Macromolecules

Three-Component Polycondensation of Bis(diazoketone) with Dicarboxylic Acids and Cyclic Ethers: Synthesis of New Types of Poly(ester ether ketone)s

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Supporting Information

ABSTRACT: New types of poly(ester ether ketone)s 3 and 8 were prepared by three-component polycondensation of bis(diazoketone) 1 with a variety of dicarboxylic acids 2 and THF or THP catalyzed by $Rh_2(OAc)_4$. THF was ring-opened and incorporated into almost every carboxyl O-H of 2 via simultaneous insertion together with a diazocarbonyl-derived carbene, resulting in the formation of a unique poly-(ester ether ketone) framework. On the other hand, when THP was used as a cyclic ether, insertion of carbene alone into the carboxyl O-H



(normal insertion) competes with the simultaneous insertion of THP and carbene, and the ratio of the two modes of insertion depends on the kind of 2 employed. The mode and selectivity of the propagation were confirmed by conducting Rh-catalyzed model reactions of diazoacetophenone 4 with 4-tert-butylbenzoic acid 5 in THF and THP.

INTRODUCTION

Recently, diazocarbonyl compounds have attracted much attention not only as highly useful reagents for organic synthesis^{1,2} but also as monomers for polymerization.^{3,4} In particular, Rh- and Pd-mediated polymerization of diazoacetates can afford C-C main chain polymers bearing an ester group on every main chain carbon atom, which generally cannot be obtained by conventional vinyl polymerization.^{3,4} On the other hand, because of their inherent unique reactivity,^{1,2} diazocarbonyl compounds can be regarded as promising monomers when they are used as a monomer for polycondensation in a form of bis(diazocarbonyl) compounds. Actually, we recently reported the first example of polycondensation of some bis(diazoketone)s with aromatic diols,⁵ where the initial objective of the examination was to utilize insertion of carbene derived from diazoketone into O-H of the diol to obtain poly(ether ketone)s (Scheme 1a). The reaction of the monomers in halogenated or hydrocarbon solvents did not proceed in an expected manner but afforded uncharacterizable polymeric products. On the other hand, the reaction of the monomers in THF gave polymers, whose well-defined structure was totally unexpected: ring-opened THF and diazocarbonylderived carbene simultaneously inserted into almost every diol O-H, resulting in the formation of a poly(ether ketone) framework (Scheme 1b). This polymerization giving a new type of poly(ether ketone) is also quite unique as a new example of threecomponent polycondensation,⁶ where a combination of monomers A (diazoketone), B (diol), and C (THF) affords a sequence regulated repeating unit of A'-C'-B'-C'. On the other hand, when tetrahydropyran (THP) or 1,4-dioxane was used as a solvent and comonomer, the analogous simultaneous insertion of ring-opened THP or 1,4-dioxane completes with an insertion

of the carbene alone (normal insertion), affording poly(ether ketone)s with a combination of repeating units of A'-C'-B'-C', A'-C'-B', A'-B'-C', and A'-B' in the main chain [A: diazoketone; B: diol; C: THP or 1,4-dioxane].

It has been reported that carbenes derived from diazocarbonyl compounds can insert into O-H of carboxylic acids, affording an ester linkage between the two components.¹ Accordingly, as shown in Scheme 2, on the assumption that similar ring-opening of THF followed by simultaneous insertion with diazocarbonylderived carbene proceeds, we can expect that the three-component polycondensation of bis(diazocarbonyl) compounds with dicarboxylic acids and THF will afford a novel type of polymer, poly(ester ether ketone), with a well-defined repeating unit sequence of A'-C'-B'-C'. Herein, we report polymerization of a bis(diazoketone) with a series of dicarboxylic acids and THF, along with analogous examination using THP in place of THF.

