Control of Chain Ends of Polyesters in Polycondensation of AA and BB Monomers by Use of Solid-Phase Reagent

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ABSTRACT: For selective synthesis of linear polyester having a functional group at one end, polycondensation between 1,4-butanediol (**1a**) and sebacoyl chloride (**2a**) and between 1,12-dodecanediol (**1b**) and isophthaloyl chloride (**2b**) was conducted in the presence of oxime resin or oxime silica gel, followed by cleavage of the formed polyester from the solid-phase support with aniline. Matrix-assisted laser desorption ionization time-of-flight mass spectra and ^{1}H NMR spectra of the cleaved polyester showed that the products contained not only polyester with anilide at one end (**poly 1**), but also polyester with anilides at both ends (**poly 2**). The product ratio of **poly 1** to **poly 2** (**poly 1**/**poly 2**) was dependent on monomers, monomer concentration, feed ratio of monomer to oxime moiety in the support, oxime content in the support, reaction solvent, and the nature of the support. Polyester with a high **poly 1**/**poly 2** ratio of 81/21 and moderate molecular weight ($M_n = 1430$ g/mol) was obtained by polycondensation of **1b** and **2b** in the presence of oxime silica gel in dichloromethane. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2015**, *53*, 1379–1386

KEYWORDS: controlled polymerization; maldi; oxime resin; polycondensation; polyesters; silica gel; solid-phase reaction

INTRODUCTION Polycondensation is a fundamental polymerization method, affording polyamides, polyesters, polyimides, and so on, which are widely used in the manufacture of textiles, engineering plastics, and other products. As polycondensation proceeds in a step-growth polymerization manner, the obtained polymers possess broad molecular weight distribution, and controlling the molecular weight is difficult. However, the polymerization mechanism can be converted from step-growth to chain-growth if the monomer selectively reacts with the polymer end group. We have developed chain-growth condensation polymerization by means of three approaches: (1) activation of polymer end group due to the difference in substituent effects between the monomer and the polymer;[1–5] (2) activation of polymer end group due to successive intramolecular transfer of catalyst to the polymer end;[6] and (3) suppression of self-condensation of monomers by dispersion of solid monomers in the reaction mixture.[7] However, these approaches are limited to polymerization of AB type monomers having nucleophilic and electrophilic sites in the molecule.

Most polycondensation is conducted with AA type monomers having two nucleophilic sites and BB type monomers having two electrophilic sites; these are generally easier to synthesize than AB type monomers. Furthermore, physical properties of the obtained polymers can be easily tuned by appropriate combination of AA and BB monomers. However, there are only a few reports of synthesis of polymers with defined molecular weight and low polydispersity by means of AA + BB polycondensation. Shaffer and Kramer[8] polymerized 1,8-dibromooctane and Na_2S with a phase transfer catalyst (PTC) in water to obtain a polysulfide with high molecular weight and low polydispersity ($M_n = 683{,}000$ g/mol, $M_w/M_n = 1.24$). Hay and coworkers[9] synthesized polyformal with high molecular weight and low polydispersity ($M_n = 250{,}000$ g/mol, $M_w/M_n = 1.3$) by polymerization of the potassium salt of bisphenol A and an excess amount of dibromomethane in *N*-methylpyrrolidone with vigorous stirring for only five minutes. Dai and coworkers[10] successfully synthesized polyamides with defined molecular weight and low polydispersity ($M_n = 3838$–18,860 g/mol, $M_w/M_n = 1.1$–1.4) by means of a novel, unconventional condensation polymerization of diisocyanate and dicarboxylic acid (sequential self-repetitive reaction [SSRR]) in the presence of a small amount of hindered carbodiimide and a catalyst for carbodiimide formation.

These controlled polycondensations of AA and BB monomers have been achieved using combinations of specific

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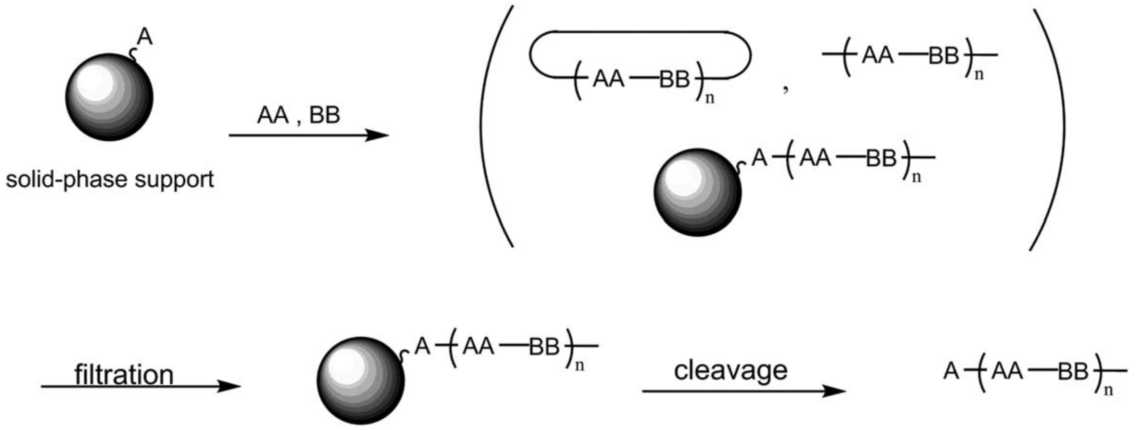


