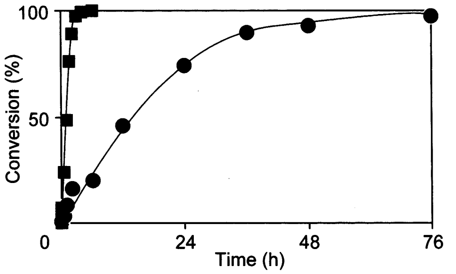


Figure 2. Time–conversion curves for the polymerization of **1h** in the presence of **19** (5 mol %) with Et_3N (circle) and *i*-Pr_2NEt (square) in CH_2Cl_2 at room temperature: $[\mathbf{1h}]_0 = [Et_3N]_0 = [i\text{-}Pr_2NEt]_0 = 0.10$ M.

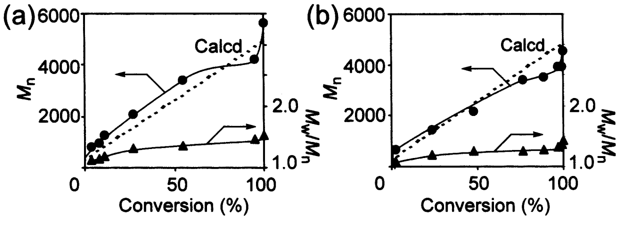


Figure 3. M_n (circle) and M_w/M_n (triangle) values of poly**1h**, obtained in the presence of **19** (5 mol %) with (a) Et_3N and (b) *i*-Pr_2NEt in CH_2Cl_2 at room temperature, as a function of monomer conversion: $[\mathbf{1h}]_0 = [Et_3N]_0 = [i\text{-}Pr_2NEt]_0 = 0.10$ M.

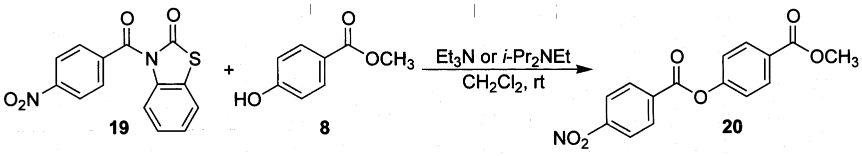
was calculated by the integral values of H_a (designated as "Int[H_a]") and H_d (Int[H_d]) in the following equation:

$$CP/(CP + SP) = 1 - Int[H_d]/Int[H_a]$$

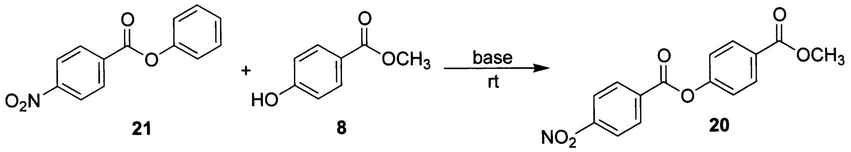
The polymerizations were carried out with varying feed ratio of $[\mathbf{1h}]_0/[\mathbf{7h}]_0 = 5$, 10, and 20. The results of the polymers obtained are listed in Table 7, and the M_n, M_w/M_n, and CP/(CP + SP) as a function of monomer conversion are shown in Figure 6. In the case of $[\mathbf{1h}]_0/[\mathbf{7h}]_0 = 5$ (Figure 6a), the M_n increased linearly in proportion to conversion with low polydispersity ($M_w/M_n \leq 1.28$), and this polymerization would progress from initiator **7h** because CP/(CP + SP) was always 1.0. Although the M_n values were a little higher than the calculated ones, these results indicate that the polymerization at this feed ratio proceeded in a chain-growth manner. On the other hand, when $[\mathbf{1h}]_0/[\mathbf{7h}]_0 \geq 10$ (Figure 6b,c), the M_n–conversion curves were shown like the polymerization with **19** in Figure 3; increase of the M_n was reduced in the middle stage of polymerization, and acceleration of the M_n and increase of the M_w/M_n occurred in the late stage of polymerization. Furthermore, deviations of CP/(CP + SP) from 1.0, which were ascribed to the increased extent of step-growth polymerization, became larger as deviations of the M_n from the calculated values were large. These tendencies enhanced as $[\mathbf{1h}]_0/[\mathbf{7h}]_0$ increased from 10 (Figure 6b) to 20 (Figure 6c). The results mentioned above suggest that transesterification between monomer and polymer chain occurred by the attack of the monomer phenoxy moiety to the ester carbonyl carbon of polymer main chain in the middle stage of polymerization. The *N*-acyl-2-benzothiazolone moiety of polymer end group is indeed a much better leaving group than the aryl ester of polymer chain, and nucleophilic attack of monomer occurred selectively at the polymer propagating end rather than at the polymer chain in the low conversion stage. In the higher conversion stage where concentration of the polymer propagating ends was much lower than that of the ester linkages in polymer chain, however, the dominant concentration of the polymer ester linkage would overcome the higher reactivity of the polymer propagating end. Consequently, the nucleophilic phenoxide of monomer might attack the phenyl ester moiety of polymer chain, and the M_n might not increase regardless of monomer consumption. This transesterification would not only give "step-growth polymer" bearing no initiator end but also cause slowdown of increase of the M_n since such a transesterification would decrease the molecular weight of the polymer. In the last stage of polymerization, the step-growth polymers would react with each other to give polymer with high molecular weight, which led steep increase of M_n.