RESULTS AND DISCUSSION

Polymerization with THF. As a bis(diazocarbonyl) compound, we employed bis(diazoketone) 1, where two acetophenone-derived diazoketone moieties are connected by a -SiMe₂CH₂CH₂SiMe₂- bridge. When 1 was reacted with terephthalic acid 2a as a dicarboxylic acid monomer in the presence of $Rh_2(OAc)_4$ ([1]/[2a]/[Rh] = 25:25:1) in THF as a solvent and also a comonomer at room temperature, we obtained a polymer **3a** with a GPC-determined (PMMA calibration) M_n of

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Scheme 1. Polycondensation of Bis(diazoketone) with Diol

a) unsuccessful attempts in CH2Cl2 or toluene



b) three-component polycondensation via simultaneous insertion of ring-opened THF and carbene into diol O-H



Scheme 2. Three-Component Polycondensation of Bis-(diazoketone) with Dicarboxylic Acid and THF



10 300, after purification by using preparative recycling GPC to remove lower molecular weight oligomers (Scheme 3, run 1 in Table 1). The ¹H NMR spectrum of **3a** shown in Figure 1 exhibits distinct signals, which can be assigned to the expected repeating unit structure resulting from simultaneous insertion of ringopened THF and diazocarbonyl-derived carbene into carboxyl O–H: in addition to the signals assignable to Hs originating from 1 and **2a**, four signals centered at 4.38, 3.64, 1.91, and 1.81 ppm with a same intensity can be assigned to the four CH₂ in the incorporated ring-opened THF framework.

In order to confirm the reactivity of diazocarbonyl and carboxyl groups in THF, a Rh-catalyzed model reaction between diazoacetophenone 4 and 4-*tert*-butylbenzoic acid 5 was conducted in THF with a feed ratio of [4]/[5]/[Rh] = 1:10:0.01 (Scheme 4). As a result, THF-incorporated product 6 was obtained in a 75% yield based on 4, along with a product of the normal insertion 7 in a 5% yield. The observed high selectivity for the THF incorporation in the model reaction is in good accordance with the predominant presence of the THF-incorporated framework in the polymer **3a** main chain. The comparison of ¹H NMR spectra of **6** (Figure 2a) and **3a** (Figure 1) allows us to confirm the aforementioned assignment of the CH₂ in the ring-opened THF framework. In addition, a

Scheme 3. Polycondensation of Bis(diazoketone) 1 with Dicarboxylic Acids 2a-f and THF



Figure 1. ¹H NMR spectrum of **3a** (run 1 in Table 1).

 CH_2 signal at 5.56 ppm derived from diazo-bearing carbon in 7 in Figure 2b indicates that a very small signal at 5.57 ppm in the spectrum of **3a** should be ascribed to the presence of the normal insertion-derived framework in a very small extent. On the basis of the signal intensities of the CH_2 signals at 4.71 and 5.57 ppm in Figure 1, the ratio of the THF incorporation and normal insertion was determined to be 97:3 in **3a**.

When adipic acid (2e) was used as a representative aliphatic dicarboxylic acid in place of 2a for the polycondensation, a polymer 3e with $M_n = 9500$ was obtained in a similar manner (run 8 in Table 1). The ¹H NMR spectrum of 3e shown in Figure 3 indicates almost quantitative incorporation (98%) of ring-opened THF as well. The formation of a well-defined polymer from an aliphatic dicarboxylic acid is in sharp contrast

to the polymerization of 1 with diols,⁵ where aliphatic diols gave unidentifiable polymeric products in THF. The successful formation of a well-defined polymer from aromatic and aliphatic dicarboxylic acids ($pK_a = 4-4.5$) and aromatic diols ($pK_a =$ \sim 10), but not from aliphatic diols (p K_a = 15–16), suggests that an acidity of the OH group higher than a certain threshold may be required for the efficient formation of well-defined polymers in these polycondensations. Scheme 5 illustrates a proposed mechanism for the Rh-catalyzed simultaneous insertion of ringopened THF and diazoketone-derived carbene into a carboxyl O-H, where the most crucial step would be a nucleophilic attack of OH to the CH₂ at α -position of a Rh-coordinated THF. In the absence of THF, the insertion of diazocarbonyl compounds into O-H bonds has been reported to proceed via a nucleophilic attack of an oxygen of the O-H group to the carbene-carbon of the intermediate Rh-carbene complex.¹

Table 1 summarizes results of polycondensation of 1 with a series of aromatic and aliphatic dicarboxylic acids 2a-f in THF catalyzed by $Rh_2(OAc)_4$. As demonstrated in runs 1–4 and 8–10 where polymerization temperature was varied, polymer yield is highest with room temperature for both aromatic (terephthalic acid) and aliphatic (adipic acid) dicarboxylic acids.