SCHEME 1 Control of chain ends in polycondensation of AA and BB monomers by use of solid-phase reagent.

monomers under unique conditions. We wanted to open up a more broadly applicable controlled polymerization method for polycondensation of conventional AA and BB monomers. Difficulty of controlling molecular weight in polycondensation may stem from cyclization of polymers. Kricheldorf et al. proposed that propagation and cyclization competitively take place during all stages of polycondensation, and finally only cyclic polymers are obtained, except for some rigid monomers.[11] Accordingly, we thought that selective synthesis of linear polymers by controlling the polymer end groups would be a way to control polycondensation. It seemed plausible that a monofunctional reagent added during polycondensation of AA and BB monomers would afford a linear polymer, and the molecular weight of the product could be controlled by adjusting the feed ratio of monofunctional reagent. However, linear oligomers or polymers attached to the monofunctional reagent at one end would not prevent reaction with other oligomers or polymers with a mono-functional end. Cyclic polymers would also be included in the products, if the monofunctional reagent did not have a chance to react with monomer and oligomers. It occurred to us that attachment of the monofunctional reagent to resin or silica gel would suppress the reaction between polymers attached to the monofunctional reagent on the solid-phase support because of the bulkiness of the support. Cyclic polymers and linear polymers not attached to the support might be formed in solution, but these polymers could easily be removed by filtration. The residual support could then be treated with a cleaving reagent to afford a linear polymer with a monofunctionalized end (Scheme 1). The molecular weight would be controlled by the feed ratio of the monomer to this solid-phase support reagent, and the molecular weight distribution could be made narrower by controlling monomer addition to the reaction mixture containing the support reagent.

In this article, we report the first attempt to achieve controlled polycondensation of diol and diacid chloride in the presence of oxime resin or silica gel. The hydroxyl group in the oxime reacts with diacid chloride monomer, and the formed oxime ester moiety is easily cleaved with a weak nucleophile, aniline,[12] after the polycondensation to afford polyester with anilide at one end.

EXPERIMENTAL

General

^{1}H and ^{13}C NMR spectra were obtained on JEOL ECA-500 and ECA-600 spectrometers. The internal standard for ^{1}H NMR spectra in $CDCl_3$ was tetramethylsilane (0.00 ppm), and the internal standard for ^{13}C NMR spectra in $CDCl_3$ was the midpoint of $CDCl_3$ (77.0 ppm). All melting points were measured with a Yanagimoto hot-stage melting point apparatus without correction. Column chromatography was performed on silica gel (Kieselgel 60, 230–400 mesh; Merck) with a specified solvent, and this silica gel was used as the solid-phase support. Commercially available dehydrated diethyl ether (Kanto), dehydrated dichloromethane (Kanto), and dehydrated toluene (Wako) were used as dry solvents. Oxime resin (cross-linking: 1% DVB; bead size: 200–400 mesh; loading: 0.54 mmol/g; ChemPep) was used as received. The M_n and M_w/M_n values of polymers were measured on a Shodex GPC-101 gel permeation chromatography unit (eluent, THF; calibration, polystyrene standards) with two Shodex KF-804L columns, Shodex UV-41, and Shodex RI-71S. Matrix-assisted laser desorption ionization time-of flight (MALDI-TOF) mass spectra were recorded on a Shimadzu/Kratos AXIMA-CFR plus in the reflectron ion mode by use of a laser ($\lambda = 337$ nm). Dithranol (1,8-dihydroxy-9[10H]-anthracenone) was used as the matrix for the MALDI-TOF mass measurements.

