SHORT COMMUNICATIONS

A Novel Synthesis of Polyesters by Insertion Reaction of Oxiranes into Polyanhydrides

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Polyester synthesis can be categorized into three different methods. The first method is polycondensations of dicarboxylic acids, dicarboxylic acid chlorides, or dicarboxylic esters with diols.¹ The second method is polycondensations of alkylene dihalides with sodium dicarboxylates using phase transfer catalysts,² or the reactions of alkylene dihalides with dicarboxylic acids using 1,8-diazabicyclo[5.4.0]-7-undecene as a strong organic base.³ The third method is ring-opening polymerization of cyclic lactone monomers,⁴ or by ring-opening alternating copolymerizations of oxiranes with carboxylic anhydrides.⁵

Recently, polyanhydrides⁶ have been of interest as biodegradable polymers,⁷ since the introduction of anhydride linkages into polymer backbones enhanced the rate of biodegradation in nature. However, there is no report on the chemical modification of polyanhydrides and synthesis of polymers using anhydride groups in the polymer main chains. We aimed at anhydride linkages in the polymer main chains, and designed a novel synthetic route of polyesters by the insertion of oxiranes into polyanhydrides. In this communication, we report on a novel and successful synthesis of polyesters by the insertion reaction of oxiranes into polyanhydrides.

EXPERIMENTAL

Materials

Solvents were dried using P₂O₅, CaH₂, or Na metal wire and purified by distillation before use. Tetrabutylammonium bromide (TBAB) was recrystallized twice from ethyl acetate. Tetrabutylphosphonium bromide (TBPB), 18-crown-6 (18-C-6), and potassium bromide (KBr) were used without further purification. Valeric anhydride (**1**) was dried using P₂O₅ and purified by distillation before use. Glycidyl phenyl ether (**2a**), butyl glycidyl ether (**2b**), styrene oxide (**2c**), and cyclohexene oxide (**2d**) were dried using CaH₂ and purified by distillation. Poly(sebacic anhydride) (**4**) (η_{red} : 0.19 dL g⁻¹, measured at 0.5 g dL⁻¹ in CHCl₃ at 30°C) donated from Okamura Oil Mill. Ltd. (Kashiwara-city, Japan) was dried *in vacuo* for 3 days. Polyanhydride (**6**) was prepared according to the reported method.⁸

Measurement

Infrared (IR) spectra were measured on a JASCO Model IR-700 spectrometer. The ¹H NMR and the ¹³C NMR spectra were recorded on a JEOL Model JNM FX-200 (200 MHz) instrument in CDCl₃ using Me₄Si (TMS) as an internal standard. The molecular weights of the polymers were estimated by gel permeation chromatography (GPC) with the use of a Tosoh Model HLC-8120 GPC equipped with a refractive index detector using TSK gel columns (eluent: tetrahydrofuran (THF), calibrated using narrow molecular weight polystyrenes as standards).

Model Reaction

The reaction of **1** (0.187 g; 1 mmol) with **2a** (0.150 g; 1 mmol) was performed using TBAB (0.016 g, 0.05 mmol) as a catalyst without solvent at 100°C for 1 h in the sealed tube. The reaction mixture was diluted with ethyl acetate, washed thrice with water, and the organic phase was dried using anhydrous MgSO₄, after which MgSO₄ was filtered off. The organic solvent was then evaporated *in vacuo* and purified by a silica gel column chromatography using chloroform as the eluent. Isolated yield of the product was 0.327 g (97%). IR (neat, cm⁻¹): 1741 (C=O, ester), 1598 (C=C, aromatic), 1239 (C–O–C, ester), and 1170 (C–O–C, ether). ¹H NMR [200 MHz, CDCl₃, TMS, (ppm)]: 0.91 (t, *J* = 7.62 Hz, 6.0H, –CH₃), 1.33 (m, 4.0H, CH₂CH₃), 1.60 (m, 4.0H, CH₂CH₂CH₂), 2.32 (m, 4.0H, OCOCH₂CH₂), 4.11 (d, *J* = 5.37 Hz, 2.0H, CHCH₂OPh), 4.49 (dd, *J* = 5.86, 11.72 Hz, 1.0H, CHCH₂OCO), 4.45 (dd, *J* = 4.39, 11.72 Hz, 1.0H, CHCH₂OCO), 5.39 (m, 1.0 H, CH₂CHO), and 6.88–7.32 (m, 5H, aromatic H). ¹³C NMR [50 MHz, CDCl₃, (ppm)]: 13.69 (CH₃), 22.21 (CH₂CH₃), 26.97 (CH₂–CH₂CH₂), 33.82, 33.98 (COCH₂), 62.28 (CHCH₂OCO), 66.07 (CHCH₂OPh), 69.56 (CH), 114.61, 121.33, 129.52, 158.34 (aromatic C), 173.06, and 173.3 (C=O). Anal. Calcd. for C₁₉H₁₈O₅: C, 67.83%; H, 8.39%. Found: C, 67.80%; H, 8.25%.