Table 1. Polycondensation of 1 with 2a-f and THF Catalyzed by $Rh_2(OAc)_4^a$

							(THF		
							incorporated		
	dicarboxylic		yield			$M_{\rm w}/$	unit)/(normal	$T_{\rm g}$	
ru	ın acid	temp	(%)	product	$M_n^{\ b}$	$M_n^{\ b}$	insertion unit) c	$(^{\circ}C)$	
1	2a	RT	43	3a	10300	1.78	97:3	16	
2	^d 2a	RT	47	3a	8400	1.26	97:3		
3	2a	0 °C	17	3a	10700	1.64	84:16		
4	2a	50 °C	36	3a	10200	1.55	95:5		
5	2b	RT	34	3b	7500	1.61	97:3	17	
6	^e 2c	RT	31	3c	25300	3.30	95:5	23	
7	2d	RT	37	3d	10800	1.37	99:1	-16	
7	2d	RT	37	3d	10800	1.37	99:1	-16	
8	2e	RT	40	3e	9500	1.83	97:3	-50	
9	2e	0 °C	29	3e	9000	2.24	90:10		
1	0 2e	50 °C	35	3e	8900	1.75	95:5		
1	1 2f	RT	37	3f	7300	1.68	98:2	-41	

^{*a*} Polymerization period = 17 h; solvent (THF) = 5 mL, **1** = ca. 0.1 g, [**1**]/[dicarboxylic acid]/[Rh₂(OAc)₄] = 25:25:1. ^{*b*}M_n and M_w/M_n were obtained by GPC calibration using standard PMMAs in THF solution. ^{*c*} Determined by ¹H NMR. ^{*d*} Polymerization period = 72 h. ^{*e*}[**1**]/[**2c**]/[Rh₂(OAc)₄] = 25:38:1. Whereas M_{n} s remain nearly consistent with the variation of reaction temperature, the selectivity for the normal insertion is slightly enhanced when the polymerization was conducted at 0 °C. A longer reaction period (72 h in run 2) did not increase the $M_{\rm n}$ value, suggesting that diazocarbonyl groups at polymer chain ends would decompose at a certain point during the polymerization. Although, because of the removal of significant amount of low $M_{\rm n}$ part by preparative recycling GPC, yields of polymers are rather low, a variety of poly(ester ether ketone)s with $M_{\rm p} > 7300$ were obtained. In their ¹H NMR spectra (see Supporting Information), all the polymers show distinct signals derived from their structures with almost quantitative incorporation of ringopened THF (>95%, for polymers obtained at room temperature). When 4,4'-biphenyldicarboxylic acid (2c) was used in a standard feed ratio of [1]/[2c] = 1:1, the resulting product was not soluble in common organic solvent, probably because of the rigidity imparted by the biphenyl framework. Accordingly, to lower the $M_{\rm n}$ of the product, the polymerization in run 6 in Table 1 was conducted in a feed ratio of [1]/[2c] =



Figure 2. ¹H NMR spectra of **6** (a) and 7 (b).

Scheme 4. Model Reaction of Diazoketone with Carboxylic Acid and THF



1:1.5, and a soluble product was obtained expectedly. The GPCdetermined M_n of 25 300 could be much higher than the actual value because the rigid main chain structure of the polymer would render the GPC measurement inappropriate for determination of M_n .

Glass transition temperatures of the polymers determined by differential scanning calorimetry (DSC) analysis are listed in Table 1. As expected, polymers derived from aromatic dicarboxylic



Figure 3. ¹H NMR spectrum of 3e (run 8 in Table 1).

Scheme 5. Proposed Mechanism for Rh-Catalyzed Simultaneous Insertion of Ring-Opened THF and Diazoketone-Derived Carbene into Carboxyl O–H



acids (2a-d) exhibit much higher $T_{\rm g}$ s than those from aliphatic ones (2e and 2f). Thus, the availability of aliphatic dicarboxylic acids as a monomer enables us to prepare polymers with a wide range of $T_{\rm g}$ (-50-23 °C) by the polymerization.

