Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 4589–4598 **4589**
DOI: 10.1021/ma100494a

Polycondensation of Bis(diazocarbonyl) Compounds with Aromatic Diols and Cyclic Ethers: Synthesis of New Type of Polyetherketones

Eiji Ihara,* Kotaro Saiki, Yuko Goto, Tomomichi Itoh, and Kenzo Inoue*

Department of Material Science and Biotechnology, Graduate School of Science and Engineering, Venture Business Laboratory, Ehime University, 3 Bunkyo-cho, Matsuyama 790-8577, Japan

Received March 4, 2010; Revised Manuscript Received April 14, 2010

ABSTRACT: A series of new polyetherketones was prepared by Rh-catalyzed polycondensation of bis(diazocarbonyl) compounds **1a**−**c** with aromatic diols **2A**−**C** in cyclic ethers (THF, THP, and 1,4-dioxane). In addition to the expected insertion of diazo-bearing carbon of **1a**−**c** into O−H of **2A**−**C** releasing N_2, unexpected incorporation of the ring-opened cyclic ethers between the diazo-bearing carbon of **1a**−**c** and phenolic oxygen of **2A**−**C** occurred, providing the polymer main chains with additional oxyalkylene units. The extent of cyclic ether incorporation relative to the expected insertion depended on the kind of the cyclic ether: THF, 95−98%; THP, 26−32%; 1,4-dioxane, 11−21%. Polyetherketones with a variety of main chain structures can be prepared by the new polycondensation.

Introduction

Diazocarbonyl compounds have been demonstrated to be versatile reagents that can be used in a variety of reactions,[1,2] mostly represented by transition-metal-catalyzed cyclopropanation of olefins. In addition, not only for organic synthesis, utility of diazocarbonyl compounds as a monomer for polymer synthesis has also been demonstrated in the metal-mediated polymerization to afford C−C main chain polymers bearing substituents on all of the main chain carbon atoms.[3] In addition to linear polymers, we have succeeded in preparing cross-linked polymers by copolymerization using bifunctional diazocarbonyl compounds [bis(diazocarbonyl) compounds] as a comonomer.[4]

To our knowledge, polycondensation using bis(diazocarbonyl) compounds as a monomer has not been reported so far, although the formation of a variety of main chain structures will be expected by using the reactions of a diazocarbonyl group with other functional groups. For example, Rh-catalyzed O−H insertion of diazocarbonyl compounds with alcohol is one of the common reactions,[1,2] which could be applied for polycondensation of bis(diazocarbonyl) compounds with diols. Interesting to note is that the resulting polymer main chain consists of carbonyl and ether linkages (Scheme 1), and variation in the combination of R^3 and R^4 groups in the monomers will enable us to control the physical properties of the products. Herein, we will describe the results of Rh-catalyzed polycondensation of bis(diazocarbonyl) compounds with aromatic diols, which indeed afforded polymers with carbonyl and ether linkages in the main chain (polyetherketones), whereas unexpected incorporation of ring-opened cyclic ether (THF, THP, and 1,4-dioxane) units accompanied to afford additional oxyalkylene [−O−$(CH_2)_n$−] units in the polymer main chain.

Results and Discussion

As a bis(diazocarbonyl) compound for the polycondensation, we first employed bis(aryldiazoketone) **1a**, in which two diazoacetophenone moieties are connected with a $SiMe_2CH_2CH_2SiMe_2$ linker to impart enough solubility to resulting polymers. By employing rhodium acetate dimer, $Rh_2(OAc)_4$, as a most commonly used catalyst for the O−H insertion,[1,2] the reaction of **1a** with bisphenol A (**2A**) was conducted in various solvents, such as CH_2Cl_2, 1,2-dichloroethane, toluene, and cyclic ethers. However, when the reaction was conducted in the chlorinated solvents and toluene at 0−80 °C, the resulting polymeric products (M_n = 1500−4300) obtained in 20−50% yields exhibited very complicated appearance in their ^{1}H NMR spectra, which did not allow us to identify the polymer structures. The results suggest that in these solvents, in addition to the expected insertion of diazo-bearing carbon into O−H, some unexpected reactions occur between the functional groups, even though CH_2Cl_2 is the most commonly used solvent for the Rh-catalyzed reaction of diazocarbonyl compounds.[1] The unexpected reactions could be N_2-releasing C=C formation between two diazocarbonyl groups and oligomerization of the diazocarbonyl group, as we have reported for monofunctional diazoketones in previous publications.[3d,4] Polymers with well-defined structures were obtained in the cyclic ethers (THF, THP, and 1,4-dioxane), as will be described in detail in the following.

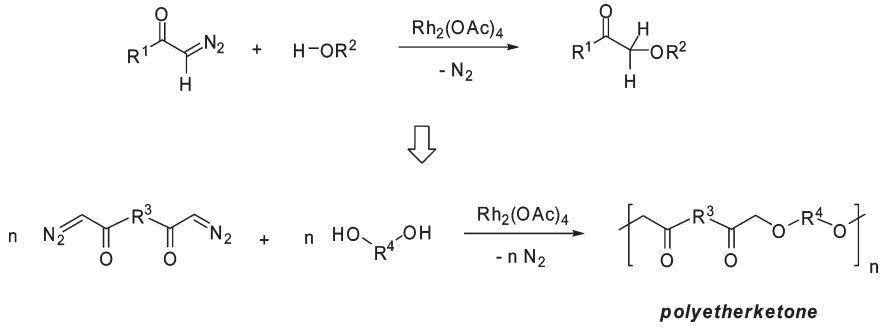
For example, when a 1:1 mixture of **1a** and **2A** was reacted in the presence of a catalytic amount of $Rh_2(OAc)_4$ in a ratio of [**1a**]/[**2A**]/[$Rh_2(OAc)_4$] 50:50:1, a polymeric product **3aA**, whose GPC-estimated M_n (PMMA standards) was 11 900, was obtained after purification with preparative recycling GPC (Scheme 2, run 1 in Table 1). In the ^{1}H NMR spectrum shown in Figure 1, in addition to signals assignable to H's derived from **1a** and **2A**, we can observe unexpected signals at 3.95, 3.62, and 1.85 ppm in a 1:1:2 ratio, which could be ascribed to the ring-opened framework of THF, as illustrated in Scheme 2.

To confirm the incorporation of the ring-opened THF framework, a model reaction for the polymerization was conducted between diazoacetophenone (monofunctional counterpart to **1a**) and 4-*t*-butylphenol (Scheme 3). Because a Rh-catalyzed equimolar reaction of the compounds in THF afforded a polymeric product with an unidentified structure as a main product, a 10-fold excess of the phenol was employed in the model reaction. As a result, along with a small amount of an undesirable polymeric product, we obtained a product of normal (expected) O−H

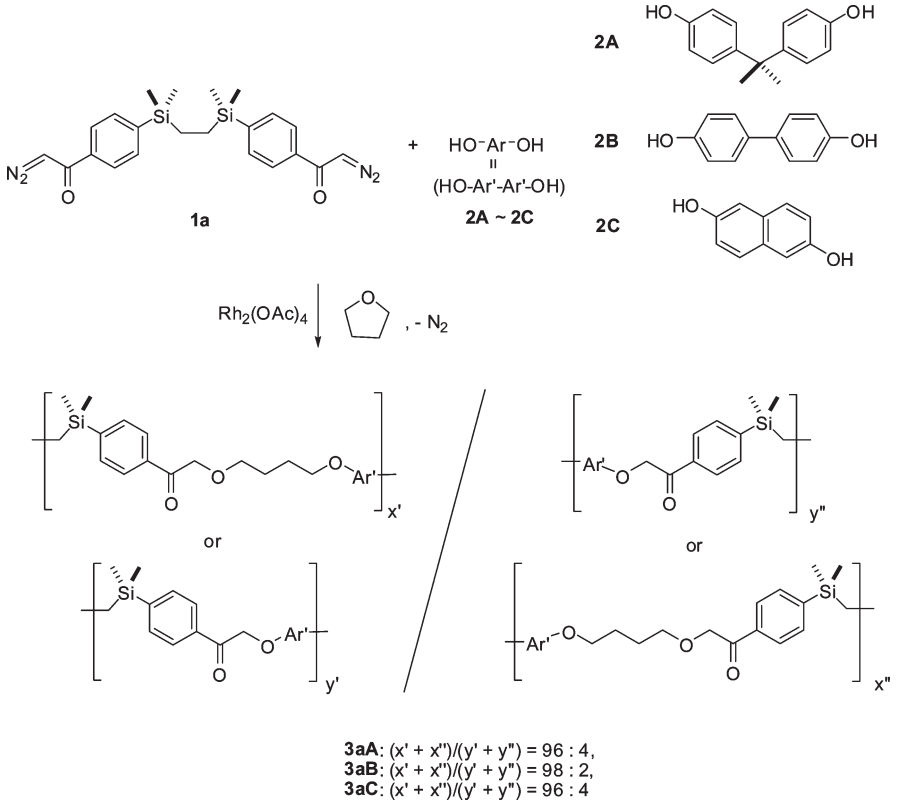
*Corresponding author. Tel/Fax: +81-89-927-8547. E-mail: ihara@eng.ehime-u.ac.jp.