Transesterification at Polymer Main Chain. Transesterification at the polymer backbone was studied by a model reaction with various bases (Scheme 8). Triester **23** was used as a polymer chain model, and this compound has two aryl ester moieties ("**a**" and "**b**"). The carbonyl carbon "**a**" is connected with two groups. One

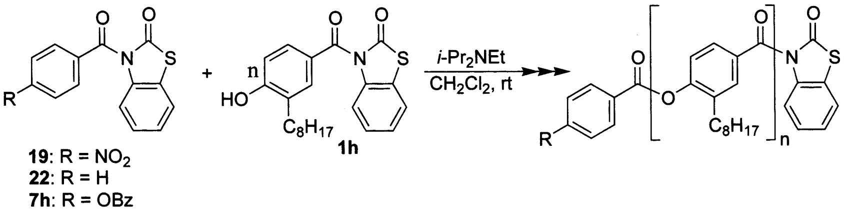
Scheme 5. Model Reaction for Initiation



Scheme 6. Model Reaction of Transesterification at Initiation End



Scheme 7. Polymerization of 1h with Various Initiators



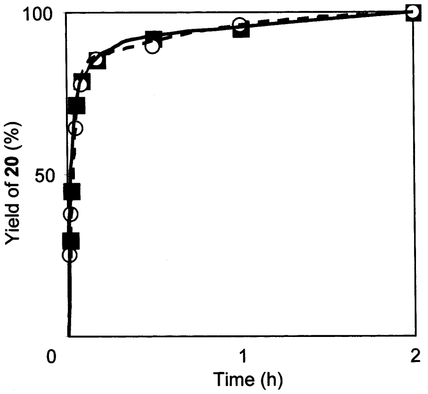


Figure 4. Yields of **20** in the reaction of **19** and **8** with Et_3N (filled cube) or *i*-Pr_2NEt (open circle) in CH_2Cl_2 at room temperature: $[\mathbf{19}]_0 = [\mathbf{8}]_0 = 83$ mM.

Table 5. Transesterification of 21 by 8[a]

entry	base	solvent	conv of **8** (%)[b]	yield of **20** (%)[b]
1	DBN	CH_2Cl_2	16.4	16.4
2	DBU	CH_2Cl_2	32.4	28.2
3	Et_3N	CH_2Cl_2	5.9	3.0
4	*i*-Pr_2NEt	CH_2Cl_2	1.6	1.2
5	Et_3SiH/CsF/18-crown-6	THF	23.1	19.6
6	*t*-BuOK/18-crown-6	THF	10.3	7.1

[a] The reaction was carried out with base (1.0 equiv) in CH_2Cl_2 (entries 1–4, $[\mathbf{21}]_0 = [\mathbf{8}]_0 = 0.10$ M) or THF (entries 5 and 6, $[\mathbf{21}]_0 = [\mathbf{8}]_0 = 0.17$ M) at room temperature for 1 h. [b] Determined by GC.

