Synthesis of Polyesters from Terephthalaldehyde and Isophthalaldehyde through Tishchenko Reaction Catalyzed by the Ethylmagnesium Bromide–(−)-Sparteine Complex and Aluminum Alkoxides

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ABSTRACT: Terephthalaldehyde (TPA) and isophthalaldehyde (IPA) were polymerized with the ethylmagnesium bromide–(−)-sparteine (EtMgBr–Sp) complex and aluminum alkoxides as catalysts to obtain polyesters through the Tishchenko reaction. The polyester prepared from TPA with the EtMgBr–Sp complex was characterized by IR, FD mass, ^{1}H and ^{13}C NMR spectroscopies, and was found to be a random copolymer composed of oxycarbonyl-1,4-phenylenemethylene and terephthaloyloxymethylene-1,4-phenylenemethyleneoxy units. The polyesters possessed terminal formyl groups and were further polymerized with the EtMgBr–Sp complex. On the basis of the results, a possible mechanism for the polymerization is discussed.

KEY WORDS Terephthalaldehyde / Isophthalaldehyde / Tishchenko Reaction / Sparteine / Polyester / Aluminum Alkoxides

Condensation reactions of aldehydes to produce esters are known as the Tishchenko reaction,[1] which are catalyzed by various metal complexes[2] including aluminum alkoxides,[3] lanthanoid complexes,[4] and ruthenium complexes.[5] The metal complexes may be used as the catalysts for the syntheses of polyesters from dialdehydes such as terephthalaldehyde (TPA) through the Tishchenko reaction. However, a few papers describe the polyester syntheses using the metal complexes. Mitin et al.[6] and later, Sweeny[7] reported the polymerization of TPA to polyesters by means of the Tishchenko reaction with aluminum ethoxide and alkylaluminums, respectively. The polyesters were examined by IR, X-ray diffraction patterns, and differential thermal analysis (DSC), and their structures were postulated to be not pure poly(oxycarbonyl-1,4-phenylenemethylene) (**1**), but a random copolymer composed of oxycarbonyl-1,4-phenylenemethylene and terephthaloyloxymethylene-1,4-phenylenemethyleneoxy (4-xylyleneterephthalate) units (**2**). Very recently, Yamamoto and co-workers also prepared polyesters with ruthenium complexes similar in structures to those reported by Sweeny from TPA through the Tishchenko reaction.[8]
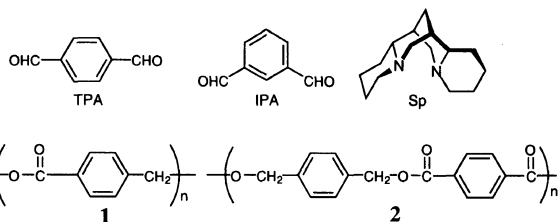
Previously, we found that an optically active poly(3-phenylpropanal) with a predominant one-handed helical structure could be obtained by the asymmetric polymerization of 3-phenylpropanal (3-PPA) with the ethylmagnesium bromide–(−)-sparteine (EtMgBr–Sp) complex in toluene at −78°C.[9] The polymerization was also initiated with 3-phenylpropoxymagnesium bromide and terminated by the Tishchenko reaction to afford the polymer having an ester terminal at ω-end. In the polymerization, a large amount of 3-phenylpropyl 3-phenylpropanoate was produced as a side product through the Tishchenko reaction. These results indicate that the EtMgBr–Sp complex can be used as a novel catalyst for the enantioselective Tishchenko reaction of racemic aldehydes such as (±)-2-phenylpropanal (2-PPA). Actually, the EtMgBr–Sp complex catalyzed the enantioselective Tishchenko reaction to afford optically active 2-phenylpropyl 2-phenylpropanoate. Enantiomeric excess of optically active 2-phenylpropyl 2-phenylpropanoate obtained achieved up to 65%.[10] In both reactions, 3-phenyl- or 2-phenylpropoxymagnesium bromide–Sp complex is a real intermediate and further reacts with 3-PPA or 2-PPA followed by the Tishchenko-type termination again with the aldehydes to afford the optically active poly(3-PPA) having an ester terminal at ω-end and 2-phenylpropyl 2-phenylpropanoate, respectively, as a cyclic mechanism.[9,10] These results led us to apply our system to prepare polyesters from dialdehydes such as TPA and isophthalaldehyde (IPA) through the Tishchenko reaction. (−)-Sparteine is a commercially available chiral diamine and has been widely used for asymmetric synthesis,[11] helix-sense-selective polymerization,[12] and enantiomer-selective polymerization of racemic methacrylates.[13]

In the present study, we performed the polymerization of TPA and IPA with the EtMgBr–Sp complex and aluminum alkoxides through the Tishchenko reaction. The structures of polyesters and the mechanism of the polymerization were elucidated on the basis of IR, 1D and 2D NMR, and FD-mass spectroscopies.