General Procedure for Polycondensation of 1a and 2a in the Presence of Solid-Phase Support

All glass apparatus were dried prior to use. Addition of reagents to a reaction flask was performed via a syringe from a three-way stopcock under a stream of nitrogen. Oxime resin (0.5 mmol oxime/g resin, 151.1 mg resin, 0.076 mmol oxime) was placed in the flask, and the atmosphere in the flask was replaced with argon. A solution of dry pyridine (0.25 ml, 3.1 mmol) and 1,4-butanediol (**1a**) (135.3 mg, 1.5 mmol) in dry dichloromethane (6 ml) was added via a syringe, and the mixture was stirred at 0 °C. A solution of sebacoyl chloride (**2a**) (358.7 mg, 1.5 mmol) in dry dichloromethane (3 ml) was added dropwise to the flask via a syringe over 5–10 min, and stirring was continued at room temperature for 3–7 days. Dry ethanol was added via a syringe, and the mixture was stirred for 30–60 min. Dichloromethane solution in the flask was removed with a pipette, and the resin was washed in the flask with six 15 ml portions of dichloromethane with stirring for 10 min for each washing. The combined dichloromethane solution was washed with 1 M hydrochloric acid and water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to afford polyester from the homogeneous solution (246.8 mg, 64.2%). The washed resin was collected and dried under reduced pressure in a vacuum desiccator. Aniline (5 ml) and dichloromethane (5 ml) were added to the resin, and stirring was continued at room temperature for 24 h to cleave polyester from the resin. After filtration of the resin, the filtrate was washed with 1 M hydrochloric acid and water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to afford polyester cleaved from the resin (23.1 mg, 6.0%).

Polycondensation of 1b and 2b in the Presence of Resin Containing a Low Concentration of Oxime Moieties

All glass apparatus were dried prior to use. Addition of reagents to a reaction flask was performed via a syringe from a three-way stopcock under a stream of nitrogen. Acetyl chloride (12 mg, 0.15 mmol) was placed in the flask, and oxime resin (0.54 mmol oxime/g resin, 416 mg resin, 0.225 mmol oxime) and dry dichloromethane (4.0 ml) were added to the flask. Then, dry pyridine (0.1 ml, 1.24 mmol) was added, and the mixture was stirred at room temperature for 24 h. Dichloromethane solution in the flask was removed with a pipette, and the resin was washed in the flask with six 15 ml portions of dichloromethane with stirring for 10 min for each washing. The washed resin was collected and dried under reduced pressure in a vacuum desiccator to afford a pale yellow powder (428 mg). The oxime content in the resin was calculated to be 0.18 mmol/g, assuming that acetyl chloride reacted quantitatively with the oxime moieties in the resin. This oxime resin (0.18 mmol/g in resin, 0.428 mg, 0.077 mmol) was placed in the flask, and the atmosphere in the flask was replaced with argon. A solution of dry pyridine (0.25 ml, 3.1 mmol) and 1,12-dodecanediol (304 mg, 1.5 mmol) in dry dichloromethane (3.5 ml) was added via a syringe, and the mixture was stirred at 0 °C. A solution of isophthaloyl chloride (305 mg, 1.5 mmol) in dry dichloromethane (1.5 ml) was added dropwise to the flask via a syringe, and stirring was continued at room temperature for 7 days. After this, a similar procedure to that described above was carried out to afford polyester from the homogeneous solution (356.3 mg, 71.4%) and polyester cleaved from the resin (32.6 mg, 6.5%).

Synthesis of [(4-Benzoylphenyl)methyl]triphenyl phosphonium Bromide (3)

4-(Bromomethyl)benzophenone (2.766 g, 10.1 mmol), triphenylphosphine (2.628 g, 10.0 mmol), and dry toluene (80 ml) were placed in a round-bottomed flask equipped with a reflux condenser, and the mixture was refluxed for 3.5 h. The mixture was then cooled to room temperature, and the precipitate was collected by filtration, washed with acetone, and dried under reduced pressure in a vacuum desiccator to afford **3** as a white solid (4.062 g, 76%).

^1H NMR (500 MHz, $CDCl_3$): ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.83–7.76$ (m, 9H), 7.72 (d, $J = 8.5$ Hz, 2H), 7.64 (td, $J = 8.2$ and 3.6 Hz, 6H), 7.60–7.55 (m, 3H), 7.46 (t, $J = 7.8$ Hz, 2H), 7.32 (dd, $J = 8.3$ and 2.6 Hz, 2H), 5.72 (d, $J = 14.9$ Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 196.0$, 137.1, 136.8, 135.0, 134.3, 132.6, 132.3, 131.6, 130.1, 130.0, 129.9, 128.2, 30.3; IR (KBr) 3053, 2870, 2769, 2361, 1648, 1603, 1438 cm^{-1}.