Table 6. Effect of Initiator in Polymerization of 1h[a]

entry	initiator	time[b] (h)	M_n calcd	M_n obsd[c]	M_w/M_n[d]
1	**19**	16	4957	3930	1.49
2	**22**	30	4754	3630	1.46
3	**7h**	24	5071	4840	1.40

[a] The reaction was carried out with *i*-Pr_2NEt (1.0 equiv) and initiator (5 mol %) in CH_2Cl_2 ($[\mathbf{1h}]_0 = 0.10$ M) at room temperature. [b] Conversion = 100%. [c] Determined by ^1H NMR. [d] Determined by GPC based on polystyrene standards.

is the aryloxy group substituted by the electron-withdrawing ester group at the para position, and the other is the aromatic ring having the electron-donating acyloxy group at the para position. Nucleophilic reaction by **8** at the "**a**" position affords ester **24** and phenol **25** as an exchanged product and a leaving component, respectively. The circumstance of the carbonyl carbon "**b**" is similar to that of "**a**", but the aryl group connecting to the carbonyl carbon "**b**" does not have the electron-donating acyloxy substituent. Therefore, electrophilicity of the carbonyl carbon "**b**" would be higher than that of "**a**", and transesterification may occur more frequently at the "**b**" position to give **26** as a exchanged product and **27** as a leaving phenol. The reactivity at the "**a**" position would reflect the electrophilicity of the ester moiety of the polyester backbone we synthesized, and transesterification at the "**b**" position would correspond to that at the initiator end of polyester when **22** or **7h** is used as an initiator.

However, the results of reaction were not so simple; not only **24**–**27** but also other products including oligomers were formed. This is because **24** and **26** having the aryl ester group could be attacked by the phenol moiety of **8**, **25**, or **27**, which led further transesterification. Indeed, the total yields of **24** and **26** were always smaller than conversions of **23** or **8**. Since the yields of **24** and **26** would not reflect the reactivities of the "**a**" and "**b**" position, respectively, the effect of base on the transesterification was estimated by the conversion of **23** and **8**.

Table 8 shows the conversion of **23** and **8** in the model transesterification reaction using equimolar amounts of **23** and **8** in the presence of a variety of bases. In a similar manner of the transesterification of initiator end model **21** by **8** as shown in Scheme 6 and Table 5, consumption of **23** was faster in the reaction with DBN, DBU, Et_3SiH/CsF/18-crown-6, and *t*-BuOK/18-crown-6, and a considerable amount of **23** reacted even in a short time (2 h). The results suggest that polymerization with these bases causes transesterification readily to yield polymers having the phenoxide moiety and the active acyl group at each ends, followed by step-growth polymerization to give polymer with a high molecular