EXPERIMENTAL

Materials

TPA, IPA, terephthalic acid, and 4-carboxybenzaldehyde were purchased from Tokyo Kasei and used as

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received. 1,4-Bis(hydroxymethyl)benzene, 4-(chloromethyl)benzoic acid, and Me_3Al in toluene (2 M) were obtained from Aldrich. (R)-$(+)$-1,1′-Bi-2-naphthol ($[\alpha]_D^{25}$ $+32°$, c 1.5 g dl^{-1}, tetrahydrofuran (THF)) was obtained from Kankyo Kagaku Center. EtMgBr was prepared by the usual method using magnesium and ethyl bromide in dry ether under nitrogen atmosphere and its concentration was determined to be 0.92 M by acid and base titration. Toluene was purified in the usual manner, mixed with a small amount of butyllithium, and distilled under high vacuum just before use. THF was dried over sodium benzophenone ketyl before distillation and further distilled over $LiAlH_4$ under high vacuum just before use. Dichloromethane and chloroform were dried over CaH_2 and distilled under high vacuum just before use. $(-)$-Sparteine (Sigma) was dried over CaH_2 for 2 h with stirring and distilled under reduced pressure (bp 92.0—93.5°C/0.06 mmHg). Aluminum isopropoxide was from Tokyo Kasei and used as a toluene solution (2 M).

Preparation of Catalysts

The EtMgBr–Sp complex was prepared by mixing EtMgBr with 1.2 equivalent ($-$)-Sp in toluene at room temperature under dry nitrogen, and the concentration of the complex was adjusted to 0.30 M. The complex ((R)-BIN-Al) of (R)-$(+)$-1,1′-bi-2-naphthol with Me_3Al was prepared by mixing (R)-$(+)$-1,1′-bi-2-naphthol in dry toluene with 1 equivalent Me_3Al in toluene at room temperature under dry nitrogen. Methane gas was produced immediately. The mixture was stirred for 1 h at room temperature and used as a catalyst for the polymerization.

Polymerization Procedure

Polymerization was carried out in a glass ampule under dry nitrogen atmosphere. A typical polymerization procedure is described below. TPA (1.0 g, 7.5 mmol) was placed in an ampule, and was dried on a vacuum line. After the ampule was flushed with dry nitrogen, a three-way stopcock was attached to the ampule. Chloroform (10 ml) was then added with a hypodermic syringe. The monomer solution was cooled to 0°C, and the prescribed initiator solution was added to the mixture to initiate the polymerization with a syringe. After 30 min, the ampule was placed in a water bath at 30°C or 50°C. The molar ratio of monomer to EtMgBr or aluminum alkoxide was 50 unless otherwise noted. The reaction was terminated with a few drops of methanol containing a small amount of HCl. The polymer was precipitated in a large amount of methanol, separated by centrifugation, and dried *in vacuo* at 50°C for 3 h.

Spectroscopic data of poly(TPA) (run 4 in Table I). IR (KBr): 1717 cm^{-1} (C=O), 1270, 1100 cm^{-1} (C–O); ^{1}H and ^{13}C NMR (see Figure 2 (a and b)). *Anal.* Calcd for $(C_8H_6O_2)_n$: C, 71.63; H, 4.51%. Found: C, 69.59; H, 4.43%.

Preparation of Model Compounds and Polymers

Poly(terephthaloyloxymethylene-1,4-phenylenemethyleneoxy). To a solution of 1,4-bis(hydroxymethyl)benzene (1.4 g, 10 mmol) and triethylamine (28 mmol) in dry dichloromethane (50 ml), terephthaloyl dichloride (2.0 g, 10 mmol) was added under nitrogen. After the mixture

was stirred at 40°C for 3 h, it was cooled to room temperature and poured into methanol (200 ml). The polymer precipitated was separated by centrifugation, washed with methanol, and dried *in vacuo* at 50°C for 3 h. The polymer obtained was not soluble in common organic solvents. The yield of the polymer was 2.6 g (98%). IR (KBr): 1717 cm^{-1} (C=O), 1272, 1102 cm^{-1} (C–O).

Poly(oxycarbonyl-1,4-phenylenemethylene) (**1**). This polymer was prepared according to the reported procedure[14] by the polymerization of 4-(chloromethyl)benzoic acid in the presence of triethylamine in THF under reflux. IR (KBr): 1717 cm^{-1} (C=O), 1272, 1102 cm^{-1} (C–O).

Model compounds, dimethyl terephthalate (**3**), 1,4-bis(acetyloxymethyl)benzene (**4**), and 4-(hydroxymethyl)benzoic acid (**5**) were prepared by usual methods or according to the reported procedure.

(**3**): mp 140—142°C; ^{1}H NMR (CDCl$_3$): δ 3.95 (s, 3H, –CH$_3$), δ 8.10 (s, 4H, –Ph); ^{13}C NMR (CDCl$_3$): 166.29, 133.92, 129.54, 52.35; IR (KBr): 1721 cm^{-1} (C=O); EI-MS: 194 (M$^+$).