Published on Web 04/23/2010

Scheme 1. O−H Insertion of Diazocarbonyl Compound with Alcohol and its Application to Polycondensation Affording Polyetherketone



Scheme 2. Polycondensation of 1a with Aromatic Diols in THF



3aA: (x' + x")/(y' + y") = 96 : 4,
3aB: (x' + x")/(y' + y") = 98 : 2,
3aC: (x' + x")/(y' + y") = 96 : 4

Table 1. Polymerization of 1a with 2A∼2C and Cyclic Ethers (THF, THP, and 1,4-Dioxane) Catalyzed by $Rh_2(OAc)_4$[a]

run	diol	ether	temp	yield (%)	product	M_n[b]	M_w/M_n[b]	$(x' + x'')/(y' + y'')$[c]
1	**2A**	THF	RT	40.8	**3aA**	11 900	2.07	96:4
2		THF	0 °C (41 h)	35.1	**3aA**	10 000	1.77	95:5
3		THF	50 °C	44.9	**3aA**	5200	1.31	96:4
4		THP	RT	27.3	**6aA**	13 400	1.64	29:71
5		1,4-dioxane	RT	24.0	**8aA**	13 100	1.44	18:82
6	**2B**	THF	RT	24.1	**3aB**	16 500	1.39	98:2
7		THP	RT	29.1	**6aB**	11 900	1.38	29:71
8	**2C**	THF	RT	28.6	**3aC**	10 400	1.86	96:4
9		THP	RT	36.1	**6aC**	14 400	1.85	27:73
10		1,4-dioxane	RT	24.7	**8aC**	11 400	1.81	11:89

[a] Polymerization period = 17 h; solvent (ether) = 5 mL, **1a** = ca. 0.1 g, [**1a**]/[diol]/[$Rh_2(OAc)_4$] = 50:50:1. [b] M_n and M_w/M_n were obtained by GPC calibration using standard PMMAs and dibutyl sebacate in THF solution. [c] $x' + x''$ = ether-incorporated unit; $y' + y''$ = normal insertion unit.

insertion **4** and a product incorporating ring-opened THF **5** in 1.3 and 86.8% isolated yields, respectively, whose ^{1}H NMR spectra are shown in Figure 2. Compared with the spectrum of **4** (Figure 2a), there appear three additional signals at 3.97, 3.64, and 1.87 ppm with an intensity ratio of 1:1:2 in the spectrum of **5** (Figure 2b). Considering the relative intensity of the additional signals to the other signals and ^{13}C and 2D (H−H and H−C) NMR spectra, the structure of **5** can be clearly identified as that having a ring-opened THF between the diazoketone- and phenol-derived moieties.

Although this type of reaction giving **5** is unprecedented at least to our knowledge, the mechanism for the formation of **5** can

be estimated from the reported mechanism for the formation of **4**.[1] The reaction would be initiated by a nucleophilic attack of a THF-oxygen to the carbene-carbon of Rh−carbene complex, which should be formed by the reaction of the Rh complex with a diazoketone. Then, the resulting oxonium ylide complex would be attacked by a phenolic-oxygen in one of two possible pathways. In path A, the attack of the phenolic-oxygen occurs at one of two carbons adjacent to the oxygen in the THF-derived five-membered ring, resulting in the ring-opening of THF to give a THF-incorporated product such as **5** after elimination of the Rh-complex. In path B, the phenolic-oxygen attacks at a Rh-bearing carbon, followed by eliminations of THF and the Rh complex to give a normal insertion product such as **4**.

Comparison of the ^{1}H NMR spectrum of **5** (Figure 2b) with that of **3aA** demonstrates that the polymer predominantly has the ring-opened THF framework in the main chain. The small signal at 5.18 ppm in the spectrum of **3aA** can be assigned to the CH_2 between carbonyl carbon and ether oxygen resulting from the normal insertion as in the formation of **4** (the related signal of **4** appears at 5.25 ppm in Figure 2a), indicating the presence of the framework in a very small extent. The selectivity for the THF-incorporation in the polymerization is in good accordance with that in the model reaction ([**4**]/[**5**] 2:98): the relative signal intensity between those at 5.18 and 4.67 ppm (the signal for −(C═O)−CH_2−O− of THF-incorporated framework) shows the ratio is 4:96 ([without THF]/[with THF]). The yield of **3aA** calculated based on the main chain structure was relatively low (40.8%), basically because a significant amount of a low-molecular-weight product was removed by preparative recycling GPC, which also brings about rather narrow molecular weight distributions for polycondensation products. In the ^{1}H NMR spectrum of the low-molecular-weight product removed by the purification, we observed additional signals that cannot be identified along with the predominant signals of **3aA**. We assume that these low-molecular-weight products derived from some side reactions such as a coupling reaction forming a −C(═O)−CH═CH−C(C═O)− linkage, polymerization as in Pd-mediated ones,[3d,4] and so on, as we also suggested as the aforementioned reason for the formation of unidentifiable products in chlorinated solvents and toluene. The low yield due to the contamination of the low M_n unidentifiable product is a common trend observed in all polymerizations in Tables 1 and 2. Polymerization at 0 °C did not affect the polymerization result (run 2 in Table 1), and raising the temperature to 50 °C afforded a lower M_n polymer (run 3). In addition, longer reaction periods at room temperature did not improve the yield or M_n of the products.

The THF-incorporating polycondensation of **1a** also proceeded with 4,4′-biphenol **2B** and 2,6-naphthalenediol **2C**, affording polymers **3aB** and **3aC** (Scheme 2, runs 6 and 8 in Table 1), respectively. (See the Supporting Information for ^{1}H NMR spectra for the polymers.) In a similar manner as with **1A**, incorporation of the ring-opened THF predominates in those polymerizations as the ratios listed in Table 1 indicate, and the isolated yields of the polymers were rather low after the removal of the low-molecular-weight products by using preparative recycling GPC.

When THP was used as a solvent instead of THF for the polycondensation of **1a** with bisphenol A (**2A**) (run 4 in Table 1), the appearance in ^{1}H NMR of the obtained polymer **6aA** with M_n = 13 400 indicated that the ether linkage in the product was totally different from the aforementioned pattern for **3aA** with THF (Scheme 5, Figure 3). Therefore, in the ^{1}H NMR spectrum of **6aA** shown in Figure 3, five signals centered at 3.91, 3.58, 1.78, 1.70, and 1.57 ppm (the last one overlaps with signals from Me derived from **2A** and H_2O) with nearly equal intensities appear, which can be ascribed to the ring-opened structure of THP. To confirm the structural assignment, a model reaction of diazoacetophenone with

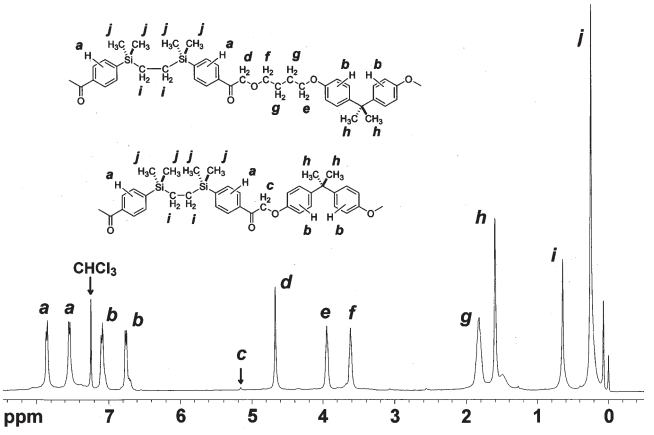


Figure 1. ^{1}H NMR spectrum for **3aA** (run 1 in Table 1).

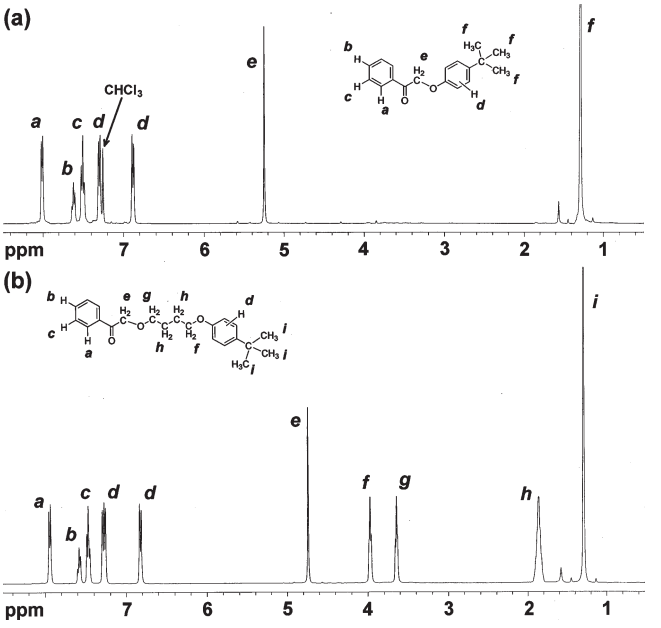


Figure 2. ^{1}H NMR spectra of (a) **4** and (b) **5**.