Synthesis of 4-Vinylbenzophenone (4)

An aqueous solution of sodium hydroxide (4 N, 25 ml, 100 mmol) was added dropwise at 0 °C to a solution of phosphonium salt **3** (687.5 mg, 1.28 mmol) and 37% formaldehyde (3.6 ml, 48 mmol). After removal of methanol *in vacuo*, the residue was dissolved in dichloromethane, and the solution was washed with water. The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel (AcOEt/hexane = 1/10) to afford **4** as a slightly yellow liquid (151 mg, 57%).

^1H NMR (500 MHz, $CDCl_3$) $\delta = 7.79$ (m, 4H), 7.58 (tt, $J = 7.4$ and 1.3 Hz, 1H), 7.49 (m, 4H), 6.78 (dd, $J = 10.5$ and 17.5 Hz, 1H), 5.89 (d, $J = 17.5$ Hz,1H), 5.40 (d, $J = 10.9$ Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 196.2$, 141.5, 137.7, 136.6, 136.0, 132.3, 130.5, 129.9, 128.2, 126.0, 116.6; IR (neat) 2921, 2359, 2342, 1655, 1604 cm^{-1}.

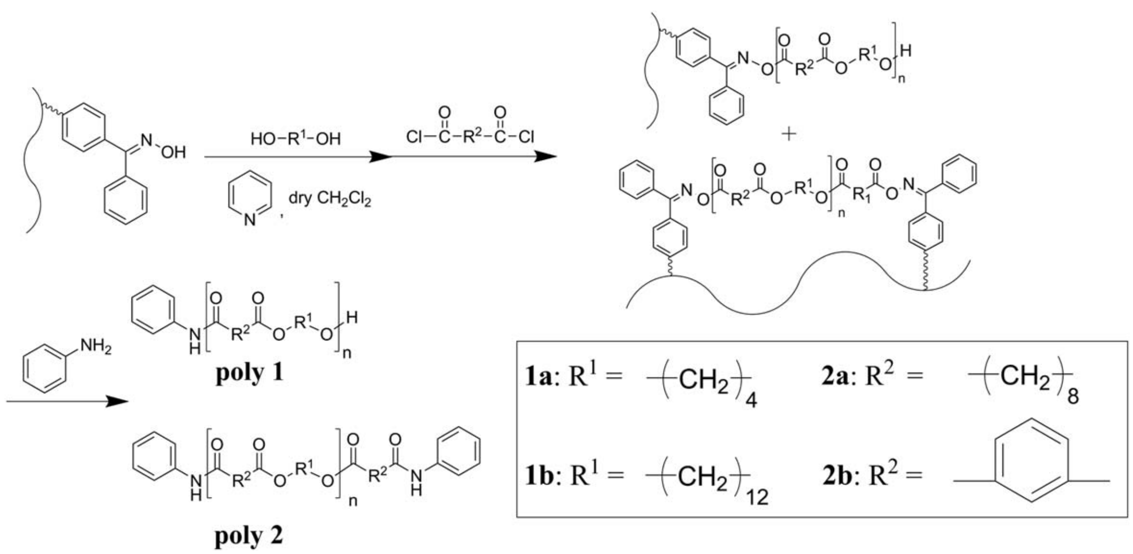
Synthesis of 5

A mixture of **4** (1.092 g, 5.24 mmol), (3-mercaptopropyl)trimethoxysilane (1.027 g, 5.23 mmol), and 2,2′-azobis(isobutyronitrile) (9.8 mg, 0.060 mmol) in dry toluene (10 ml) was charged in a glass tube. The tube was degassed by means of five freeze–pump–thaw cycles, filled with argon, sealed, and heated at 70 °C for 26 h. The reaction mixture was concentrated *in vacuo* to give **5** as a slightly yellow viscose liquid (2.232 g, 105%).

^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.81–7.77$ (m, 4H), 7.58 (t, $J = 7.0$ Hz, 1H), 7.48 (dd, $J = 7.5$ and 1.5 Hz, 2H), 7.33 (dd, $J = 6.3$ and 1.7 Hz, 2H), 3.58 (s, 9H), 2.97 (t, $J = 7.7$ Hz, 2H), 2.81 (t, $J = 7.2$ Hz, 2H), 2.57 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 191.6$, 142.5, 138.4, 133.1, 130.3, 130.2, 128.4, 125.3, 50.5, 36.2, 33.5, 32.9, 25.1, 21.6; IR (neat) 2940, 2361, 1704, 1657, 1605, 1278 cm^{-1}.

Synthesis of 6 (Immobilization of 5 onto SiO_2)

A suspension of silica gel (1.304 g), dried under reduced pressure in the presence of P_2O_5 in a desiccator overnight, and **5** (407 mg, 1.0 mmol) in dry toluene (12 ml) was heated under reflux for 24 h. The resulting solid was collected by filtration and dried under reduced pressure in a vacuum desiccator to afford **6** as a white solid (1.552 g).