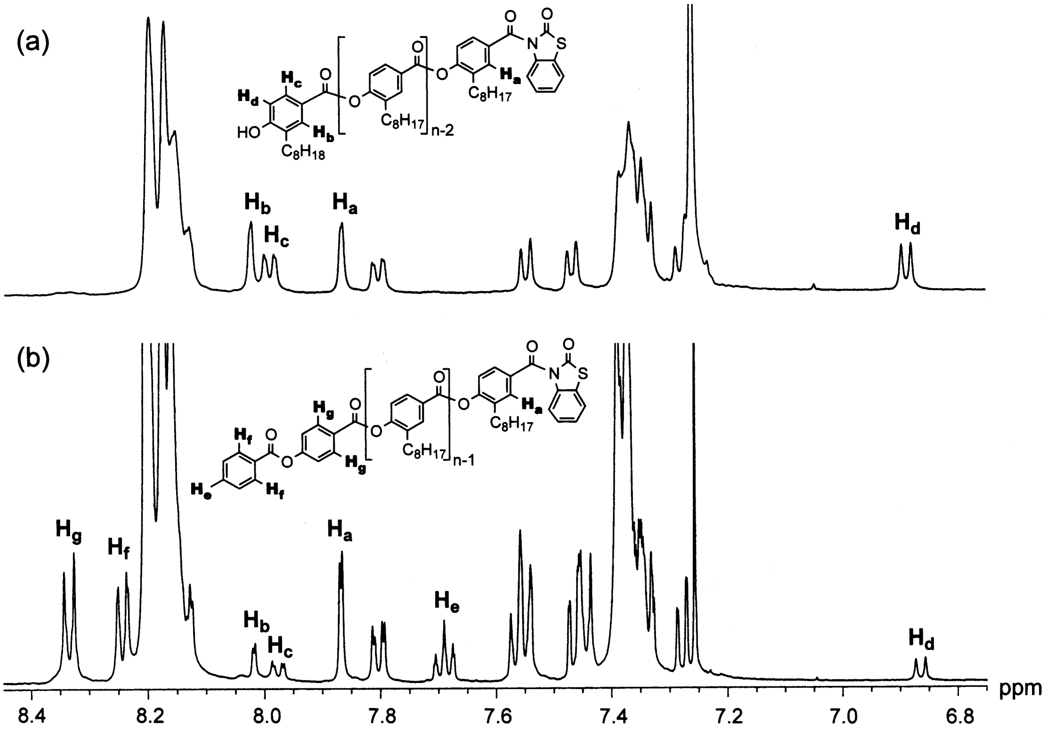


Figure 5. ^{1}H NMR spectra of the polyesters obtained by the polymerization of **1h** in the (a) absence and (b) presence of initiator **7h** (500 MHz, $CDCl_3$).

Table 7. Polymerization of 1h in the Presence of 7h[a]

entry	feed ratio $[\mathbf{1h}]_0/[\mathbf{7h}]_0$	time (h)[b]	M_n calcd	M_n obsd[c]	M_w/M_n[d]	CP/(CP + SP) (%)[c,e]
1	5	24	1546	1950	1.28	100
2	10	30	2699	3000	1.30	92
3	20	30	5071	5810	1.45	69

[a] The polymerization was carried out in the presence of **7h** with i-Pr_2NEt (1.0 equiv) in CH_2Cl_2 ([**1h**] = 0.10 M) at room temperature. [b] Conversion = 100%. [c] Determined by ^{1}H NMR. [d] Determined by GPC based on polystyrene standards. [e] Ratio of the number of chain-growth polymers to that of total polymers.

weight and a broad molecular weight distribution. This assumption agrees with the results of polymerization of **1h** with **19** shown in Table 4 in which reactions with these bases gave polymers with a high molecular weight and a broad molecular weight distribution. On the other hand, transesterifications with Et_3N or i-Pr_2NEt were very slow. Trace amounts of **23** and **8** were consumed for 2 h (entries 3 and 5). When the reaction was prolonged to 24 h, the conversions of **23** and **8** increased up to 3−4% (entries 4 and 6). These results suggest that transesterification indeed occur even by use of weak tertiary amines such as Et_3N and i-Pr_2NEt and is one of the factors of difficulty in achieving the chain-growth polycondensation of **1h** from a small amount of initiators.