Scheme 3. Model Reaction of Diazoketone with Phenol in THF

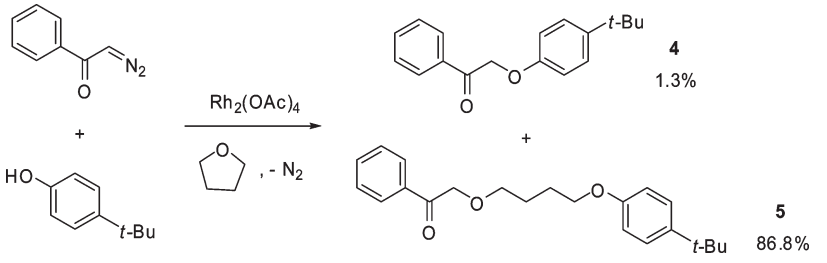
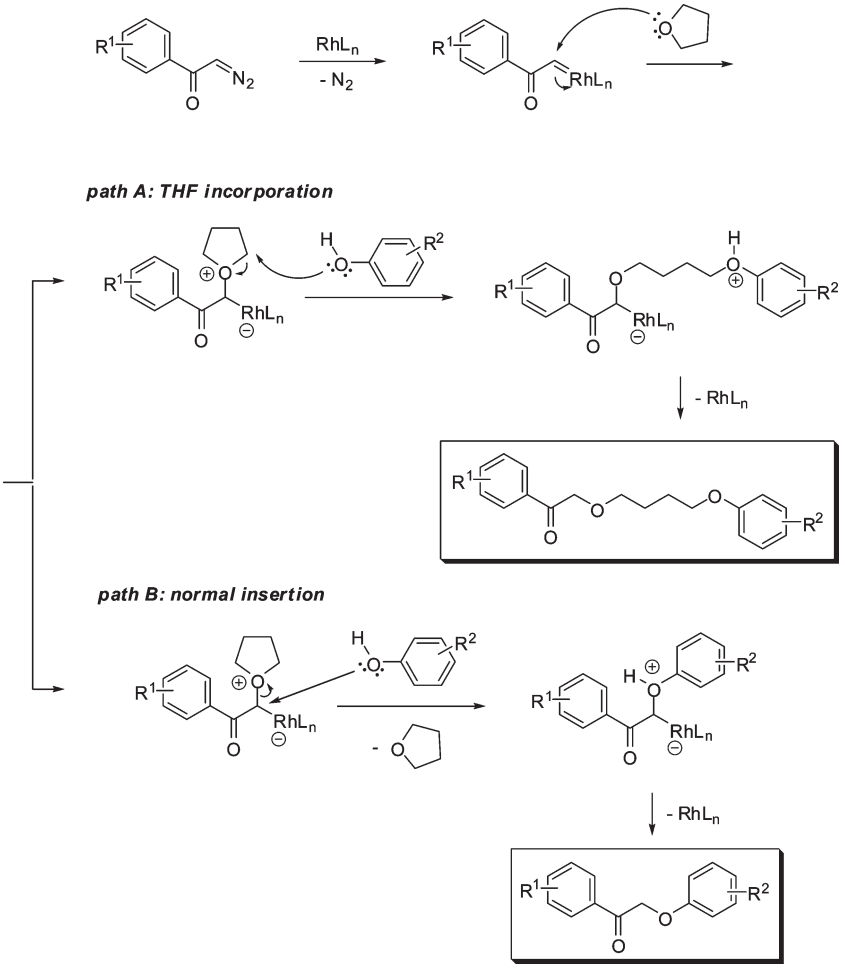


Table 2. Polymerization of 1b and 1c with 2A∼2C and Cyclic Ethers (THF, THP, and 1,4-Dioxane) Catalyzed by $Rh_2(OAc)_4$[a]

run	**1b** or **1c**	diol	ether[b]	product	yield (%)	M_n[b]	M_w/M_n[b]	$(x' + x'')/(y' + y'')$[c]
1	**1b**	**2A**	THF	**3bA**	30.8	10 500	1.23	97:3
2			THP	**6bA**	40.4	12 000	1.63	27:73
3			1,4-dioxane	**8bA**	40.1	15 400	1.78	11:89
4		**2B**	THF	**3bB**	37.7	14 700	1.43	98:2
5			THP	**6bB**	35.7	16 700	1.82	27:73
6		**2C**	THF	**3bC**	28.2	27 000	2.05	96:4
7			THP	**6bC**	25.3	17 500	1.92	26:74
8	**1c**	**2A**	THF	**3cA**	27.6	10 400	1.36	97:3
9			THP	**6cA**	26.2	7600	1.21	32:68
10			1,4-dioxane	**8cA**	25.5	9000	1.25	21:79
11		**2B**	THF	**3cB**	38.7	13 400	1.41	98:2
12			THP	**6cB**	27.8	10 700	1.54	32:68
13		**2C**	THF	**3cC**	35.7	17 200	1.69	98:2
14			THP	**6cC**	36.5	12 200	2.44	37:63

[a] Polymerization period = 17 h; solvent (ether) = 5 mL, **1b** or **1c** = ca. 0.1 g, [**1b,c**]/[diol]/[$Rh_2(OAc)_4$] = 50:50:1. [b] M_n and M_w/M_n were obtained by GPC calibration using standard PMMAs and dibutyl sebacate in THF solution. [c] $x' + x''$ = ether-incorporated unit; $y' + y''$ = normal insertion unit.

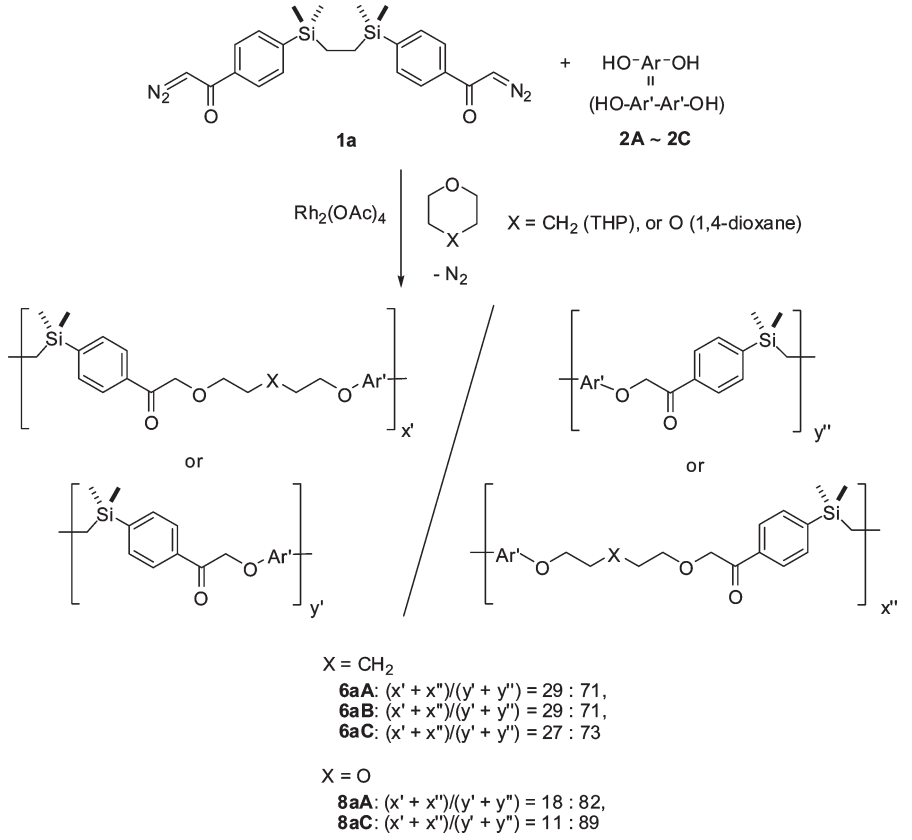
Scheme 4. Proposed Mechanism for Propagation in the Presence of THF



4-*t*-butylphenol was conducted in THP under a similar condition ([diazoketone]/[phenol] 1:10) as that in THF described above. As a result, a mixture of **4** and a THP-incorporated product **7** was obtained in 51.8 and 26.8% yields, respectively, and a ^{1}H NMR spectrum for **7** is shown in Figure 4, whose comparison with Figure 3 allowed us to confirm the presence of the ring-opened THP in the polymer main chain of **6aA**. Corresponding to the ratio of the yields of **4** and **7** ([**4**]/[**7**] 66:34), the composition in the polymerization determined by the relative signal intensity between the signals at 5.18 and 4.67 ppm in Figure 3 shows the predominance of the normal insertion: [without THP]/[with THP] 71:29. The observed difference between THF and THP in the selectivity with respect to the ring-opening incorporation can be reasonably ascribed to the higher propensity for the ring-opening reaction for THF than for THP under the condition. It is interesting to note that THP and 1,4-dioxane (see below) participate in the ring-opening reaction, which, we propose, proceeds in a mechanism analogous to cationic ring-opening polymerization of cyclic ethers, although THP and 1,4-dioxane have very low cationic ring-opening homopolymerizability.[5]

The polycondensation of **1a** with **2B** and **2C** as aromatic diols in THP also proceeded to give polymers **6aB** and **6aC**, respectively, having ring-opened THP in their main chains with similar incorporation selectivities of THP (runs 7 and 9 in Table 1).

Scheme 5. Polycondensation of 1a with Aromatic Diols in THP and 1,4-Dioxane



X = CH_2
6aA: (x' + x")/(y' + y") = 29 : 71,
6aB: (x' + x")/(y' + y") = 29 : 71,
6aC: (x' + x")/(y' + y") = 27 : 73

X = O
8aA: (x' + x")/(y' + y") = 18 : 82,
8aC: (x' + x")/(y' + y") = 11 : 89

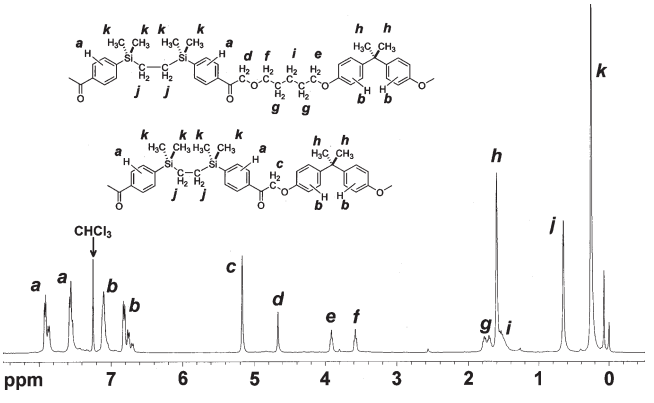


Figure 3. ^{1}H NMR spectrum for **6aA** (run 4 in Table 1).

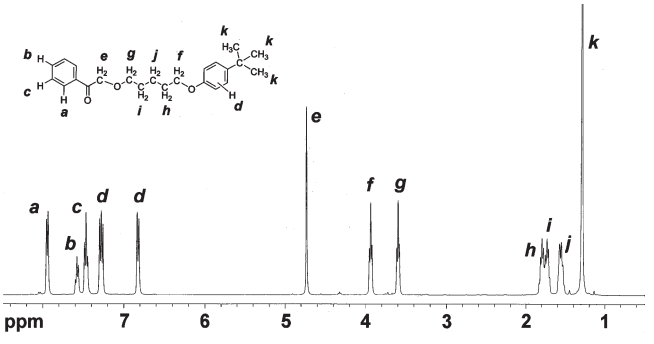


Figure 4. ^{1}H NMR spectrum for **7**.