SCHEME 2 Polycondensation of diol and diacid chloride in the presence of oxime resin or silica gel.

Synthesis of Oxime Silica Gel 7

A suspension of **6** (507 mg, 0.319 mmol), dry pyridine (0.45 ml, 5.59 mmol), and hydroxylamine hydrochloride (440 mg, 6.3 mmol) in dry methanol (10 ml) was heated under reflux for 3 days. The resulting solid was collected by filtration, washed successively with methanol, 50% aqueous methanol, acetone, and dichloromethane, and dried under reduced pressure to give **7** as a white solid (476 mg).

RESULTS AND DISCUSSION

Polymerization of 1,4-Butanediol 1a and Sebacoyl Chloride 2a

Polycondensation of 1,4-butanediol (**1a**) and sebacoyl chloride (**2a**) was first performed in dichloromethane in the presence of commercially available oxime resin ($[\text{monomer}]_0/[\text{oxime moiety}]_0 = 20$) and pyridine at room temperature, according to the reported method for homogeneous solution polymerization of **1a** and **2a**.[11] The monomer addition method was modified as follows: a solution of **2a** in dichloromethane was added dropwise to the reaction mixture of **1a**, pyridine, and the resin in dichloromethane. After stirring, the polymerization mixture was filtered, and the residual oxime resin was thoroughly washed with dichloromethane. The resin was placed in an excess amount of aniline and dichloromethane, and stirred for 24 h to cleave polyester from the resin. The solution was washed with hydrochloric acid to remove excess aniline and concentrated to afford polyester in 6.0% yield (Scheme 2; Table 1, Entry 1). The molecular weight was unexpectedly low

TABLE 1 Polymerization of **1a** and **2a** in the Presence of Oxime Resin

Entry	Excess Amount of Acid Chloride (mol %)	$[\mathbf{1a}]_0$ (mol/L)	$[\mathbf{1a}]_0$ / $[\text{oxime}]_0$	Reaction Time (days)	Yield (%)	M_n[a] (g/mol) (GPC)	M_n[b] (g/mol) (NMR)	M_w/M_n[a]	**poly 1** : **poly 2**[b] (mol %)
1	0	0.33	20	7	6.0	813	572	1.73	32:68
2	2.3	0.33	20	7	6.2	1,210	1,050	1.71	39:61
3	4.4	0.33	20	9	6.5	1,320	1,020	1.97	18:82
4	7.7	0.33	20	7	7.1	1,150	608	1.50	31:69
5	0	1.0	20	7	4.9	1,410	1,420	1.94	39:61
6	0	1.0	10	7	9.4	1,200	1,360	1.76	52:48
7	0	1.0	6.7	7	17.3	1,070	1,460	2.07	64:36
8[c)]	0	1.0	20	0.21	2.3	1,330	1,560	2.18	84:16

Polymerization of **1a** and **2a** was performed in the presence of 1.03 equiv of pyridine and oxime resin in dichloromethane at rt.

[a] Estimated by GPC based on polystyrene standards (eluent: THF).

[b] Estimated from the ^{1}H NMR spectrum.

[c] Oxime resin was added to the polymerization mixture after it had been stirred for 10 min.

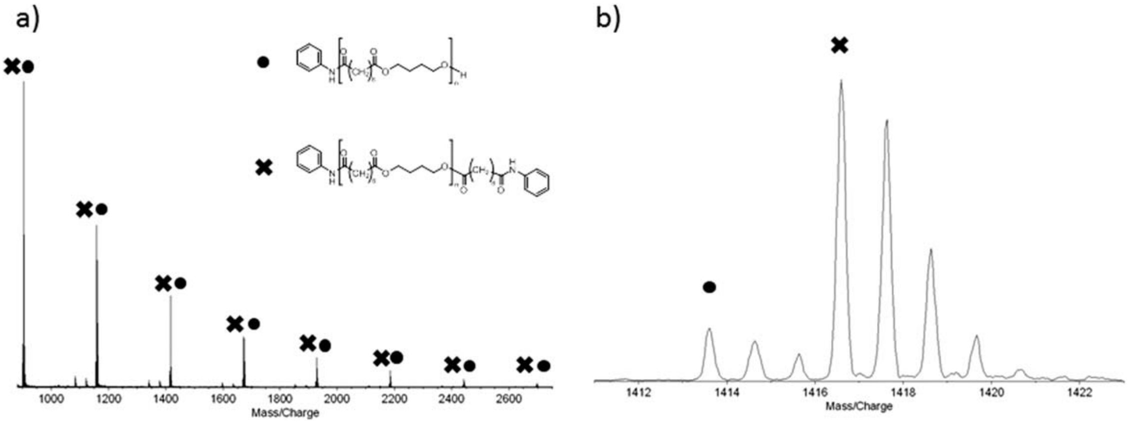


FIGURE 1 MALDI-TOF mass spectra of products cleaved from oxime resin (Table 1, Entry 1): (a) mass/charge range is between 900 and 2800 g/mol, (b) enlargement of a peak around the mass/charge ratio of 1416 g/mol.