Conclusions. Model reactions of esterification revealed that 2-benzothiazolone was the most suitable leaving group for the synthesis of aryl polyesters by chain-growth polycondensation, and we synthesized **1h** and investigated its polymerization. When **19** was used as an initiator, the most suitable base was i-Pr_2NEt, but the polymerization did not proceed in a chain-growth manner completely. The results of model reaction suggest that transesterification occurred at the initiator end. We examined the effect of initiators to find that the polymerization with **7h** as an initiator gave better results than that with **19**. When the polymerization of **1h** was carried out in the presence of 20 mol % of **7h**, it proceeded in a chain-growth manner to give polymer with a controlled molecular weight and a low polydispersity. However, the polymerization with 10 mol % or less of **7h** could not be controlled to give a certain amount of step-growth polymer as well as chain-growth polymer. Analysis of the polymerization behavior and the results of model reactions suggest that transesterification at the polymer main chain interfered with chain-growth polycondensation. We are currently investigating the reaction conditions preventing the transesterification so as to synthesize aryl polyester with a higher molecular weight and a low polydispersity by chain-growth polycondensation.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were obtained on JEOL A-500, EX-270, and FX-200 spectrometers using tetramethylsilane as an internal standard. 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-8120 gel-permeation chromatography (GPC) unit (eluent: tetrahydrofuran (THF); calibration: polystyrene standards) using two TSK-gel columns (2 × Multipore H_{XL}-M). Isolation of polyesters was carried out with a Japan Analytical Industry LC-908 recycling preparative HPLC (eluent: $CHCl_3$) using two TSK-gel column (2 × G2000H_{HR}). All melting points were measured with a Yanagimoto hot stage melting point apparatus and were uncorrected. Column chromatography was performed on silica gel (Kieselgel 60, 230−400 mesh, Merck) with a specified solvent. Commercially available (Kanto) dehydrated dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF, stabilizer free) were used as dry solvents. *N*,*N*-Dimethylformamide (DMF), 1-methyl-2-pyridone (NMP), pyridine, triethylamine (Et_3N), *N*,*N*-diisopropylethylamine (i-Pr_2NEt), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), and triethylsilane (Et_3SiH) were distilled by standard procedure.[16] 4-(Dimethylamino)pyridine (DMAP), cesium fluoride (CsF), and potassium *tert*-butoxide (t-BuOK) were used as received. 18-

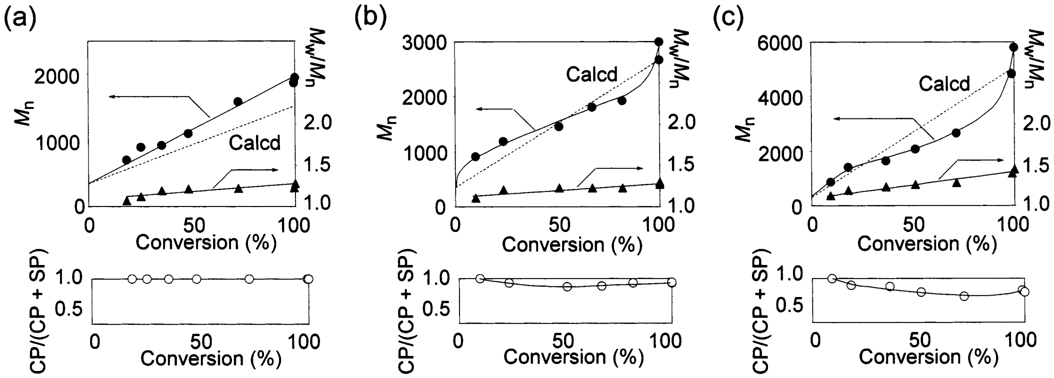


Figure 6. M_n (filled circle), M_w/M_n (filled triangle), and CP/(CP + SP) (open circle) values of poly**1h**, obtained in the presence of **7h** with *i*-Pr_2NEt at room temperature, as a function of monomer conversion: $[\mathbf{1h}]_0 = [i\text{-}Pr_2NEt]_0 = 0.10$ M, $[\mathbf{1h}]_0/[\mathbf{7h}]_0 =$ (a) 5, (b) 10, and (c) 20.