Similarly, when 1,4-dioxane was used as another six-membered cyclic ether as a solvent for the polymerization of **1a** with

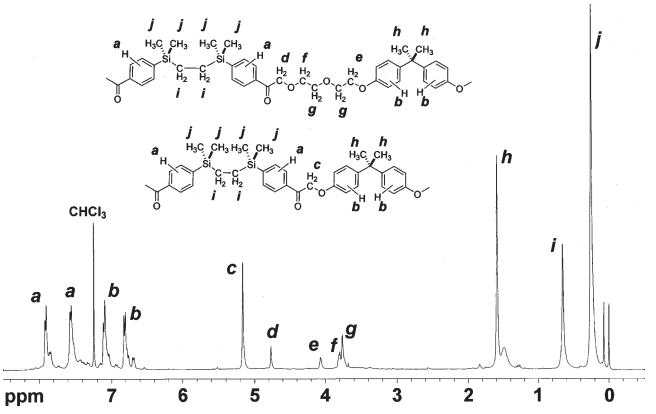


Figure 5. ^{1}H NMR spectrum for **8aA** (run 5 in Table 1).

2A, a ring-opened framework of 1,4-dioxane was incorporated in the main chain of the product **8aA** (Scheme 5, run 5 in Table 1). The assignment of the signals derived from the ring-opened 1,4-dioxane structure in the ^{1}H NMR spectrum in Figure 5 was again confirmed by comparison of the signals to those of an 1,4-dioxane incorporated model product **9** (Figure 6) obtained from the model reaction described in Scheme 7. The ratio of the yield of **4** to 1,4-dioxane-incorporated compound **9** ([**4**]/[**9**] 90:10) is even higher than that observed in the model reaction in THP (Scheme 6), and the selectivity for the reaction was reflected in the polymerization, where the composition between the two types of the linkages was 82:18 ([without 1,4-dioxane]/[with 1,4-dioxane]). The composition was determined from the relative signal intensity between those at 5.17 and 4.77 ppm in Figure 5. The analogous 1,4-dioxane-incoporated polymer **8aC** was obtained from the polymerization using **2C** as an aromatic diols (run 10 in Table 1),

although a product of the polymerization of **1a** with **2B** was an insoluble solid because of its low solubility derived from the low degree of 1,4-dioxane incorporation.

Whereas we can expect that similar polymerization should proceed with the use of another six-membered cyclic ether trioxane[6] and a three-membered ether 1,2-epoxybutane, which have high reactivity for cationic ring-opening polymerization, the reaction of **1a** with **2A** under similar conditions using these cyclic ethers afforded polymeric products, whose structures cannot be identified from their ^{1}H NMR spectra. For the reaction with trioxane, which is solid at room temperature (mp 59−62 °C), the reaction was conducted at >65 °C or at room temperature by using Et_2O, CH_2Cl_2, or toluene as a solvent. The model reaction of diazoacetophenone with 4-*t*-butylphenol and trioxane in CH_2Cl_2 as a solvent gave **4** alone in a 63.6% yield, whereas the reaction in 1,2-epoxybutane did not afford any identifiable product. These results suggest that the efficient incorporation of the ring-opened cyclic ether is the essential condition for the polymerization to afford well-defined main chain structures. In addition, although our proposed mechanism for THF-incorporation described in Scheme 4 is closely related to the propagation mechanism for the cationic polymerization of THF, the reactivities of cyclic ethers for cationic polymerization and ring-opening insertion in this study are not simply related.

The polymerizations of **1b** and **1c** bearing −$SiMe_2$− and −$SiMe_2$−O−$SiMe_2$− linkers, respectively, as bis(diazocarbonyl) compounds with aromatic diols **2A**∼**2C** in the cyclic ethers were examined, and the results are summarized in Table 2. For these polymerizations, the incorporation of ring-opened ethers employed as a solvent was observed in similar manners as described with **1a**, furnishing a variety of polyetherketones (Scheme 8). (See the Supporting Information for ^{1}H NMR spectra for the polymers in Table 2.) However, when 1,4-dioxane was used as a solvent, because of low solubility of the products derived from the low degree of solvent incorporation, well-defined polymers were not obtained, except in the case of using bisphenol A as a diol (**8bA** (run 3) and **8cA** (run 10)).

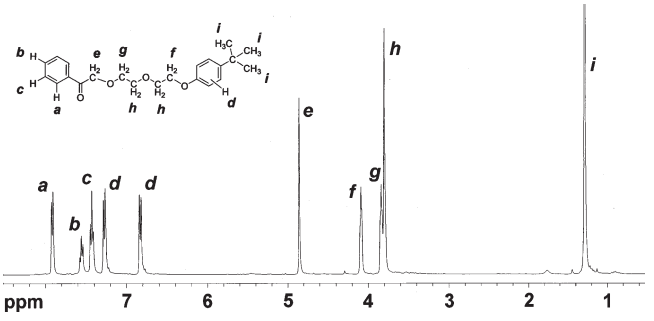
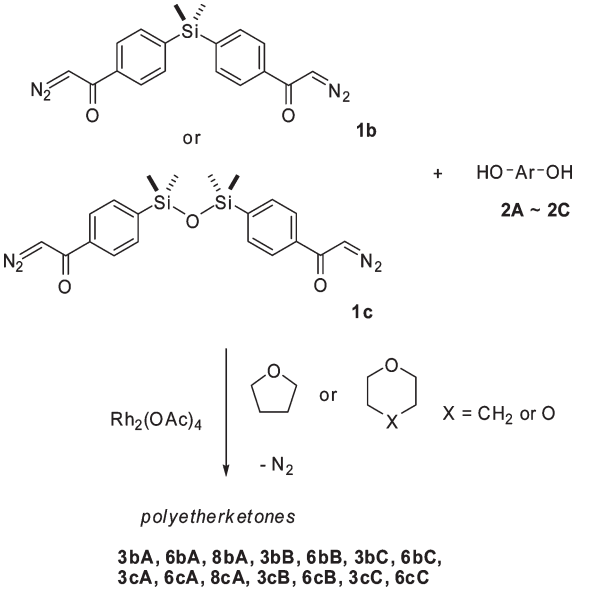


Figure 6. ^{1}H NMR spectrum for **9**.

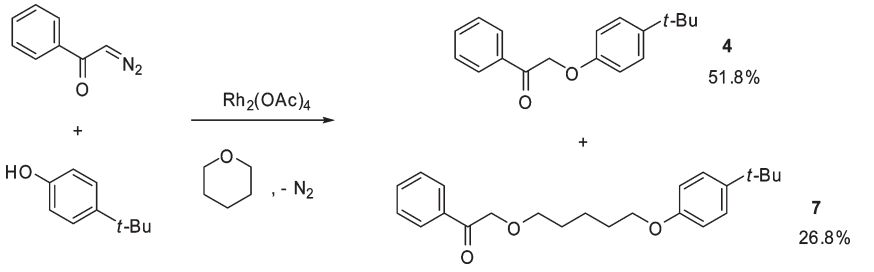
Conclusions

We have demonstrated that bis(diazocarbonyl) compounds can be utilized as a monomer for polycondensation for the first time. The reaction of bis(diazocarbonyl) compounds with aromatic

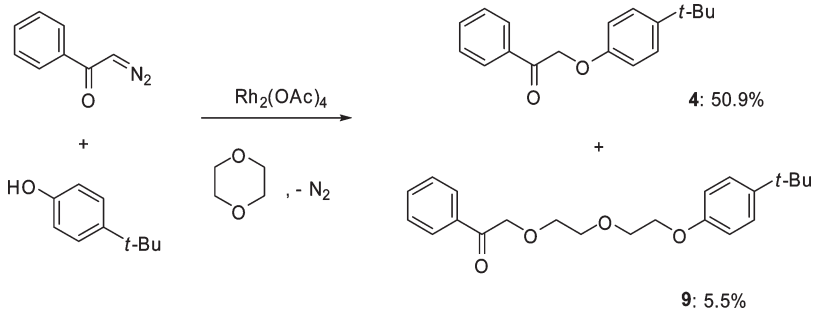
Scheme 8. Polycondensation of 1b and 1c with Aromatic Diols in THF, THP, and 1,4-Dioxane



Scheme 6. Model Reaction of Diazoketone with Phenol in THP



Scheme 7. Model Reaction of Diazoketone with Phenol in 1,4-Dioxane



diols in cyclic ethers afforded polyetherketones with a variety of structures as a result of incorporation of ring-opened cyclic ethers. Despite the rather low polymer yields in this study, bis(diazocarbonyl) compounds can be regarded as a useful class of monomers for polycondensation because of their versatile reactivities with various functional groups. The further investigation along this course is underway in our laboratory.

Experimental Section

Materials. THF was dried over Na/K alloy and distilled before use. THP (TCI, > 98.0%) and 1,2-epoxybutane (TCI, > 99.0%) were dried over CaH_2 and used without further purification. 1,3,5-Trioxane (TCI, > 99.0%), dehydrated 1,4-dioxane (Kanto Chemical, > 99.5%), bisphenol A (Wako, > 95%), 4,4′-biphenol (TCI, > 99.0%), 2,6-dihydroxynaphthalene (Wako), 4-*t*-butylphenol (Nacalai, 98%), and $Rh_2(OAc)_4$ (AZmax, 99%) were used as received. Diazoacetophenone was prepared according to the literature.[7]

Measurements. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker Avance 400 spectrometer using tetramethysilane as an internal standard in chloroform-*d* ($CDCl_3$) at room temperature (monomers) or at 50 °C (polymers).

Molecular weights (M_n) and molecular weight distributions (M_w/M_n) were measured by means of gel permeation chromatography (GPC) on a Jasco-ChromNAV system equipped with a differential refractometer detector using tetrahydrofuran as eluent at a flow rate of 1.0 mL/min at 40 °C, calibrated with poly(MMA). The column used for the GPC analyses was a combination of Styragel HR4 (Waters; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 600K for polystyrene) and Styragel HR2 (Waters; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 20K for polystyrene), and poly(MMA) standards (Shodex M-75, M_p = 212 000, M_w/M_n = 1.05, M_p = 50 000, M_w/M_n = 1.02, M_p = 22 00, M_w/M_n = 1.02, M_p = 5720, M_w/M_n = 1.06, M_p = 2400, M_w/M_n = 1.08) and dibutyl sebacate (MW = 314.5) were used for the calibration.