Polymerization with THP. Next, polymerization of 1 with dicarboxylic acids was conducted in tetrahydropyran (THP) (Scheme 6, Table 2). As shown in run 1 in Table 2, the polymerization of 1 with terephthalic acid (2a) in THP catalyzed by $Rh_2(OAc)_4$ proceeded to give a polymer 8a with $M_p = 11600$. The ¹H NMR spectrum of 8a in Figure 4 exhibits five signals with a same intensity at 4.35, 3.60, 1.82, 1.74, and 1.56 ppm, which can be assigned to CH₂s of ring-opened framework of THP. In contrast to the spectrum of 3a and 3e in Figures 1 and 3, the intensity of the signal at 5.57 ppm derived from the normal insertion unit is obviously higher than that of the signal at 4.69 ppm derived from THP incorporation, indicating that normal insertion is preferred in this polymerization, as observed in the polymerization of 1 with aromatic diols in THP.⁵ The ratio calculated from the signal intensities in this case is [THPincorporation]/[normal insertion] = 33:67. Again, a model reaction of 4 with 5 in THP was performed, in order to check

Table 2. Polymerization of 1 with 2a, 2b, 2d-f, and THP Catalyzed by $Rh_2(OAc)_4$ at Room Temperature^{*a*}

					(THP			
						incorporated		
	dicarboxylic	yield			$M_{\rm w}/$	unit)/(normal	T_{g}	
run	acid	(%)	product	$M_{\rm n}^{\ b}$	$M_n^{\ b}$	insertion unit) ^c	$(^{\circ}C)$	
1	2a	46	8a	11600	1.41	33:67	24	
2	2b	33	8b	6600	1.52	35:65	16	
3	2d	40	8d	11500	1.32	41:59	12	
5	2e	29	8e	9000	1.45	41:59	-5	
6	2f	45	8f	6200	1.37	51:49	-7	

^{*a*} Polymerization period = 17 h; solvent (THP) = 5 mL, **1** = ca. 0.1 g, [1]/[dicarboxylic acid]/[Rh₂(OAc)₄] = 25:25:1. ^{*b*} M_n and M_w/M_n were obtained by GPC calibration using standard PMMAs in THF solution. ^{*c*} Determined by ¹H NMR.

Scheme 6. Polycondensation of Bis(diazoketone) with Dicarboxylic Acids and THP



8a, 8b, 8d-f: (x' + x") / (y' + y") = 33:67 ~ 51:49







the selectivity of this reaction and to confirm the assignments of the repeating unit signals. As expected from the above polymerization result, THP-incorporated (9) and normal insertion (7) products were obtained in 55% and 45% yields, respectively, clearly indicating the higher normal insertion selectivity in THP compared to that in THF. The selectivity trend was generally retained in the polymerizations in Table 2, although the selectivity varies considerably depending on the dicarboxylic acids employed. Peak assignments for the THP-incorporated repeating unit were confirmed from comparison between the spectra of 8a in Figure 4 and 9 in Figure 5.

As summarized in Table 2, polymers with $M_n = 6000-12\,000$ were obtained in 30–50% yields after removing the low M_n part by preparative recycling GPC. The structures of the polymers were characterized by their ¹H NMR spectra (see Supporting Information). As for T_g s of the polymers in Table 2, a similar trend as that in Table 1 is observed with a narrower temperature range (-7 to 24 °C).

CONCLUSIONS

We have demonstrated that bis(diazoketone) (1) can be used as a monomer for three-component polycondensation with dicarboxylic acid and THF to afford a totally new type of poly(ester ether ketone) as a result of a unique propagation with simultaneous insertion of ring-opened THF and diazoketonederived carbene into carboxyl O–H. When THP was used as a solvent and comonomer in place of THF, normal insertion of diazoketone-derived carbene alone into the carboxyl O–H competes with the simultaneous insertion. Although the polymerization mechanism is basically similar to that reported in our previous publication using aromatic diols,⁵ the availability of aliphatic dicarboxylic acids as a monomer for the polymerization here is an important advantage, which allows us to prepared polymers with a wide range of $T_{\rm g}$ s, for example. These results show the potential of bis(diazocarbonyl) compounds as a monomer for polycondensation, where the characteristic reactivity of diazocarbonyl group can be utilized for the formation of new polymers. Further application of the use of bis-(diazocarbonyl) compounds for polymer synthesis is underway in our laboratory.