Typical Procedure for the Insertion Reaction of Oxirane into Polyanhydride

Polymer **4** (0.184 g; 1 mmol as anhydride group), oxirane **2a** (0.150 g; 1 mmol), and TBAB (0.016 g, 0.05 mmol) were all charged into a glass tube in a dry

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Scheme 1.

Scheme 2.

box, after which the tube was evacuated, then sealed using a gas torch. Then, the reaction was carried out in the sealed tube at 100°C for 24 h under stirring. The reaction mixture was dissolved with chloroform, washed three times with water. The organic phase was then poured into *n*-hexane to precipitate the polymer. The resulting polymer was reprecipitated twice from chloroform into *n*-hexane, and dried *in vacuo*. The yield of the corresponding polymer (**5a**) was 0.332 g. The number-average molecular weight (M_n) of polymer **5a**, estimated by GPC based on polystyrene standards, was 9820 (M_w/M_n : 1.70). The reduced viscosity of the obtained polymer, measured at a concentration of 0.5 g dL⁻¹ in CHCl₃ at 30°C, was 0.18 dL g⁻¹. The degree of insertion (D.I.) of oxirane into the polymer was 100%, which was calculated from the intensity ratio of ¹H NMR spectrum. IR (film, cm⁻¹): 1740 (C=O, ester), 1598 (C=C, aromatic), 1239 (C-O-C, ester), and 1171 (C-O-C, ether). ¹H NMR [200 MHz, CDCl₃, TMS, (ppm)]: 1.26 (bs, 8H, CH₂), 1.35–1.79 (m, 4.0H, OCO-CH₂CH₂), 2.10–2.21 (m, 4.0H, OCOCH₂CH₂), 4.10 (d, *J*=5.37 Hz, 2.0H, CHCH₂OPh), 4.28 (dd, *J*=5.86, 11.72 Hz, 1.0H, CHCH₂OCO), 4.43 (dd, *J*=3.91, 11.72 Hz, 1.0H, CHCH₂OCO), 5.37 (m, 1.0H, CH₂-CHO), and 6.87–7.36 (m, 5.0H, aromatic H). ¹³C NMR [50 MHz, CDCl₃, (ppm)]: 24.76 (CH₂), 29.00 (COCH₂CH₂CH₂), 33.96 (COCH₂CH₂CH₂), 34.04, 34.13 (COCH₂), 62.25 (CHCH₂OCO), 65.97 (CH-CH₂OPh), 69.56 (CH₂CHO), 114.50, 121.26, 129.45, 158.24 (aromatic C), 172.96, and 173.23 (C=O). Anal. Calcd. for C₁₉H₂₆O₅: C, 68.24%; H, 7.84%. Found: C, 67.95%; H, 7.83%.

RESULTS AND DISCUSSION

The addition reaction of oxirane **2a** with low molecular weight acid anhydride **1** was examined as a model reaction for the insertion reaction of oxirane into the anhydride linkage in the polymer main chain. The reaction proceeded without solvent at 100°C for 1 h to give a product in 97% yield. The obtained product was identified by IR, ¹H NMR, and ¹³C NMR spectra,

and elemental analysis, and it was found that the corresponding ester (**3**) was obtained as shown in Scheme 1.