($M_n = 813$ g/mol). Polyester formed in solution, not connected to the resin, was obtained in 64% yield, and its M_n was 2140 g/mol. The low yield of polyester on the resin might be a consequence of the low nucleophilicity of the hydroxyl group on the oxime resin due to the electron-withdrawing imino group attached to the hydroxyl group and the steric hindrance of the resin. These results were disappointing, as we had anticipated that the molecular weight of the polyester on the resin would be as high as that of the polyester obtained in solution, because the polymer end functional groups of the elongated polyester chains on the resin could react with monomers and oligomers in a similar manner to that in the case of the polymerization in solution.

To establish why the polyester cleaved from the resin had low molecular weight, we analyzed the polymer end groups by means of MALDI-TOF mass spectrometry. The spectrum seemed to show only one series of peaks [Fig. 1(a)], but when the spectrum was enlarged, it turned out that two series of peaks were present: the minor peaks are due to the desired polymers having an anilide at one end and a hydroxyl group at the other (**poly 1**), and the major peaks are due to polymers with anilides at both ends (**poly 2**) [Fig. 1(b)]. The ratio of **poly 1** to **poly 2** was estimated to be 32/68 from the ^{1}H NMR spectra. As mentioned in Introduction section, we had anticipated that the reaction between the polymer end groups of polymers on the resin would be suppressed because of the bulkiness of the resin. However, **poly 2**, in which the oxime moieties in the resin had reacted with both polymer ends, was formed. We speculated that the oxime moieties in resin beads would have reacted intramolecularly with the acid chloride moiety of polyester to afford **poly 2**. This intramolecular reaction in a resin bead might account for the low molecular weight of the polymer cleaved from the resin.

Since Kricheldorf et al.[11] reported that 1% excess of diacid chloride in polycondensation with diol resulted in the highest molecular weight, we conducted polycondensation using excess **2a** (Entries 2–4). The polymer yield was slightly increased with increasing amount of **2a**, and the molecular weight reached the highest value when a 4.4% excess of **2a** was used ($M_n = 1320$ g/mol, Entry 3). However, the selectivity for **poly 1** decreased with increasing amount of **2a**. When the monomer concentration was increased from 0.33 to 1.0 mol/L, the M_n value reached 1410 g/mol, but **poly 2** became the major product (Entry 5). To decrease formation of **poly 2**, polycondensation was performed with increasing amounts of oxime resin, although the molecular weight would be decreased under these conditions (Entries 5–7). As expected, the ratio of **poly 2** was decreased from 61% to 36%, and the polymer yield was increased to 17.3%. The molecular weight was not greatly decreased, implying that the oxime moieties in the resin are not as reactive as monofunctional reagent in homogeneous solution.

Furthermore, oxime resin was added to the polymerization mixture after stirring for 10 min, because we expected that the ratio of **poly 1** would be increased if we reacted polyester that had already been elongated to some degree with the oxime resin. Indeed, the ratio of **poly 1** was increased to 84% (Supporting Information Fig. S1), and the molecular weight was increased to 1330 g/mol. However, the yield was decreased, implying that reaction of oxime moiety in the resin with the terminal acyl chloride moiety of polyester might be slow because of steric hindrance between resin and polyester (Entry 8).

Polymerization of 1,12-Dodecanediol 1b and Isophthaloyl Chloride 2b in the Presence of Oxime Resin

As we expected that a rigid polymer backbone would decrease the probability of reaction of the end groups of polymers attached on the resin to afford **poly 2**, the diacid chloride was changed from sebacoyl chloride (**2a**) to isophthaloyl chloride (**2b**). We wanted to use 1,4-butanediol (**1a**), but polyester derived from **1a** and **2b** was not soluble in dichloromethane. Accordingly, the polycondensation of 1,12-dodecanediol (**1b**) and **2b** was investigated under the conditions of Entry 5, Table 1. Polyester was not precipitated