EXPERIMENTAL SECTION

Materials. THF was dried over Na/K alloy and distilled before use. THP (TCI, >98.0%) was dried over CaH₂ and used without further purification. Terephthalic acid (Nacalai, 98%), 1,4-naphthalenedicarboxylic acid (Wako, 95%), 4,4'-biphenyldicarboxylic acid (TCI, >95%), adipic acid (Nacalai, 99.5%), succinic acid (Wako, 99%), 4-*tert*-butylbenzoic acid (Kanto Chemical, 98%), and Rh₂(OAc)₄ (AZmax, 99%) were used as received. Bis(diazoketone) (1),⁵ diazoacetophenone (4),⁷ and bis(4-carboxyphenyl)dimethylsilane (2d)⁸ were prepared according to the literature.

Measurements. ¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded on a Bruker Avance 400 spectrometer using tetramethysilane as an internal standard in chloroform-d (CDCl₃) 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 μ m average particle size, exclusion molecular weight of 600K for polystyrene) and Styragel HR2 (Waters; 300 mm × 7.8 mm i.d., 5 μ m 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 = 22 600, M_w/M_n = 1.02, M_p = 5720, M_w/M_n = 1.06, M_p = 2400, M_w/M_n = 1.08) 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 \times 20 mm i.d., exclusion molecular weight of 70K for polystyrene) and a JAIGEL-2H (600 mm \times 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 \times 20 mm i.d., exclusion molecular weight of 1K for polystyrene) for the products of model reactions **6**, **7**, and **9**, using CHCl₃ 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.

Thermal properties of the polymers were measured using a differential scanning calorimeter, Seiko DSC 6200, under a nitrogen atmosphere at a $10 \,^{\circ}$ C/min heating rate.

Elemental analyses were performed on a YANAKO MT-5 analyzer at Integrated Center for Science (INCS) in Ehime University.

Detailed characterization data for all the polymers and model reaction products are described in the Supporting Information.

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

Under a N_2 atmosphere, 1 (84.1 mg, 0.193 mmol), 2a (32.1 mg, 0.193 mmol), and $Rh_2(OAc)_4$ (1.7 mg, 3.9×10^{-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 (1 N, 10 mL), aqueous solution of HCl (1 N, 10 mL), and CHCl₃ (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 CHCl₃. After the combined organic layer was washed with 50 mL of 1 N aqueous solution of HCl, 50 mL of saturated aqueous solution of NaCl, it was dried over Na₂SO₄. 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 (56 mg, 43%).

Other Rh-catalyzed polymerizations of bis(diazocarbonyl) compounds with dicarboxylic acids in cyclic ether were carried out in a similar procedure.

Procedure for Model Reactions. Under a N₂ atmosphere, diazoacetophenone (4) (308 mg, 2.11 mmol), 4-*tert*-butylbenzoic acid (5) (3.76 g, 21.1 mmol), and Rh₂(OAc)₄ (10.3 mg, 2.32×10^{-2} mmol) were placed in a Schlenk tube. After THF (45 mL) was added, the mixture was stirred at room temperature for 17 h. After work-up procedure for the above polymerization was applied, purification with preparative recycling GPC in CHCl₃ afforded **6** (583 mg, 1.58 mmol) and 7 (31.9 mg, 0.107 mmol) in 75% and 5% yield, respectively.

The model reaction of 4 and 5 in THP was carried out in a similar procedure.

ASSOCIATED CONTENT

Supporting Information. ¹H and ¹³C NMR spectra and elemental analysis data for products of model reactions **6**, **7**, and **9**; ¹H NMR spectra for all the polymers in Tables 1 and 2; peak assignments of NMR spectra for all the model reaction products

and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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