(**4**): mp 42—43°C; ^{1}H NMR (CDCl$_3$) δ 2.10 (s, 3H, –CH$_3$), δ 5.10 (s, 4H, –CH$_2$–Ph), δ 8.10 (s, 4H, –Ph); ^{13}C NMR (CDCl$_3$) 170.85, 136.04, 128.45, 65.85, 20.89; IR (KBr) 1723 cm^{-1} (C=O); EI-MS: 222 (M$^+$).

(**5**): mp 175—177°C (lit.[15] 174—180°C); ^{1}H NMR (dimethyl sulfoxide (DMSO)-d_6): δ 3.38 (s, 2H, –CH$_2$OH), δ 5.20 (s (broad), 1H, –OH), δ 7.44—7.92 (d, –Ph, 4H); ^{13}C NMR (DMSO-d_6): 167.59, 148.04, 129.46, 129.36, 126.46; IR (KBr): 3420 (–OH), 1720 cm^{-1} (C=O); EI-MS: 152 (M$^+$).

Alkaline Hydrolysis of the Polyester Obtained with the EtMgBr–Sp Complex

Poly(TPA) (0.50 g, run 4 in Table I) was dispersed in ethanol (15 ml) containing KOH (1 g) at room temperature. After 6 h stirring, the solution was poured into H_2O, and then extracted with ether. The ether solution was dried over Mg_2SO_4, and the ether was removed by evaporation, yielding oily residues (ca. 0.06 g, ca. 10% yield based on the poly(TPA)). The aqueous layer was acidified with 1N HCl solution and the mixture was extracted with ether. The ether solution was dried over Mg_2SO_4, and the ether was removed by evaporation, giving a crystalline residue (ca. 0.5 g, ca. 88%). Each product obtained from the ether layer and aqueous layer was dissolved in DMSO-d_6, and ^{1}H, ^{13}C NMR, and electron impact (EI) mass spectra were measured. The data are given in Figure 3.

Measurements

One dimensional ^{1}H and ^{13}C NMR and two dimensional COSY spectra were taken on a Varian VXR-500S (500 MHz for ^{1}H and 125 MHz for ^{13}C) or a Varian GEMINI 2000 (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer in CDCl$_3$ or DMSO-d_6. TMS was the internal standard. Field desorption (FD) and EI mass spectra were recorded on a JEOL JMS-AX505HA spectrometer. Thermogravimetric analysis (TGA) was made on a Regaku DSC-8230 apparatus with heating rate 10°C min^{-1} in the temperature range of 30—500°C. IR spectra were recorded using a JASCO Fourier Trans-

form IR-7000 spectrophotometer with a JASCO PTL-396 data processor. Gel permeation chromatography (GPC) was performed using a JASCO 880-PU chromatography equipped with a UV-visible (254 nm; JASCO 875-UV) detector. GPC columns, Shodex KF-802.5 (30 × 0.72 (i.d.) cm) and AC-80 (50 × 0.72 (i.d.) cm) were connected in series and chloroform was used as the eluent at a flow rate of 1.0 ml min^{-1}. The molecular weight calibration curve was obtained with standard polystyrenes (Tosoh).

RESULTS AND DISCUSSION

Polymerization of TPA and IPA with the EtMgBr–Sp Complex and Structure of Polymers

Table I shows the results of polymerization of TPA and IPA with the EtMgBr–Sp complex under various reactions conditions together with those of polymerization by uncomplexed EtMgBr in chloroform. In THF at 0°C, methanol-insoluble polymers were not obtained with the EtMgBr–Sp complex. However, poly(TPA) was obtained in a good yield in chloroform and dichloromethane at 0°C or at higher temperatures, although the number-average molecular weight (M_n) of poly(TPA)s was relatively low (1500—2800) compared with reported values (900—5200)[8] probably because the polymers precipitated during the polymerization in the solvents used. The poly(TPA)s obtained with the EtMgBr–Sp complex were soluble in chloroform and dichloromethane, but insoluble in benzene, toluene, and THF. However, poly(TPA)s precipitated during the polymerization even in chloroform. This may be due to aggregation of the active species of the polymer chain ends, since the polymers were soluble in chloroform after isolation. The molecular weight of poly(TPA)s increased when a mixture of chloroform and THF was used as the solvent (run 9—12 in Table I). No polymer was obtained using uncomplexed EtMgBr alone as the catalyst in chloroform (run 6 in Table I). Moreover, polymeric products were not produced by polymerization of TPA with the EtMgBr-(+)-(2S,3S)-2,3-dimethoxy-1,4-bis(dimethylamino)butane or -N,N,N',N'-tetramethylethylene-

diamine complexe in chloroform at 30°C. These results clearly indicate that sparteine is essential and very specific for the production of poly(TPA).[9,10] Polymerizability of IPA with the EtMgBr–Sp complex in dichloromethane at 30°C was lower than that of TPA and a very small amount of polymer was obtained (runs 15 and 16 in Table I).