TABLE 2 Polymerization of **1b** and **2b** in the Presence of Oxime Resin

Entry	Oxime Content in Resin (mmol/g)	Solvent	Reaction Time (days)	Yield (%)	M_n[a] (g/mol) (GPC)	M_n[b] (g/mol) (NMR)	M_w/M_n[a]	**poly 1** : **poly 2**[b] (mol %)
1	0.54	CH_2Cl_2	7	8.6	1,820	1,880	2.48	21:79
2[c]	0.54	CH_2Cl_2	7	8.4	1,660	1,280	2.50	0:100
3	0.18	CH_2Cl_2	7	6.5	888	908	1.41	66:34
4	0.14	CH_2Cl_2	10	3.5	654	1,240	1.28	79:21
5	0.11	CH_2Cl_2	9	8.5	561	1,100	1.42	82:18
6	0.54	CH_2Cl_2/Et_2O (2/1 (v/v))	7	8.8	2,390	1,720	1.63	39:61
7	0.54	Et_2O	9	9.9	3,000	2,970	2.27	38:62

Polymerization of **1b** and **2b** was performed in the presence of 1.03 equiv of pyridine and oxime resin $[\mathbf{1b}]_0/[\text{oxime}]_0 = 20$ in dry solvent ($[\mathbf{1b}]_0 = 1.0$ mol/L) at rt.

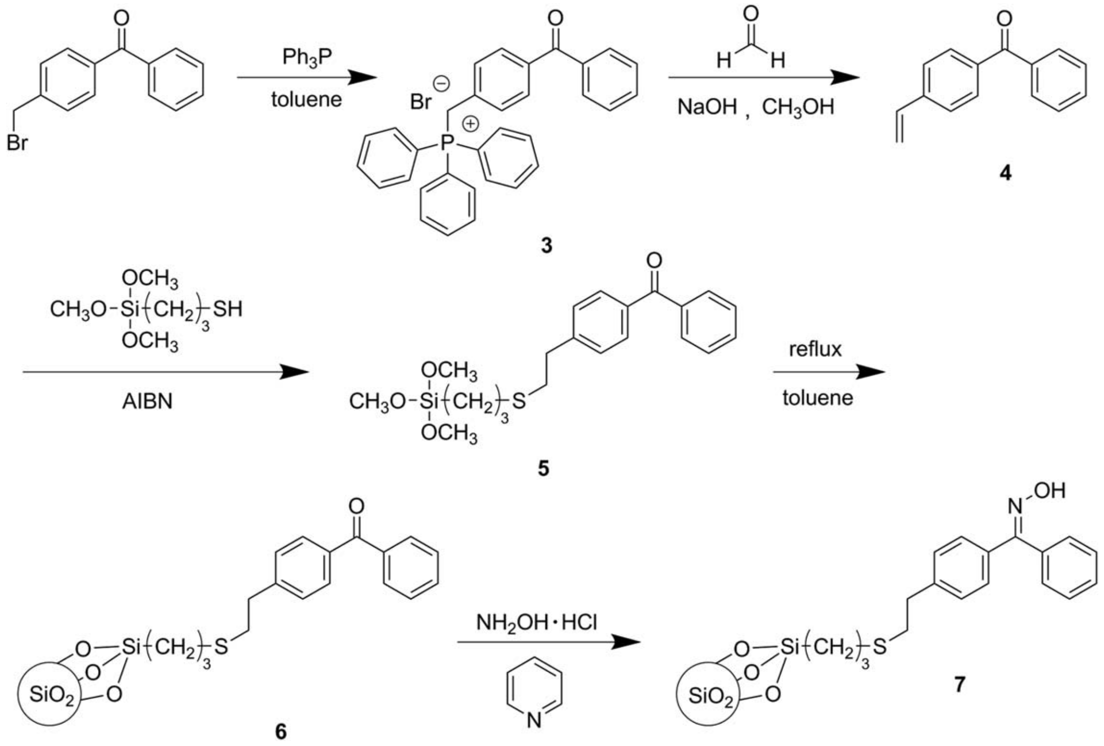
[a] Estimated by GPC based on polystyrene standards (eluent: THF).

[b] Estimated from the ^1H NMR spectrum.

[c] Reverse addition method: diol **1b** was added to the reaction mixture of acid chloride **2b**, pyridine, and resin.

during the polymerization,[11] and the molecular weight was higher than that of the polyester from **1a** and **2a**. Contrary to our expectation, however, the selectivity for **poly 1** was decreased to 21% (Table 2, Entry 1). When diol **1b** was added to the reaction mixture of **2b**, pyridine, and resin, which is the reverse of the addition method in Table 1, only **poly 2** was obtained (Entry 2).