Purification by preparative recycling GPC was performed on a JAI LC-918R equipped with a combination of columns of a JAIGEL-3H (600 mm × 20 mm i.d., exclusion molecular weight of 70K for polystyrene) and a JAIGEL-2H (600 mm × 20 mm i.d., exclusion molecular weight of 5K for polystyrene) for polymers and a combination of columns of a JAIGEL-2H and a JAIGEL-1H (600 mm × 20 mm i.d., exclusion molecular weight of 1K for polystyrene) for monomers **1a**−**c** and the products of model reactions **4**, **5**, **7**, and **9**, using $CHCl_3$ as eluent at a flow rate of 3.8 mL/min at 25 °C. The sample solution (3 mL containing ca. 0.3 g of the crude product) was injected and recycled before fractionation.

Elemental analyses were performed on a YANAKO MT-5 analyzer at Integrated Center for Science (INCS) in Ehime University. Probably because of the presence of Si-containing or aromatic moiety in the main chains, elemental analyses of all the polymers in this study did not give satisfactory results.

Preparation of Bis(diazocarbonyl) Compounds (1a−1c). The preparation of bis(4-diazoacetylphenyl)dimethylsilane (**1b**) by diazo-transfer reaction[7] of bis(4-acetylphenyl)dimethylsilane was described in our previous publication.[4] 1,2-Bis[(4-diazoacetylphenyl)dimethylsilyl]ethane (**1a**) and 1,3-bis(4-diazoacetylphenyl)-1,1,3,3-tetramethyldisiloxane (**1c**) were prepared by applying the procedure for **1b** to 1,2-bis[(4-acetylphenyl)dimethylsilyl]ethane[8] and 1,3-bis(4-acetylphenyl)-1,1,3,3-tetramethyldisiloxane,[9] respectively. Yields for the diazo-transfer reactions were 75.1% for **1a** and 32.4% for **1b**. **1a**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.70 (d, J = 7.6 Hz, 4H, Ph−*H*), 7.52 (d, J = 6.8 Hz, 4H, Ph−*H*), 5.92 (s, 2H, −C*H*=N_2), 0.62 (s, 4H, −$SiMe_2$−[CH_2]$_2$−$SiMe_2$−), 0.26 (s, 12H, −-Si[CH_3]$_2$−). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 186.5 (*C*=O), 145.4 (Ph), 136.8 (Ph), 133.8 (Ph), 125.6 (Ph), 54.2 (−*C*H=N_2), 7.6 (−$SiMe_2$−[CH_2]$_2$−$SiMe_2$−), −3.8 (−Si[CH_3]$_2$−). Anal. Calcd for $C_{22}H_{26}N_4O_2Si_2\cdot 0.3H_2O$: C, 60.05; H, 6.09; N, 12.73. Found: C, 60.78; H, 5.89; N, 11.74. **1c**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.71 (d, J = 7.6 Hz, 4H, Ph−*H*), 7.58 (d, J = 6.8 Hz, 4H, Ph−*H*), 5.91 (s, 2H, −C*H*=N_2), 0.35 (s, 12H, −Si[CH_3]$_2$−). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 186.5 (*C*=O), 145.3 (Ph), 137.3 (Ph), 133.3 (Ph), 125.8 (Ph), 54.3 (−*C*H=N_2), 0.72 (−Si[CH_3]$_2$−). Anal. Calcd for $C_{20}H_{22}N_4O_3Si_2\cdot 0.8H_2O$: C, 54.97; H, 5.44; N, 12.82. Found: C, 54.23; H, 5.05; N, 12.01.

Polymerization Procedure. As a typical procedure, copolymerization of **1a** with **2A** in THF (run 1 in Table 1) was described as follows.

Under a N_2 atmosphere, **1a** (106 mg, 0.244 mmol), **2A** (55.7 mg, 0.244 mmol), and $Rh_2(OAc)_4$ (2.2 mg, 4.9 × 10^{-3} mmol) were placed in a Schlenk tube. After THF (5.0 mL) was added, the mixture was stirred at room temperature for 17 h. After the volatiles were removed under reduced pressure, a MeOH solution of HCl (1N, 10 mL), aqueous solution of HCl (1N, 10 mL), and $CHCl_3$ (20 mL) were added to the residue. The organic layer was extracted with a separatory funnel, and the aqueous layer was extracted with 30 mL of $CHCl_3$. The combined organic layer was washed with 50 mL of 1 N aqueous solution of HCl and 50 mL of saturated aqueous solution of NaCl, dried over Na_2SO_4. The solid obtained after removal of volatiles under reduced pressure was purified by using preparative recycling GPC to give a polymer as a brownish yellow solid (67.8 mg, 40.8%).

Other Rh-catalyzed polymerizations of bis(diazocarbonyl) compounds with diols in cyclic ether were carried out in a similar procedure. **3aA**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.85 (d, J = 7.2 Hz, −$SiMe_2$−Ph[−*H*]−[C=O]−), 7.54 (d, J = 7.2 Hz, −$SiMe_2$−Ph[−*H*]−[C=O]−), 7.09 (d, J = 8.0 Hz, −O−Ph-[−*H*]−CMe_2−), 6.76 (d, J = 8.0 Hz, −O−Ph[−*H*]−CMe_2−), 5.16 (s, −[C=O]−CH_2−O−Ph− [minor repeating unit without THF incorporation]), 4.67 (s, −[C=O]−CH_2−O−CH_2− [major repeating unit with THF incorporation]), 4.0−3.9 (m, −CH_2−O−Ph−CMe_2−), 3.7−3.5 (m, −[C=O]−CH_2−O−CH_2−), 1.9−1.7 (br, −O−CH_2−[CH_2]$_2$−CH_2−O−), 1.61 (s, −Ph−C[CH_3]$_2$−Ph−), 0.65 (s, −$SiMe_2$−[CH_2]$_2$−$SiMe_2$−), 0.25 (s, −Si[CH_3]$_2$−). **6aA**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.95−7.82 (m, −$SiMe_2$−Ph[−*H*]−[C=O]−), 7.61−7.49 (m, −$SiMe_2$−Ph[−*H*]−[C=O]−), 7.15−7.03 (m, −O−Ph[−*H*]−CMe_2−), 6.85−6.67 (m, −O−Ph[−*H*]−CMe_2−), 5.17 (s, −[C=O]−CH_2−O−Ph− [major repeating unit without THP incorporation]), 4.67 (s, −[C=O]-−CH_2−O−CH_2− [minor repeating unit with THP incorporation]), 3.91 (t, J = 5.8 Hz, −CH_2−O−Ph−CMe_2−), 3.58 (t, J = 6.2 Hz, −[C=O]−CH_2−O−CH_2−), 1.82−1.74 (m, −CH_2−CH_2−O−Ph−CMe_2−), 1.74−1.66 (m, −[C=O]−CH_2−O−CH_2−CH_2−), 1.60 (s, −Ph−C[CH_3]$_2$−Ph−), 1.65−1.46 (m, −O−CH_2−CH_2−CH_2−CH_2−CH_2−O−), 0.66 (s, −$SiMe_2$−[CH_2]$_2$−$SiMe_2$−), 0.26 (s, −Si[CH_3]$_2$−). **8aA**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.95−7.80 (m, −$SiMe_2$−Ph[−*H*]−[C=O]−), 7.61−7.47 (m, −$SiMe_2$−Ph[−*H*]−[C=O]−), 7.14−7.01 (m, −O−Ph[−*H*]-−CMe_2−), 6.86−6.66 (m, −O−Ph[−*H*]−CMe_2−), 5.17 (s, −[C=O]−CH_2−O−Ph− [major repeating unit without 1,4-dioxane incorporation]), 4.77 (s, −[C=O]−CH_2−O−CH_2− [minor repeating unit with 1,4-dioxane incorporation]), 4.09−4.04 (m, −CH_2−O−Ph−CMe_2−), 3.83−3.78 (m, −[C=O]−CH_2−O−CH_2−), 3.78−3.71 (m, −O−CH_2−CH_2−O−CH_2−CH_2−O−), 1.60 (s, −Ph−C[CH_3]$_2$−Ph−), 0.66 (s, −$SiMe_2$−[CH_2]$_2$−$SiMe_2$−), 0.26 (s, −Si[CH_3]$_2$−). **3aB**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.86 (d, J = 7.2 Hz, −$SiMe_2$−Ph[−*H*]−[C=O]−), 7.54 (d, J = 7.6 Hz, −$SiMe_2$−Ph[−*H*]−[C=O]−), 7.42 (d, J = 8.0 Hz, −O−Ph[−*H*]−), 6.91 (d, J = 7.6 Hz, −O−Ph[−*H*]−), 5.24 (s, −[C=O]-−CH_2−O−Ph− [minor repeating unit without THF incorporation]), 4.69 (s, −[C=O]−CH_2−O−CH_2− [major repeating unit with THF incorporation]), 4.01 (t, J = 5.6 Hz, −CH_2−O−Ph−CMe_2−), 3.64 (t, J = 5.6 Hz, −[C=O]−CH_2−O−CH_2−), 1.95−1.79 (br, −O−CH_2−[CH_2]$_2$−CH_2−O−), 0.65