Figure 1 shows the IR spectrum of poly(TPA) obtained with the EtMgBr–Sp complex in chloroform at 30°C for 28 h (run 4 in Table I). The spectrum exhibited a characteristic absorption at 1717, and 1270 and 1100 cm^{-1} due to C=O and C–O stretchings, respectively. The IR spectral pattern of the polymer closely resembles the IR spectra of poly(oxycarbonyl-1,4-phenylenemethylene) (1) prepared from the polymerization of 4-bromomethylbenzoic acid by Pinkus, et al.[14] and polyesters prepared from TPA with alkylaluminums by Sweeny.[7] This indicates that the poly(TPA) obtained with the EtMgBr–Sp complex is a polyester. The polyester appears to be produced by the Tishchenko reaction which can catalytically convert formyl groups into ester groups.[9,10] The EtMgBr–Sp complex is found to be a novel catalyst to the polyester synthesis from a dialdehyde.

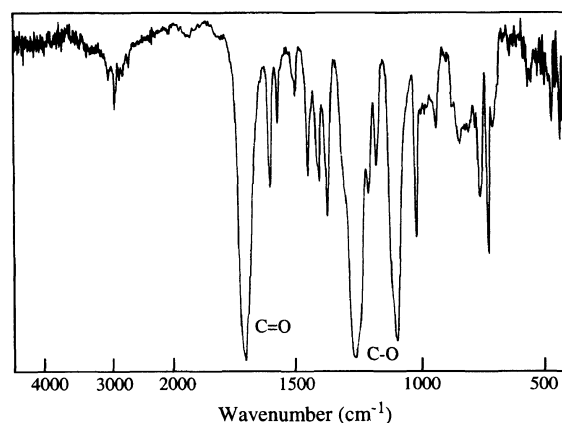The ^1H (a) and ^{13}C (b) NMR spectra of poly(TPA)

Figure 1. IR spectrum of poly(TPA) (run 4 in Table I) obtained with the EtMgBr–Sp complex.

Table I. Polymerization of TPA and IPA with the EtMgBr–Sp complex under various reaction conditions[a]

Run	Solvent[b]	Catalyst/mol%	Temp/°C	Time/h	Yield/%[c]	$\bar{M}_n \times 10^{-3}$[d]	$\bar{M}_w/\bar{M}_n$[d]
1	THF	2	0	28	0	—	—
2	THF	2	30	28	7.8	1.5	1.28
3	CHCl$_3$	2	0	28	67.0	1.9	1.33
4	CHCl$_3$	2	30[e]	28	79.5	2.0	1.28
5	CHCl$_3$	4	50[e]	18	53.0	2.0	1.26
6[f]	CHCl$_3$	2	30[e]	118	0	—	—
7	CH$_2$Cl$_2$	2	30[e]	18	53.1	2.1	1.21
8	CH$_2$Cl$_2$	4	30[e]	18	65.3	2.1	1.23
9	A	2	25[e]	18	9.2	2.5	1.28
10	A	2	50[e]	18	74.3	2.6	1.25
11	A	2	50[g]	18	71.0	2.7	1.23
12	A	2	60[e]	118	82.3	2.6	1.46
13	B	2	40[e]	118	52.8	1.8	1.33
14	C	2	60[e]	118	85.0	2.3	1.40
15[h]	CH$_2$Cl$_2$	2	30[e]	18	1	1.6	1.53
16[h]	CH$_2$Cl$_2$	4	30[e]	18	4.2	2.8	1.10

[a] TPA (1.0 g, 7.5 mmol), [Sp]/[EtMgBr] = 1.2, solvent 10 ml. [b] A = CHCl$_3$–THF (7:3), B = CH$_2$Cl$_2$–THF (9:1), C = CHCl$_3$–THF (9:1). [c] MeOH-insoluble fraction. [d] Estimated by GPC (polystyrene standards). [e] Initiation was performed at 0°C. [f] EtMgBr (0.15 mmol) was used as the catalyst. [g] Initiation was performed at 30°C. [h] IPA (1.0 g, 7.5 mmol) was used.

(run 4 in Table I) obtained with the EtMgBr–Sp complex are shown in Figure 2. Proton resonances were assigned on the basis of 2D COSY spectrum (Figure 4), comparison of NMR data of model compounds with those of the poly(TPA) and hydrolyzed compounds derived
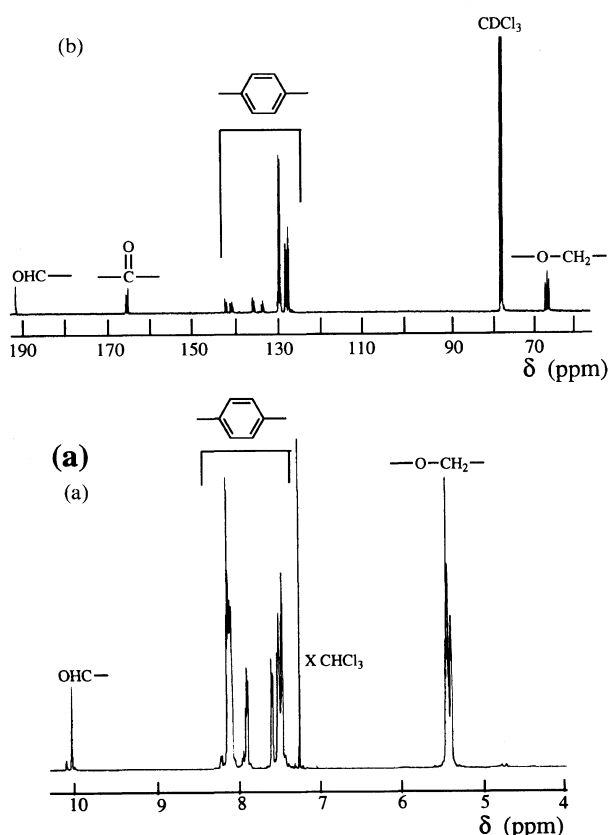