If the amount of oxime moiety in the resin is decreased (i.e., if the concentration of oxime moieties in the resin is low), the polymer chains attached to resin would be less able to react with each other, resulting in suppression of **poly 2** formation. On the basis of this idea, oxime resin was reacted with a certain amount of acetyl chloride, and then used for polycondensation. The selectivity for **poly 1** increased up to 82% with decreasing oxime content in the resin, although the molecular weight was decreased (Entries 3–5). Furthermore, polymerization in diethyl ether or a mixed solvent of diethyl ether and dichloromethane, which does not swell the resin as much as dichloromethane does, improved the



SCHEME 3 Synthesis of oxime silica gel **7**.

TABLE 3 Polymerization of **1b** and **2b** in the Presence of Oxime Silica Gel

Entry	Oxime Content in SiO_2 (mmol/g)	Reaction Time (days)	Yield (%)	M_n[a] (g/mol) (GPC)	M_n[b] (g/mol) (NMR)	M_w/M_n[a]	**poly 1** : **poly 2**[b] (mol %)
1	0.63	7	1.3	1,320	1,220	1.66	73:27
2	0.14	7	1.6	1,430	1,520	1.58	81:19

Polymerization of **1b** and **2b** was performed in the presence of 1.02 equiv of pyridine and oxime silica gel $[\mathbf{1b}]_0/[\text{oxime}]_0 = 10$ in dichloromethane ($[\mathbf{1b}]_0 = 1.0$ mol/L) at rt for 7 days.

[a] Estimated by GPC based on polystyrene standards (eluent: THF).

[b] Estimated from the ^{1}H NMR spectrum.

selectivity for **poly 1** up to 39% (Entry 6) and increased the M_n of polyester up to 3000 g/mol (Entry 7), compared to the reaction in dichloromethane (Entry 1). These results imply that low content of oxime moiety and low mobility of the solid-phase support would be effective for increasing the selectivity for **poly 1** and the polymer molecular weight. We next investigated polycondensation of **1b** and **2b** using oxime silica gel.

Polymerization of 1,12-Dodecanediol 1b and Isophthaloyl Chloride 2b in the Presence of Oxime Silica Gel

Oxime siilca gel **7**[12] was synthesized as described (Scheme 3). Commercially available 4-bromomethylbenzophenone was converted to phosphonium salt **3**,[13] which was subjected to Wittig reaction with formaldehyde to give 4-vinylbenzophenone (**4**). Radical addition of 3-(trimethoxysilyl)propanethiol to **4** was conducted in the presence of 2,2′-azobis(isobutyronitrile) (AIBN) at 70 °C to afford a silane coupling agent **5**,[14] which was reacted with silica gel in toluene under reflux for 24 h to give benzophenone silica gel **6**.[15] Finally, the carbonyl group of **6** was converted to oxime with hydroxylamine to obtain oxime silica gel **7**. Two kinds of **7** with different oxime content were prepared.

Polycondensation of equimolar **1b** and **2b** was performed in the presence of the obtained oxime silica gel in dichloromethane at rt (Table 3). As we had expected, the selectivity for **poly 1** was high even with high-oxime-content silica gel (Entry 1) and was increased to 81% with decreasing oxime content (Entry 2). The molecular weight was the highest in the case of the polymerization affording **poly 1** as a major product (Entry 2 vs. Table 2, Entries 4 and 5). However, the polymer yield was less than 2%. Oxime moieties with no mobility on the hydrophilic silica surface, in contrast to polymer resin in swelling solvent, might have less chance to react with acid chloride **2b**, resulting in the low yield of polyester on silica gel.

CONCLUSIONS

We investigated polycondensation of diol and diacid chloride in the presence of oxime resin or silica gel, followed by cleavage of the formed polyester from the solid-phase support with aniline, to synthesize mono-end functionalized linear polyester, as an approach to controlling the polymer end groups and molecular weight in AA + BB polycondensation. We expected that a bulky solid-phase support would prevent the polyester formed on the support from reacting with another polyester on the support, so that mono-functionalized polyester (**poly 1**) would be formed after cleavage from the support. However, double-end functionalized polyester (**poly 2**) was also formed. On the basis of the results that the selectivity for **poly 1** was increased when the oxime content in the support was decreased and when silica gel support with no mobility was used, **poly 2** was presumably formed intramolecularly on the support. Low yield of polyester cleaved from the support might be accounted for by the low nucleophilicity of the hydroxyl group in the oxime moiety, compared to that of the hydroxyl group in the diol monomer. We are now investigating polycondensation of AA and BB monomers for the synthesis of mono-end functionalized polyester in the presence of a silica gel support containing a more nucleophilic hydroxyl group.

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