(s, $-SiMe_2-[CH_2]_2-SiMe_2-$), 0.25 (s, $-Si[CH_3]_2-$). **6aB**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.96−7.82 (m, $-SiMe_2-Ph-[-H]-[C=O]-$), 7.61−7.49 (m, $-SiMe_2-Ph[-H]-[C=O]-$), 7.46−7.33 (m, $-O-Ph[-H]-$), 7.00−6.87 (m, $-O-Ph[-H]-$), 5.23 (s, $-[C=O]-CH_2-O-Ph-$ [major repeating unit without THP incorporation]), 4.67 (s, $-[C=O]-CH_2-O-CH_2-$ [minor repeating unit with THP incorporation]), 3.97 (t, J = 5.6 Hz, $-CH_2-O-Ph-CMe_2-$), 3.59 (t, J = 5.6 Hz, $-[C=O]-CH_2-O-CH_2-$), 1.86−1.77 (br, $-CH_2-CH_2-O-Ph-CMe_2-$), 1.76−1.67 (br, $-[C=O]-CH_2-O-CH_2-CH_2-$), 1.62−1.52 (m, $-O-CH_2-CH_2-CH_2-CH_2-CH_2-O-$), 0.70−0.60 (m, $-SiMe_2-[CH_2]_2-SiMe_2-$), 0.26 (s, $-Si[CH_3]_2-$). **3aC**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.90−7.80 (m, $-SiMe_2-Ph[-H]-[C=O]-$), 7.61−7.46 (m, $-SiMe_2-Ph[-H]-[C=O]-$ and $-O-$naphthalene$[-H]-$), 7.11−7.00 (m, $-O-$naphthalene$-[-H]-$), 5.26 (s, $-[C=O]-CH_2-O-$naphthalene− [minor repeating unit without THF incorporation]), 4.69 (s, $-[C=O]-CH_2-O-CH_2-$ [major repeating unit with THF incorporation]), 4.11−4.01 (m, $-CH_2-O-$naphthalene−), 3.69−3.59 (m, $-[C=O]-CH_2-O-CH_2-$), 1.98−1.79 (br, $-O-CH_2-[CH_2]_2-CH_2-O-$), 0.64 (s, $-SiMe_2-[CH_2]_2-SiMe_2-$), 0.25 (s, $-Si[CH_3]_2-$). **6aC**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.99−7.81 (m, $-SiMe_2-Ph[-H]-[C=O]-$), 7.63−7.49 (m, $-SiMe_2-Ph[-H]-[C=O]-$ and $-O-$naphthalene$[-H]-$), 7.22−7.02 (m, $-O-$naphthalene$[-H]-$), 5.23 (s, $-[C=O]-CH_2-O-$naphthalene− [major repeating unit without THP incorporation]), 4.67 (s, $-[C=O]-CH_2-O-CH_2-$ [minor repeating unit with THP incorporation]), 4.06−3.99 (m,$-CH_2-O-$naphthalene−), 3.63−3.55 (m, $-[C=O]-CH_2-O-CH_2-$), 1.89−1.79 (br, $-CH_2-CH_2-O-$naphthalene−), 1.77−1.68 (br, $-[C=O]-CH_2-O-CH_2-CH_2-$), 1.63−1.54 (m, $-O-CH_2-CH_2-CH_2-CH_2-CH_2-O-$), 0.72−0.59 (m, $-SiMe_2-[CH_2]_2-SiMe_2-$), 0.27 (s, $-Si[CH_3]_2-$). **8aC**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.99−7.79 (m, $-SiMe_2-Ph[-H]-[C=O]-$), 7.63−7.43 (m, $-SiMe_2-Ph[-H]-[C=O]-$ and $-O-$naphthalene$[-H]-$), 7.22−7.02 (m, $-O-$naphthalene$[-H]-$), 5.27 (s, $-[C=O]-CH_2-O-$naphthalene− [major repeating unit without 1,4−dioxane incorporation]), 4.79 (s, $-[C=O]-CH_2-O-CH_2-$ [minor repeating unit with 1,4−dioxane incorporation]), 4.21−4.15 (m, $-CH_2-O-$naphthalene−), 3.90−3.84 (m, $-[C=O]-CH_2-O-CH_2-$), 3.81−3.76 (m, $-O-CH_2-CH_2-O-CH_2-CH_2-O-$), 0.71−0.58 (m, $-SiMe_2-[CH_2]_2-SiMe_2-$), 0.26 (s, $-Si[CH_3]_2-$). **3bA**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.88 (d, J = 8.0 Hz, $-SiMe_2-Ph[-H]-[C=O]-$), 7.58 (d, J = 8.0 Hz, $-SiMe_2-Ph[-H]-[C=O]-$), 7.09 (d, J = 8.8 Hz, $-O-Ph-[-H]-CMe_2-$), 6.75 (d, J = 9.2 Hz, $-O-Ph[-H]-CMe_2-$), 5.15 (s, $-[C=O]-CH_2-O-Ph-$ [minor repeating unit without THF incorporation]), 4.66 (s, $-[C=O]-CH_2-O-CH_2-$ [major repeating unit with THF incorporation]), 3.94 (t, J = 5.8 Hz, $-CH_2-O-Ph-CMe_2-$), 3.61 (t, J = 6.2 Hz, $-[C=O]-CH_2-O-CH_2-$), 1.91−1.75 (m, $-O-CH_2-[CH_2]_2-CH_2-O-$), 1.61 (s, $-Ph-C[CH_3]_2-Ph-$), 0.59 (s, $-Si[CH_3]_2-$). **6bA**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.05−7.77 (m, $-SiMe_2-Ph[-H]-[C=O]-$), 7.65−7.43 (m, $-SiMe_2-Ph[-H]-[C=O]-$), 7.14−6.97 (m, $-O-Ph[-H]-CMe_2-$), 6.85−6.64 (m, $-O-Ph-[-H]-CMe_2-$), 5.15 (s, $-[C=O]-CH_2-O-Ph-$ [major repeating unit without THP incorporation]), 4.65 (s, $-[C=O]-CH_2-O-CH_2-$ [minor repeating unit with THP incorporation]), 3.95−3.85 (m, $-CH_2-O-Ph-CMe_2-$), 3.60−3.51 (m, $-[C=O]-CH_2-O-CH_2-$), 1.82−1.73 (m, $-CH_2-CH_2-O-Ph-CMe_2-$), 1.73−1.65 (m, $-[C=O]-CH_2-O-CH_2-CH_2-$), 1.60 (s, $-Ph-CMe_2-Ph$), 1.64−1.43 (m, $-O-CH_2-CH_2-CH_2-CH_2-CH_2-O-$), 0.59 (s, $-Si[CH_3]_2-$). **8bA**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.99−7.79 (m, $-SiMe_2-Ph[-H]-[C=O]-$), 7.67−7.43 (m, $-SiMe_2-Ph[-H]-[C=O]-$), 7.15−6.98 (m, $-O-Ph[-H]-CMe_2-$), 6.86−6.64 (m, $-O-Ph[-H]-CMe_2-$), 5.15 (s, $-[C=O]-CH_2-O-Ph-$ [major repeating unit without 1,4−dioxane incorporation]), 4.76 (s, $-[C=O]-CH_2-O-CH_2-$ [minor repeating unit with 1,4−dioxane incorporation]), 4.09−4.02 (m, $-CH_2-O-Ph-CMe_2-$), 3.84−3.78 (m, $-[C=O]-CH_2-O-CH_2-$), 3.78−3.70 (s, $-O-CH_2-CH_2-O-CH_2-CH_2-O-$), 1.59 (s, $-Ph-C[CH_3]_2-Ph-$), 0.59 (s, $-Si[CH_3]_2-$). **3bB**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.88 (d, J = 7.6 Hz, $-SiMe_2-Ph[-H]-[C=O]-$), 7.58 (d, J = 8.0 Hz, $-SiMe_2-Ph-[-H]-[C=O]-$), 7.41 (d, J = 8.4 Hz, $-O-Ph[-H]-$), 6.91 (d, J = 8.0 Hz, $-O-Ph[-H]-$), 5.21 (s, $-[C=O]-CH_2-O-Ph-$ [minor repeating unit without THF incorporation]), 4.67 (s, $-[C=O]-CH_2-O-CH_2-$ [major repeating unit with THF incorporation]), 4.06−3.94 (m, $-CH_2-O-Ph-CMe_2-$), 3.68−3.56 (m, $-[C=O]-CH_2-O-CH_2-$), 1.94−1.77 (m, $-O-CH_2-[CH_2]_2-CH_2-O-$), 0.58 (s, $-Si[CH_3]_2-$). **6bB**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.01−7.80 (m, $-SiMe_2-Ph[-H]-[C=O]-$), 7.68−7.48 (m, $-SiMe_2-Ph[-H]-[C=O]-$), 7.47−7.31 (m, $-O-Ph[-H]-$), 7.01−6.79 (m, $-O-Ph[-H]-$), 5.22 (s, $-[C=O]-CH_2-O-Ph-$ [minor repeating unit without THP incorporation]), 4.66 (s, $-[C=O]-CH_2-O-CH_2-$ [major repeating unit with THP incorporation]), 4.01−3.89 (m, $-CH_2-O-$naphthalene−), 3.63−3.52 (m, $-[C=O]-CH_2-O-CH_2-$), 1.87−1.75 (br, $-CH_2-CH_2-O-$naphthalene−), 1.75−1.63 (br, $-[C=O]-CH_2-O-CH_2-CH_2-$), 1.61−1.39 (m, $-O-CH_2-CH_2-CH_2-CH_2-CH_2-O-$), 0.60 (s, $-Si[CH_3]_2-$). **3bC**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.93−7.83 (m, $-SiMe_2-Ph[-H]-[C=O]-$), 7.63−7.52 (m, $-SiMe_2-Ph[-H]-[C=O]-$ and $-O-$naphthalene$[-H]-$), 7.11−7.01 (m, $-O-$naphthalene$-[-H]-$), 5.26 (s, $-[C=O]-CH_2-O-$naphthalene− [major repeating unit without THF incorporation]), 4.67 (s, $-[C=O]-CH_2-O-CH_2-$ [minor repeating unit with THF incorporation]), 4.11−4.00 (m, $-CH_2-O-$naphthalene−), 3.68−3.58 (m, $-[C=O]-CH_2-O-CH_2-$), 1.97−1.79 (m, $-O-CH_2-[CH_2]_2-CH_2-O-$), 0.58 (s, $-Si[CH_3]_2-$). **6bC**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.01−7.76 (m, $-SiMe_2-Ph[-H]-[C=O]-$), 7.67−7.35 (m, $-SiMe_2-Ph[-H]-[C=O]-$ and $-O-$naphthalene$[-H]-$), 7.21−6.96 (m, $-O-$naphthalene$[-H]-$), 5.26 (s, $-[C=O]-CH_2-O-$naphthalene− [major repeating unit without THP incorporation]), 4.65 (s, $-[C=O]-CH_2-O-CH_2-$ [minor repeating unit with THP incorporation]), 4.07−3.95 (m, $-CH_2-O-$naphthalene−), 3.62−3.50 (m, $-[C=O]-CH_2-O-CH_2-$), 1.89−1.77 (br, $-CH_2-CH_2-O-$naphthalene−), 1.76−1.64 (br, $-[C=O]-CH_2-O-CH_2-CH_2-$), 1.63−1.37 (m, $-O-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-O-$), 0.58 (s, $-Si[CH_3]_2-$). **3cA**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.03−7.78 (m, $-SiMe_2-Ph[-H]-[C=O]-$), 7.73−7.48 (m, $-SiMe_2-Ph[-H]-[C=O]-$), 7.09 (d, J = 7.6 Hz, $-O-Ph[-H]-CMe_2-$), 6.75 (d, J = 8.0 Hz, $-O-Ph-[-H]-CMe_2-$), 5.18 (s, $-[C=O]-CH_2-O-Ph-$ [minor repeating unit without THF incorporation]), 4.69 (s, $-[C=O]-CH_2-O-CH_2-$ [major repeating unit with THF incorporation]), 3.99−3.89 (m, $-CH_2-O-Ph-CMe_2-$), 3.67−3.58 (m, $-[C=O]-CH_2-O-CH_2-$), 1.91−1.76 (br, $-O-CH_2-[CH_2]_2-CH_2-O-$), 1.61 (s, $-Ph-C[CH_3]_2-Ph-$), 0.35 (s, $-Si[CH_3]_2-$). **6cA**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.97−7.83 (m, $-SiMe_2-Ph[-H]-[C=O]-$), 7.68−7.56 (m, $-SiMe_2-Ph[-H]-[C=O]-$), 7.14−7.03 (m, $-O-Ph[-H]-CMe_2-$), 6.85−6.67 (m, $-O-Ph[-H]-CMe_2-$), 5.18 (s, $-[C=O]-CH_2-O-Ph-$ [major repeating unit without THP incorporation]), 4.67 (s, $-[C=O]-CH_2-O-CH_2-$ [minor repeating unit with THP incorporation]), 3.92 (t, J = 6.0 Hz, $-CH_2-O-Ph-CMe_2-$), 3.58 (t, J = 6.6 Hz, $-[C=O]-CH_2-O-CH_2-$), 1.82−1.74 (m, $-CH_2-CH_2-O-Ph-CMe_2-$), 1.74−1.67 (m, $-[C=O]-CH_2-O-CH_2-CH_2-$), 1.60 (s, $-Ph-C[CH_3]_2-Ph-$), 1.64−1.51 (m, $-O-CH_2-CH_2-CH_2-CH_2-CH_2-O-$), 0.39−0.30 (m, $-Si[CH_3]_2-$). **8cA**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.96−7.82 (m, $-SiMe_2-Ph[-H]-[C=O]-$), 7.68−7.51 (m, $-SiMe_2-Ph[-H]-[C=O]-$), 7.14−7.01 (m, $-O-Ph[-H]-CMe_2-$), 6.85−6.66 (m, $-O-Ph[-H]-CMe_2-$), 5.17 (s, $-[C=O]-CH_2-O-Ph-$ [major repeating unit without 1,4−dioxane incorporation]), 4.78 (s, $-[C=O]-CH_2-O-CH_2-$ [minor repeating unit with 1,4−dioxane incorporation]), 4.09−4.05 (m, $-CH_2-O-Ph-CMe_2-$), 3.84−3.79 (m, $-[C=O]-CH_2-O-CH_2-$), 3.79−3.75 (m, $-O-CH_2-CH_2-O-CH_2-CH_2-O-$), 1.60 (s, $-Ph-C[CH_3]_2-Ph-$), 0.36 (s, $-Si[CH_3]_2-$). **3cB**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.88 (d, J = 8.4 Hz,