Scheme 8. Model Reaction of Transesterification at Polymer Chain

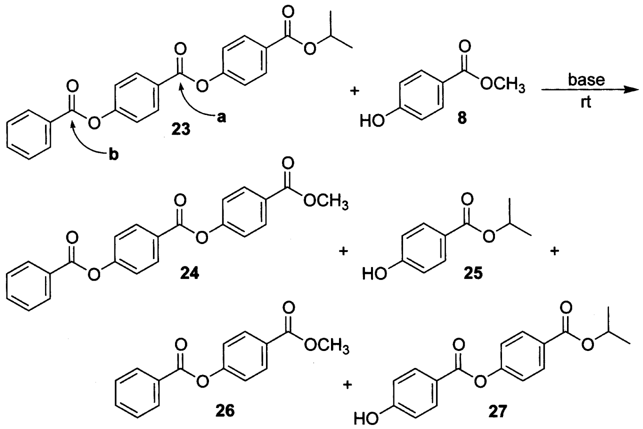


Table 8. Transesterification of 23 by 8[a]

entry	base	solvent	time (h)	conv (%)[b]	
				23	**8**
1	DBN	CH_2Cl_2	2	82	75
2	DBU	CH_2Cl_2	2	42	50
3	Et_3N	CH_2Cl_2	2	0.2	0.6
4			24	4	3
5	*i*-Pr_2NEt	CH_2Cl_2	2	0.2	0.4
6			24	3	3
7	Et_3SiH/CsF/18-crown-6	THF	2	94	76
8	*t*-BuOK/18-crown-6	THF	2	92	58

[a] The reaction was carried out with base (1.0 equiv) in CH_2Cl_2 (entries 1−6, $[\mathbf{1h}]_0 = 0.10$ M) or THF (entries 7 and 8, $[\mathbf{1h}]_0 = 0.17$ M) at room temperature. [b] Determined by GC.

Crown-6 was dried under reduced pressure at 40 °C for more than 6 h prior to use.

Model Reaction for Leaving Group. Typical Procedure for the Reaction of 8 with 6 and 7. To a solution of **8** (0.076 g, 0.50 mmol), Et_3N (0.08 mL, 0.6 mmol), and phenanthrene (internal standard for GC analysis, 0.36 g, 0.20 mmol) in dry CH_2Cl_2 (2 mL) was added a solution of **6** (0.5 mmol) and **7** (0.5 mmol) in dry CH_2Cl_2 (19 mL). The mixture was stirred at room temperature for 48 h, and the conversion of **8** and the yields of **9** and **10** were determined by GC analysis of the reaction mixture.

Step-Growth Polycondensation of 1h. A solution of **1h** (0.192 g, 0.500 mmol) and naphthalene (internal standard for HPLC analysis, 64 mg, 0.50 mmol) in dry CH_2Cl_2 (5 mL) was placed in a round-bottomed flask equipped with a three-way stopcock under an Ar atmosphere. Into the flask was added Et_3N (0.070 mL, 0.50 mmol) or *i*-Pr_2NEt (0.087 mL, 0.50 mmol) via a syringe from the three-way stopcock with a stream of N_2. A small portion of the reaction mixture was withdrawn by a syringe via the three-way stopcock with a stream of N_2 during a certain period and analyzed by HPLC to determine the degree of consumption of **1h** and by GPC to determine M_n and M_w/M_n of polymer formed. As **1h** disappeared, 1 M hydrochloric acid was added to the reaction mixture, which was extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by preparative HPLC (eluent: $CHCl_3$) using polystyrene gel column to give step-growth poly**1h**. ^1H NMR (500 MHz, $CDCl_3$) δ: 8.20−8.17 (m, 2 H), 7.37 (br s, 1 H), 2.70 (br s, 2 H), 1.70 (br s, 2 H), 1.37−1.26 (m, 10 H), 0.87 (br s, 3 H). IR (KBr): 3455, 2925, 1742, 1587, 1498, 1246, 1167, 1090 cm^{-1}.