Figure 2. ^{1}H (a) and ^{13}C (b) NMR spectra of poly(TPA) (run 4 in Table I) in CDCl$_3$ at 60°C obtained with the EtMgBr–Sp complex.
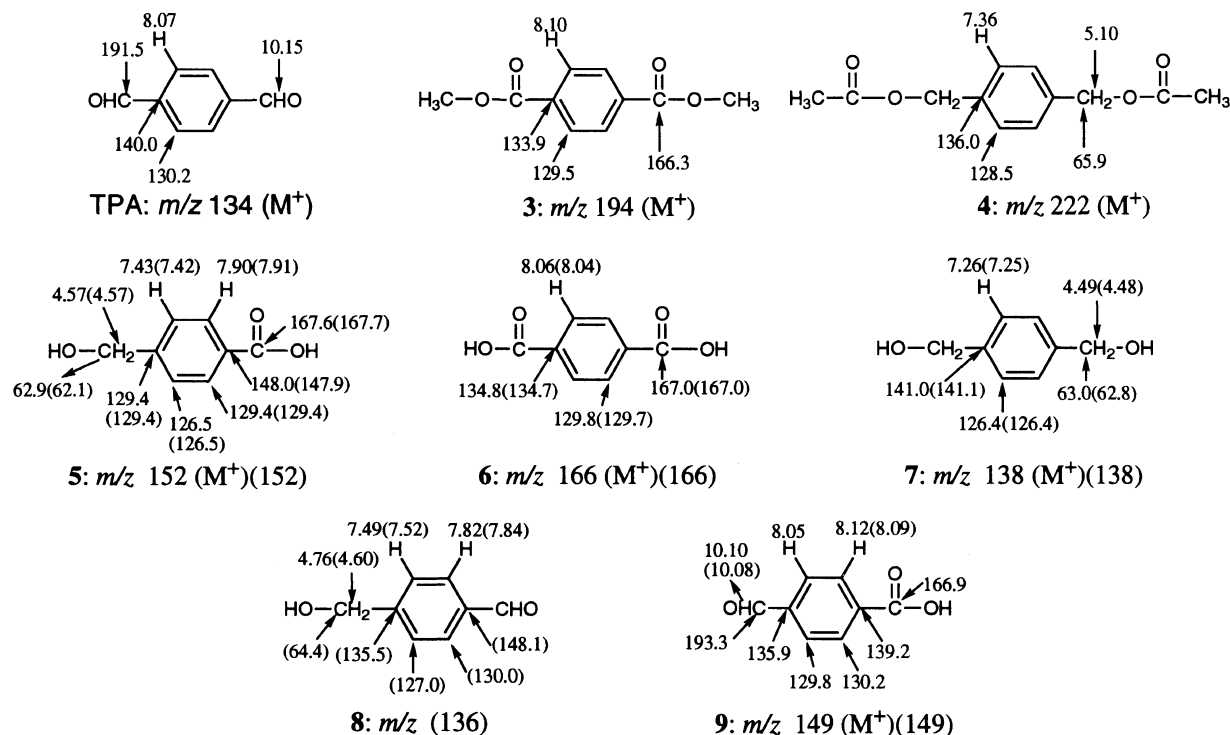
from the poly(TPA) in alkaline solution (see below). In the spectra, characteristic peaks due to the ester carbonyl carbons and O–CH_2 carbon and proton resonances appeared at around 166 and 66 ppm in the ^{13}C NMR and 5.4 ppm in the ^{1}H NMR spectrum, respectively, although the spectral patterns were not simple but rather complicated, indicating that the structure of poly(TPA) is not pure poly(oxycarbonyl-1,4-phenylenemethylene) (**1**), but may be a random copolymer composed of oxycarbonyl-1,4-phenylenemethylene and terephthaloyloxymethylene-1,4-phenylenemethyleneoxy units (**2**). Clear resonances due to the proton and carbon resonances due to a formyl group appeared at around 10 and 192 ppm in the ^{1}H and ^{13}C NMR spectra, respectively. This suggests that the poly(TPA) obtained with the EtMgBr–Sp complex probably has formyl terminals, while peaks due to other possible end groups such as hydroxymethyl groups were not observed. In the present polymerization, poly- or oligoaldehydes were not detected, since the reaction of benzaldehyde with a catalytic amount of the EtMgBr–Sp complex (2 mol%) in chloroform gave benzyl benzoate almost quantitatively (95% yield).