−$SiMe_2$−Ph[−*H*]−[C=O]−), 7.60 (d, *J* = 8.0 Hz, −$SiMe_2$−Ph-[−*H*]−[C=O]−), 7.42 (d, *J* = 8.8 Hz, −O−Ph[−*H*]−), 6.91 (d, *J* = 8.4 Hz, −O−Ph[−*H*]−), 5.24 (s, −[C=O]−CH_2−O−Ph− [minor repeating unit without THF incorporation]), 4.69 (s, −[C=O]−CH_2−O−CH_2− [major repeating unit with THF incorporation]), 4.01 (t, *J* = 5.8 Hz, −CH_2−O−naphthalene−), 3.65 (t, *J* = 6.2 Hz, −[C=O]−CH_2−O−CH_2−), 1.94−1.80 (m, −O−CH_2−[CH_2]$_2$−CH_2−O−), 0.35 (s, −Si[CH_3]$_2$−). **6cB**: ^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.98−7.83 (m, −$SiMe_2$−Ph[−*H*]−[C=O]−), 7.68−7.56 (m, −$SiMe_2$−Ph[−*H*]−[C=O]−), 7.47−7.33 (m, −O−Ph-[−*H*]−), 7.00−6.81 (m, −O−Ph[−*H*]−), 5.24 (s, −[C=O]−CH_2−O−Ph− [minor repeating unit without THP incorporation]), 4.68 (s, −[C=O]−CH_2−O−CH_2− [major repeating unit with THP incorporation]), 3.97 (t, *J* = 5.2 Hz, −CH_2−O−Ph−), 3.60 (t, *J* = 6.2 Hz, −[C=O]−CH_2−O−CH_2−), 1.86−1.77 (br, −CH_2−CH_2−O−Ph−), 1.76−1.67 (br, −[C=O]−CH_2−O−CH_2−CH_2−), 1.62−1.52 (m, −O−CH_2−CH_2−CH_2−CH_2−CH_2−O−), 0.36 (s, −Si[CH_3]$_2$−). **3cC**: ^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.92−7.83 (m, −$SiMe_2$−Ph[−*H*]−[C=O]−), 7.64−7.54 (m, −$SiMe_2$−Ph[−*H*]−[C=O]−), (m, −O−naphthalene[−*H*]−), 7.11−7.04 (m, −O−naphthalene[−*H*]−), 5.28 (s, −[C=O]−CH_2−O−naphthalene− [major repeating unit without THF incorporation]), 4.69 (s, −[C=O]−CH_2−O−CH_2− [minor repeating unit with THF incorporation]), 4.07 (t, *J* = 6.0 Hz,−CH_2−O−naphthalene−), 3.65 (t, *J* = 6.0 Hz, −[C=O]−CH_2−O−CH_2−), 1.98−1.81 (m, −O−CH_2−[CH_2]$_2$−CH_2−O−), 0.35 (s, −Si[CH_3]$_2$). **6cC**: ^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 8.01−7.81 (m, −$SiMe_2$−Ph[−*H*]−[C=O]−), 7.71−7.41 (m, −$SiMe_2$−Ph[−*H*]−[C=O]− and −O−naphthalene[−*H*]−), 7.22−6.98 (m, −O−naphthalene[−*H*]−), 5.28 (s, −[C=O]−CH_2−O−naphthalene− [major repeating unit without THP incorporation]), 4.68 (s, −[C=O]−CH_2−O−CH_2− [minor repeating unit with THP incorporation]), 4.06−3.97 (m, −CH_2−O−naphthalene−), 3.63−3.54 (m, −[C=O]−CH_2−O−CH_2−), 1.88−1.78 (br, −CH_2−CH_2−O−naphthalene−), 1.77−1.66 (br, −[C=O]−CH_2−O−CH_2−CH_2−), 1.63−1.51 (m, −O−CH_2−CH_2−CH_2−CH_2−CH_2−O−), 0.35 (s, −Si[CH_3]$_2$−).

Procedure for Model Reactions. As a typical procedure, a reaction of diazoacetophenone with 4-*t*-butylphenol in THF was described as follows.

Under a N_2 atmosphere, diazoacetophenone (100.9 mg, 0.690 mmol), 4-*t*-butylphenol (1.03 g, 6.84 mmol), and $Rh_2(OAc)_4$ (3.3 mg, 7.5×10^{-3} mmol) were placed in a Schlenk tube. After THF (14.0 mL) was added, the mixture was stirred at room temperature for 17 h. After workup procedure for the above polymerization was applied, purification with recycling-GPC in $CHCl_3$ afforded **4** (34.1 mg, 0.127 mmol) and **5** (172.4 mg, 0.506 mmol) in 1.3 and 86.8% yield, respectively.