On the basis of the above result, the insertion reaction of various oxiranes into the anhydride linkage of **4** was examined under certain conditions, and these results are summarized in Table I. When the insertion reaction of **2a** into **4** was carried out using 5 mol% of TBAB as a catalyst at 100°C for 24 h without solvent, the polymer **5a** was obtained in good yield. The IR spectrum of the obtained polymer showed new peaks at 1740 cm⁻¹ due to C=O stretching of ester linkage and at 1599 cm⁻¹ due to C=C stretching of aromatic group, and showed complete disappearance of the peak at 1810 cm⁻¹ due to C=O stretching of anhydride linkage. In the ¹H NMR spectrum of the polymer, corresponding aromatic proton signals and aliphatic proton signals due to the ring-opened structure of **2a** and starting polymer skeleton were observed, in which the intensity ratio of the aromatic protons and the aliphatic protons was equal to the calculated value assuming the quantitative insertion reaction. In the ¹³C NMR spectrum of the polymer, the signal of the C=O carbon of anhydride at 169.38 ppm of **4** shifted to 172.92 and 173.23 ppm due to the C=O carbon of the ester group. Furthermore, the elemental analysis of the polymer agreed with the calculated value. Thus, it was found that the insertion reaction of **2a** into **4** proceeded quantitatively to give the corresponding polyester **5a** as shown in Scheme 2.

As summarized in Table I, the reaction of **2a** with **4** proceeded quantitatively, when TBPB or crown ether complex (18-C-6/KBr) were used as catalysts under the same conditions. The insertion reaction of **2a** into **4** also occurred with 100% degree of insertion, when the reactions were performed in various organic solvents such as toluene, anisole, *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), and *N*-methylpyrrolidone (NMP). However, M_n s of the resulting **5a** were lower than that of the polymer obtained without solvent. It seems that hydrolysis of anhydride linkage in **4** might occur as a side reaction induced by a little water in the solvent during the insertion reaction of **3a**.

Table I. Insertion reaction of oxiranes into poly(sebacic anhydride)^a

Oxirance	Cat.	Solv.	Yield ^b		D.I. ^c %	$M_n^d \times 10^{-3}$	M_w/M_n^d	η_{red}^e dL g ⁻¹
			g	%				
2a	TBAB	None	0.332	99	100	9.82	1.70	0.18
2a	TBPB	None	0.331	99	100	9.57	1.60	0.18
2a	18-C-6/KBr	None	0.335	100	100	9.21	1.63	0.18
2a	TBAB	Toluene	0.328	98	100	7.66	1.71	0.13
2a	TBAB	Anisole	0.329	99	100	8.54	1.58	0.14
2a	TBAB	DMF	0.325	97	100	7.13	1.61	0.13
2a	TBAB	DMAc	0.313	94	100	7.04	1.71	0.14
2a	TBAB	NMP	0.312	93	100	6.56	1.66	0.13
2b	TBAB	None	0.294	88	100	7.58	1.46	0.18
2c	TBAB	None	0.293	88	100	5.90	1.40	0.13
2d	TBAB	None	0.274	82	100	4.71	1.36	0.14

^a The reaction was carried out with **2a** (0.150 g; 1 mmol) and **4** (0.184 g; 1 mmol as anhydride linkage) using 5 mol% of catalyst in bulk at 100°C for 24 h or in solvent (2 mol L⁻¹) at 80°C for 24 h. ^b Insoluble parts in *n*-hexane. ^c Degree of insertion was calculated by ¹H NMR. ^d Estimated by GPC (THF) based on polystyrene standards. ^e Measured at a concentration of 0.5 g dL⁻¹ in CHCl₃ at 30°C.

Scheme 3.

The insertion reactions of various oxiranes such as **2b**, **2c**, and **2d** into **4** were examined without solvent using 5 mol% of TBAB as the catalyst under the same conditions. As a result, it was found that the insertion reactions of such oxiranes into **4** also proceeded quantitatively to give the corresponding polyesters (**5b**, **5c**, and **5d**).

The reaction of poly(aromatic anhydride) (**6**) with **2a** was conducted using 5 mol% of TBAB in chlorobenzene at 110°C for 24 h. The IR and ¹H NMR data of the obtained polymer proved that **2a** was inserted into the anhydride linkage of **6** with 100% degree of insertion to produce the corresponding polyester as shown in Scheme 3. Moreover, the M_n of the resulting polymer was 11000 which was higher than that of the starting **6** (8600). This means that the insertion reaction of **2a** into **6** proceeded quantitatively without side reactions such as hydrolysis of anhydride linkage.

From all these results, it is concluded that novel synthetic method for polyesters by the insertion reaction of oxiranes into polyanhydrides was found, and this method can be successfully applied to the synthesis of various functional polyesters.

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