Poly(IPA) (run 16 in Table I) gave similar IR and NMR spectra to those of poly(TPA). The polymer showed the absorption at 1720, and 1274 and 1100 cm^{-1} due to C=O and C–O stretchings, respectively in its IR spectrum and characteristic peaks due to the O–CH_2 proton resonances appeared at around at 5.4 ppm in addition to the formyl proton resonances at $ca.$ 10 ppm in the ^{1}H NMR spectrum.

To determine the structure of poly(TPA)s and polymerization mechanism, the poly(TPA) obtained with the EtMgBr–Sp complex (run 4 in Table I) was hydrolyzed with KOH in ethanol and spectroscopic data including

Figure 3. Spectroscopic data of TPA and model compounds (**3**—**9**). Experimental data from hydrolysis of poly(TPA) (run 4 in Table I) obtained with the EtMgBr–Sp complex are shown in parentheses. NMR spectra of TPA, **3**, and **4** were measured in CDCl$_3$ and those of **5**—**9** were in DMSO-d_6. NMR data of **8** in CDCl$_3$ was taken from ref 14.

^{1}H and ^{13}C NMR and mass spectra of the hydrolyzed compounds derived from the poly(TPA) together with those of model compounds (3—9) are shown in Figure 3. The hydrolyzed products were identified by comparison of the ^{1}H NMR and mass spectral data with those of the authentic samples and were found to be a mixture of 4-(hydroxymethyl)benzoic acid (5), terephthalic acid (6), 1,4-bis(hydroxymethyl)benzene (7), and 4-(hydroxymethyl)benzaldehyde (8), and their molar ratio was roughly estimated to be 4.8 : 2 : 1 : 0.5 judging from the integral ratio of the corresponding proton resonances in DMSO-d_6. 4-Carboxybenzaldehyde (9) was hardly detected in the hydrates. These results support the speculation above that the poly(TPA) is not pure poly-(oxycarbonyl-1,4-phenylenemethylene) (1), but a random copolymer composed of oxycarbonyl-1,4-phenylenemethylene and terephthaloyloxymethylene-1,4-phenylenemethyleneoxy units (2). However, the above molar ratio of 5—8 was not directly correlated with the exact composition of the poly(TPA), since it is well known that two benzaldehyde molecules react to give one benzoic acid molecule and one benzyl alcohol molecule in aqueous alkaline solution (Cannizzaro reaction).[16] Therefore, portions of 8 and 9 may be converted to 7 and 6 during the alkaline hydrolysis, respectively, and the amount of formyl group and degree of polymerization (DP) of the poly(TPA) could not be determined from the hydrolysis results. In fact, compound 9 (0.5 g) yielded 5 (34%), 6 (48%), and unreacted 9 (18%) under the same conditions in the hydrolysis of the poly(TPA). Excess of 6 may be due to oxidation of 9 during the reaction. Moreover, it was difficult to recover 7 completely with ether from an aqueous solution of 7. A control experiment of the extraction of an aqueous solution of 7 (0.5 g/15 ml H$_2$O) with ether suggested the recovery of 7 to be ca. 80% even after three times extraction with ether (50 ml).

For comparison, poly(oxycarbonyl-1,4-phenylenemethylene) (1) was prepared according to the method reported by Pinkus, et al.[14] As reported in their paper, the obtained polymer was not soluble in common organic solvents including chloroform, THF, DMSO, and acetone (see Experimental). However, they measured the ^{1}H NMR of the polymer in a mixture of DMSO and hexafluoroisopropanol and reported the spectrum; aromatic and methylene protons appeared as broad doublet at 7.5 and 8.0 ppm and broad singlet at 5.4 ppm, respectively. These chemical shift values agreed with those assigned in Figures 2(a) and 4.

Figure 4 shows the COSY spectrum of the poly(TPA) obtained with the EtMgBr–Sp complex (run 4 in Table I); a number of cross peaks (A—F) and diagonal peaks