Other model reactions were carried out in similar procedures. **4**: ^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.99 (d, *J* = 7.6 Hz, 2H, *o*-Ph−*H*−[C=O]−), 7.59 (t, *J* = 7.2 Hz, 1H, *p*-Ph−*H*−[C=O]−), 7.47 (t, *J* = 7.6 Hz, 2H, *m*-Ph−*H*−[C=O]−), 7.29 (d, *J* = 8.0 Hz, 2H, −O−Ph−*H*−*t*Bu), 6.88 (d, *J* = 8.0 Hz, 2H, −O−Ph−*H*−*t*Bu), 5.23 (s, 2H, −[C=O]−CH_2−O−), 1.28 (s, 9H, −C[CH_3]$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, *δ*): 194.8 (*C*=O), 155.8 (Ph), 144.4 (Ph), 134.7 (Ph), 133.9 (Ph), 128.9 (Ph), 128.2 (Ph), 126.4 (Ph), 114.5 (Ph), 71.0 (−[C=O]−CH_2−O−), 34.2 (−CMe_3), 31.5 (−C[CH_3]$_3$). Anal. Calcd for $C_{18}H_{20}O_2 \cdot 0.2H_2O$: C, 79.50; H, 7.56. Found: C, 79.41; H, 7.30. **5**: ^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.94 (d, *J* = 7.6 Hz, 2H, *o*-Ph[−*H*]−[C=O]−), 7.58 (t, *J* = 7.4 Hz, 1H, *p*-Ph[−*H*]−[C=O]−), 7.47 (t, *J* = 7.2 Hz, 2H, *m*-Ph[−*H*]−[C=O]−), 7.28 (d, *J* = 8.4 Hz, 2H, −O−Ph-[−*H*]−*t*Bu), 6.82 (d, *J* = 8.4 Hz, 2H, −O−Ph[−*H*]−*t*Bu), 4.74 (s, 2H, −[C=O]−CH_2−O−), 3.97 (t, *J* = 5.0 Hz, 2H, −CH_2−O−Ph−*t*Bu), 3.64 (t, *J* = 5.4 Hz, 2H, −[C=O]−CH_2−O−CH_2−), 1.93−1.80 (m, 4H, −O−CH_2−[CH_2]$_2$−CH_2−O−), 1.29 (s, 9H, −C[CH_3]$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, *δ*): 196.64 (*C*=O), 156.76 (Ph), 143.21 (Ph), 135.01 (Ph), 133.51 (Ph), 128.71 (Ph), 127.97 (Ph), 126.19 (Ph), 113.94 (Ph), 73.86 (−[C=O]−CH_2−O−), 71.47 (−[C=O]−CH_2−O−CH_2−), 67.46 (−CH_2−O−Ph−*t*Bu), 34.06 (−*C*[CH_3]$_3$), 31.55 (−C-[CH_3]$_3$), 26.35 (−O−CH_2−[CH_2]$_2$−CH_2−O−), 26.05 (−O−CH_2− [CH_2]$_2$−CH_2−O−). Anal. Calcd for $C_{22}H_{28}O_3 \cdot 0.2\ H_2O$: C, 76.80; H, 8.32. Found: C, 76.70; H, 7.60. **7**: ^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.95 (d, *J* = 7.6 Hz, 2H, *o*-Ph[−*H*]−[C=O]−), 7.58 (t, *J* = 7.4 Hz, 1H, *p*-Ph[−*H*]−[C=O]−), 7.47 (t, *J* = 7.2 Hz, 2H, *m*-Ph[−*H*]−[C=O]−), 7.28 (d, *J* = 8.0 Hz, 2H, −O−Ph-[−*H*]−*t*Bu), 6.82 (d, *J* = 8.8 Hz, 2H, −O−Ph[−*H*]−*t*Bu), 4.73 (s, 2H, −[C=O]−CH_2−O−), 3.94 (t, *J* = 6.4 Hz, 2H, −CH_2−O−Ph−*t*Bu), 3.60 (t, *J* = 6.4 Hz, 2H, −[C=O]−CH_2−O−CH_2−), 1.84−1.77 (m, 2H, −CH_2−CH_2−O−Ph−*t*Bu), 1.77−1.69 (m, 2H, −[C=O]−CH_2−O−CH_2−CH_2−), 1.61−1.51 (m, 2H, −O−CH_2−CH_2−CH_2−CH_2−CH_2−O−), 1.29 (−C[CH_3]$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, *δ*): 196.70 (*C*=O), 156.81 (Ph), 143.16 (Ph), 135.02 (Ph), 133.51 (Ph), 128.71 (Ph), 127.98 (Ph), 126.19 (Ph), 113.94 (Ph), 73.92 (−[C=O]−CH_2−O−), 71.77 (−[C=O]−CH_2−O−CH_2−), 67.72 (−CH_2−O−Ph−*t*Bu), 34.07 (−*C*[CH_3]$_3$), 31.58 (−C[CH_3]$_3$), 29.42 (−[C=O]−CH_2−O− CH_2−CH_2−), 29.15 (−CH_2−CH_2−O−Ph−*t*Bu), 22.70 (−O−CH_2−CH_2−CH_2−CH_2−CH_2−O−). Anal. Calcd for $C_{23}H_{30}O_3 \cdot 0.1\ H_2O$: C, 77.54; H, 8.54. Found: C, 77.39; H, 8.34. **9**: ^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.91 (d, *J* = 7.6 Hz, 2H, *o*-Ph[−*H*]−[C=O]−), 7.56 (t, *J* = 7.2 Hz, 1H, *p*-Ph[−*H*]− [C=O]−), 7.43 (t, *J* = 7.4 Hz, 2H, *m*-Ph[−*H*]−[C=O]−), 7.27 (d, *J* = 8.4 Hz, 2H, −O−Ph[−*H*]−*t*Bu), 6.83 (d, *J* = 8.4 Hz, 2H, −O−Ph[−*H*]−*t*Bu), 4.86 (s, 2H, −[C=O]−CH_2−O−), 4.12−4.05 (m, 2H, −CH_2−O−Ph−*t*Bu), 3.87−3.82 (m, 2H, −[C=O]−CH_2−O−CH_2−), 3.82−3.76 (m, 4H, −O−CH_2−CH_2−O−CH_2−CH_2−O−), 1.29 (−C-[CH_3]$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, *δ*): 195.42 (*C*=O), 155.44 (Ph), 142.49 (Ph), 133.87 (Ph), 132.43 (Ph), 127.65 (Ph), 126.84 (Ph), 125.15 (Ph), 113.04 (Ph), 73.23 (−[C=O]−CH_2−O−), 70.10 (−O−CH_2−CH_2−O−CH_2−CH_2−O−), 69.90 (−O−CH_2−CH_2−O−CH_2−CH_2−O−), 68.80 (−[C=O]−CH_2−O−CH_2−), 66.33 (−CH_2−O−Ph−*t*Bu), 30.02 (−*C*[CH_3]$_3$), 30.49 (−C[*C*-H_3]$_3$). Anal. Calcd for $C_{22}H_{28}O_4$: C, 74.13; H, 7.92. Found: C, 73.74; H, 7.48.

Acknowledgment. This research was supported by the Grants-in-Aid for Scientific Research (B) (no. 18350066) from Japan Society for the Promotion of Science (JSPS).

Supporting Information Available: ^{13}C NMR spectra for products of model reactions **4**, **5**, **7**, and **9**. ^{1}H NMR spectra for polymers all the polymers in Tables 1 and 2 except for **3aA**, **6aA**, and **8aA**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Doyle, M. P.; Mckervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; John Wiley & Sons: New York, 1998.
(2) Zhang, Z.; Wang, J. *Tetrahedron* **2008**, *64*, 6577–6605.
(3) (a) Noels, A. F. *Angew. Chem., Int. Ed.* **2007**, *46*, 1208–1210. (b) Liu, L.; Song, Y.; Li, H. *Polym. Int.* **2002**, *51*, 1047–1049. (c) Ihara, E.; Haida, N.; Iio, M.; Inoue, K. *Macromolecules* **2003**, *36*, 36–41. (d) Ihara, E.; Fujioka, M.; Haida, N.; Itoh, T.; Inoue, K. *Macromolecules* **2005**, *38*, 2101–2108. (e) Hetterscheid, D. G. H.; Hendriksen, C.; Dzik, W. I.; Smits, J. M. M.; van Eck, E. R. H.; Rowan, A. E.; Busico, V.; Vacatello, M.; Van Axel Castelli, V.; Segre, A.; Jellema, E.; Bloemberg, T. G.; de Bruin, B. *J. Am. Chem. Soc.* **2006**, *128*, 9746–9752. (f) Ihara, E.; Nakada, A.; Itoh, T.; Inoue, K. *Macromolecules* **2006**, *39*, 6440–6444. (g) Ihara, E.; Kida, M.; Itoh, T.; Inoue, K. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 5209–5214. (h) Jellema, E.; Budzelaar, P. H. M.; Reek, J. N. H.; de Bruin, B. *J. Am. Chem. Soc.* **2007**, *129*, 11631–11641. (i) Bai, J.; Burke, L. D.; Shea, K. J. *J. Am. Chem. Soc.* **2007**, *129*, 4981–4991. (j) Ihara, E.; Hiraren, T.; Itoh, T.; Inoue, K. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 1638–1648. (k) Ihara, E.; Hiraren, T.; Itoh, T.; Inoue, K. *Polym J.* **2008**, *40*, 1094–1098. (l) Rubio, M.; Jellema, E.; Siegler, M. A.; Spek, A. L.; Reek, J. N. H.; de Bruin, B. *Dalton Trans* **2009**, 8970–8976. (m) Ihara, E.; Ishiguro, Y.; Yoshida, N.;

Hiraren, T.; Itoh, T.; Inoue, K. *Macromolecules* **2009**, *42*, 8608–8610.
(4) Ihara, E.; Goto, Y.; Itoh, T.; Inoue, K. *Polym. J.* **2009**, *41*, 1117.
(5) Odian, G. Ring-Opening Polymerization; *Principles of Polymerization*, 4th ed.; John Wiley & Sons: Hoboken, NJ, 2004; p 544.
(6) (a) Shieh, Y.-T.; Lay, M.-L.; Chen, S.-A. *J. Polym. Res.* **2003**, *10*, 151–160. (b) Shieh, Y.-T.; Yeh, M.-J.; Chen, S.-A. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 4198–4204. (c) Shieh, Y.-T.; Chen, S.-A. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 483–492.
(7) Danheiser, R. L.; Miller, R. F.; Brisbois, R. G.; Park, S. Z. *J. Org. Chem.* **1990**, *55*, 1959–1964.
(8) Itsuno, S.; Watanabe, H. *Polym. Bull.* **2003**, *51*, 183–190.
(9) Shinoda, T.; Nishiwaki, T.; Anda, K.; Hida, M. Jpn. Kokai Tokkyo Koho JP62057466 A 19870313, **1987**.