Chain-Growth Polycondensation of 1h. Method A (Base = Et_3N, *i*-Pr_2NEt, DBU, or DBN). A solution of **1h** (0.192 g, 0.500 mmol), initiator (0.025 mmol), and naphthalene (internal standard for HPLC analysis, 64 mg, 0.50 mmol) in dry CH_2Cl_2 (4 mL) was placed in a round-bottomed flask equipped with a three-way stopcock under an Ar atmosphere. Into the flask was added at room temperature a solution of a base (0.50 mmol) in dry CH_2Cl_2 (1 mL) via a syringe from the three-way stopcock with a stream of N_2, and the mixture was stirred at room temperature. A small portion of the reaction mixture was withdrawn by a syringe during a certain period and analyzed by HPLC to determine the degree of consumption of **1h** and by GPC to determine M_n and M_w/M_n of polymer formed. When initiator was **7h**, M_n was determined by ^1H NMR. As **1h** disappeared, 1 M hydrochloric acid was added to the reaction mixture, which was extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by preparative HPLC (eluent: $CHCl_3$) using a polystyrene gel column.

Method B (Base = Et_3SiH/CsF/18-Crown-6). CsF (0.076 g, 0.50 mmol) was placed in a round-bottomed flask equipped with a three-way stopcock and dried at 250 °C under reduced pressure for 20 min. The flask was cooled to room temperature under an Ar atmosphere. Into the flask was added at room temperature a solution of **1h** (0.192 g, 0.500 mmol), initiator (0.025 mmol), Et_3SiH (0.058 g, 0.50 mmol), and naphthalene (internal standard for HPLC analysis, 64 mg, 0.50 mmol) in dry THF (2.5 mL) and then a solution of 18-crown-6 (0.264 g, 1.00 mmol) in THF (0.5 mL) successively via syringes from the three-way stopcock with a stream of N_2, and the mixture was stirred at room temperature. Analysis and workup of the reaction were carried out in the same manner as method A.

Method C (Base = *t*-BuOK/18-Crown-6). A solution of *t*-BuOK (0.056 g, 0.50 mmol) and 18-crown-6 (0.132 g, 0.500 mmol) in THF (1.5 mL) was placed in a round-bottomed flask equipped with a three-way stopcock under an Ar atmosphere. Into the flask was added at room temperature a solution of **1h** (0.192 g, 0.500 mmol), initiator (0.025 mmol), and naphthalene (internal standard for HPLC analysis, 64 mg, 0.50 mmol) in dry THF (1.5 mL) via a syringe from the three-way stopcock with a stream of N_2, and the mixture was stirred at room temperature. Analysis and workup of the reaction were carried out in the same manner as method A.

Model Reaction for Initiation. A solution of **8** (0.076 g, 0.50 mmol), **19** (0.150 g, 0.500 mmol), and naphthalene (internal standard for GC analysis, 64 mg, 0.50 mmol) in dry CH_2Cl_2 (4 mL) was placed in a round-bottomed flask equipped with a three-way stopcock under an Ar atmosphere. Into the flask was added at room temperature a solution of base (0.50 mmol) in dry CH_2Cl_2 (1 mL) via a syringe from the three-way stopcock with a stream of N_2, and the mixture was stirred at room temperature. A small portion of the reaction mixture was withdrawn by a syringe during a certain period and analyzed by GC to determine the yield of **20**.

Model Reaction of Transesterification at Initiator End. Transesterification of 21 by 8. The reactions were carried out in the same manner as chain-growth polycondensation of **1h** using **21** (0.50 mmol) and **8** (0.50 mmol) as starting materials instead of **1h** and initiator. The yield of **20** was determined by GC analysis of the reaction mixture.

Model Reaction of Transesterification at Polymer Chain Transesterification of 23 by 8. The reactions were carried out in the same manner as chain-growth polycondensation of **1h** using **23** (0.50 mmol) and **8** (0.50 mmol) as starting materials instead of **1h** and initiator. The conversions of **23** and **8** were determined by GC analysis of the reaction mixture.

Supporting Information Available: Experimental procedures and spectral data of the compounds in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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