showing no shift correlation (G and H) were observed in the region of aromatic–aromatic proton resonances. Based on the ^{1}H NMR data of the hydrolyzed compounds derived from the poly(TPA) and those of the model compounds (3—9), the signals could be tentatively assigned and a possible structure of poly(TPA) is proposed in Figure 5. The aromatic peaks (G and H) were unambiguously assigned to the proton resonances of Hf and He, respectively, because the protons are almost
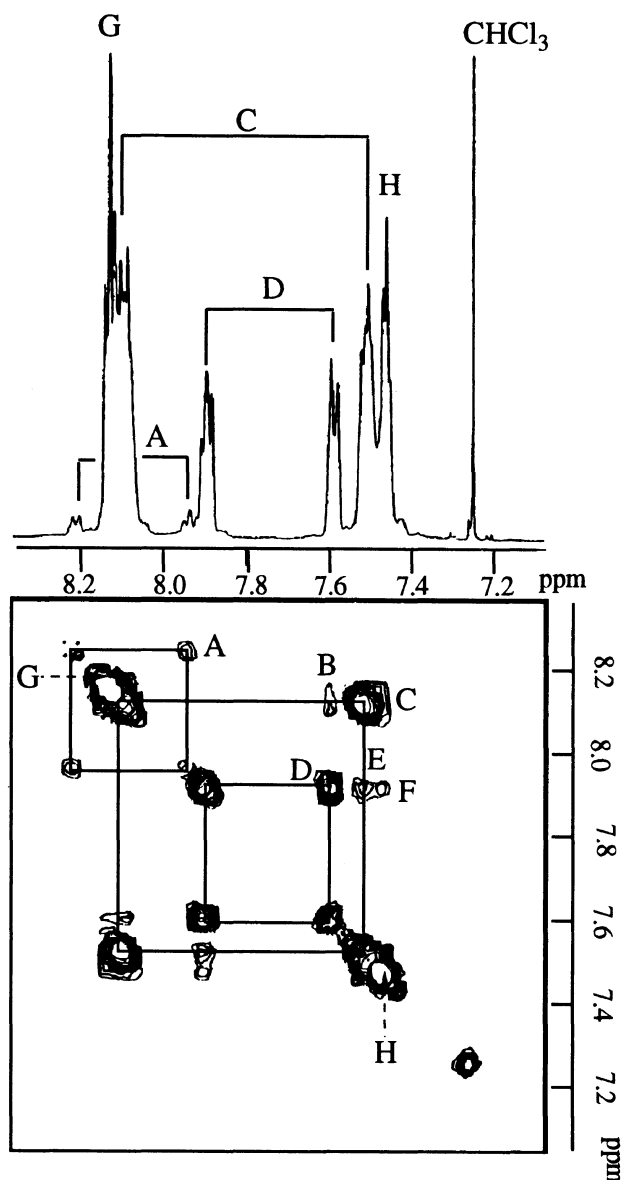

Figure 4. ^{1}H–^{1}H COSY spectrum of poly(TPA) (run 4 in Table I) in CDCl$_3$ obtained with the EtMgBr–Sp complex.
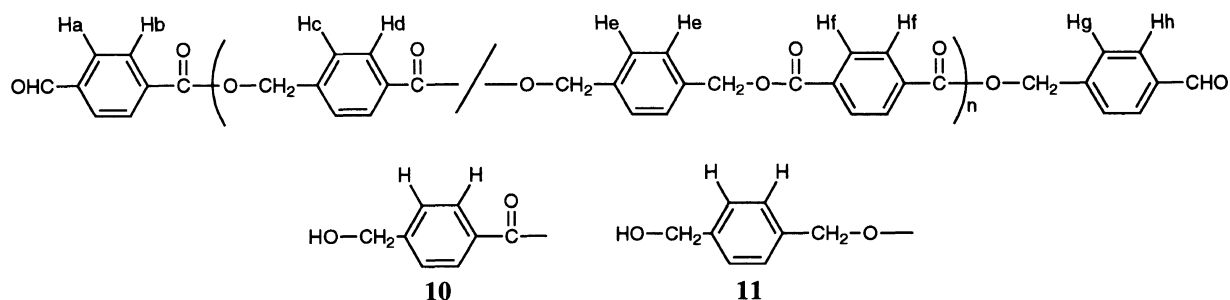

Figure 5. Possible structure of poly(TPA) obtained with the EtMgBr–Sp complex and hydroxymethyl terminal ends (10 and 11).
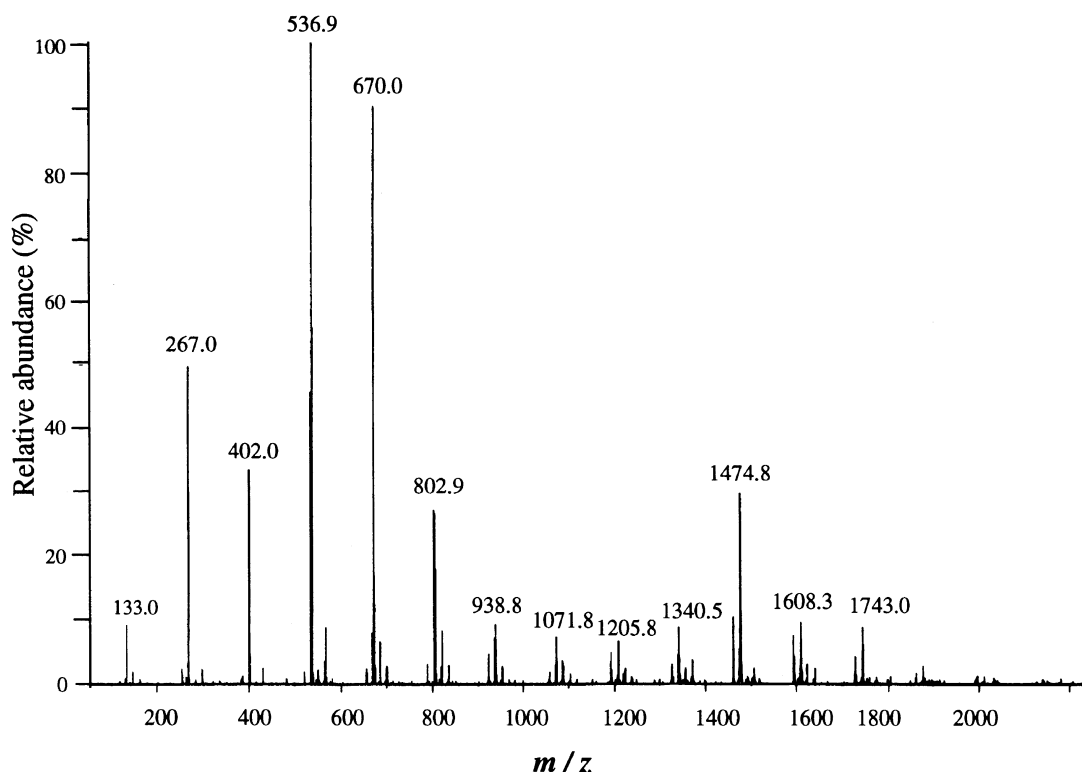
Figure 6. FD mass spectrum of poly(TPA) (run 2 in Table I) obtained with the EtMgBr–Sp complex in THF at 30°C.

equivalent, while the cross peaks A, C, and D may be correlated between Ha and Hb, Hc and Hd, and Hg and Hh proton resonances, respectively. The cross peak B, E, and F could not be assigned at present. The peaks may be derived from lower molecular weight poly(TPA). Other possible terminal ends such as 10 and 11 in Figure 5 were not detected in the NMR spectra. The existence of carboxy groups as terminal ends may be excluded according to the mechanism of polymerization (see below).

From the integral ratio of the formyl terminal proton and the aromatic and methylene proton resonances, DP and composition of the poly(TPA) were roughly obtained; $DP = ca.$ 10 and $5:6:7:8:9 = 2:1:1:1:0.2$, respectively, assuming that the polymer has formyl terminals at both ends and compositions of 6 and 7 to be at 1 : 1. These results indicate that the poly(TPA) may be a 2 : 1 random copolymer of 1 and 2 units. The above compositions of 5—8 differed from those estimated from the hydrolysis results of poly(TPA) $(5:6:7:8 = 4.8:2:1:0.5)$. This may be ascribed to side reactions such as the Cannizzaro reaction and oxidation of the formyl groups of 8 and 9 during the alkaline hydrolysis as mentioned above and difficulty in complete recovery of water soluble 7 by ether extraction from the hydrates in aqueous layer.

Figure 6 shows the FD mass spectrum of the low molecular weight poly(TPA) obtained with the EtMgBr–Sp complex (run 2 in Table I). The spectrum showed peaks corresponding to the molecular mass of the polymers (2—13 mers) with the possible structure of poly(TPA) having formyl groups at the terminal ends. The main peaks were assigned to oligomers (4 and 5 mers), and higher molecular weight polymers were also detected.

As reported previously for the asymmetric polymerization of 3-PPA and enantioselective Tishchenko reaction of ($\pm$)-2-PPA with the EtMgBr–Sp complex in toluene at $-78°C$, EtMgBr is not the real initiator of most molecules, but 3-phenyl- or 2-phenylpropoxymagnesium bromide is a real intermediate and further reacts with 3-PPA or 2-PPA followed by the Tishchenko-type termination again with the aldehydes to afford optically active poly(3-PPA) having an ester terminal at ω-end or 2-phenylpropyl 2-phenylpropanoate as a cyclic mechanism, respectively.[9,10] Similar cyclic mechanism may also operate for the present reaction system. According to the previously proposed mechanism,[9,10] the present polyester formation through the Tishchenko reaction may be considered as shown in Scheme 1. Part of the EtMgBr–($-$)-Sp complex reacts with TPA as a nucleophile to afford 1-(4-formylphenyl)propoxymagnesium bromide, and complex A may be formed by the coordination of TPA. The hydride transfer from an alkoxy group to a carbonyl group of TPA may produce ethyl 4-formylphenyl ketone and 4-formylbenzylalkoxymagnesium bromide in complex B through the Meerwein–Ponddorf–Verley reduction as reported by Saegusa et al. for the reaction of diethylaluminum sec-butoxide and n-butyraldehyde.[17] This reaction is reversible. Another route to the formation of 4-formylbenzylalkoxymagnesium bromide is an alkoxy group transfer to the carbonyl group of TPA (C), followed by the coordination of TPA (D) and the hydride transfer reaction by the Tishchenko reaction (E). The resulting 4-formylbenzylalkoxymagnesium–($-$)-Sp complex (F) must be a real nucleophile and further reacts with TPA followed by the Tishchenko-type termination again with TPA to afford poly(TPA) (Scheme 1(b)). The FD mass spectrum of the methanol soluble fraction of run 4 in Table I showed main peaks
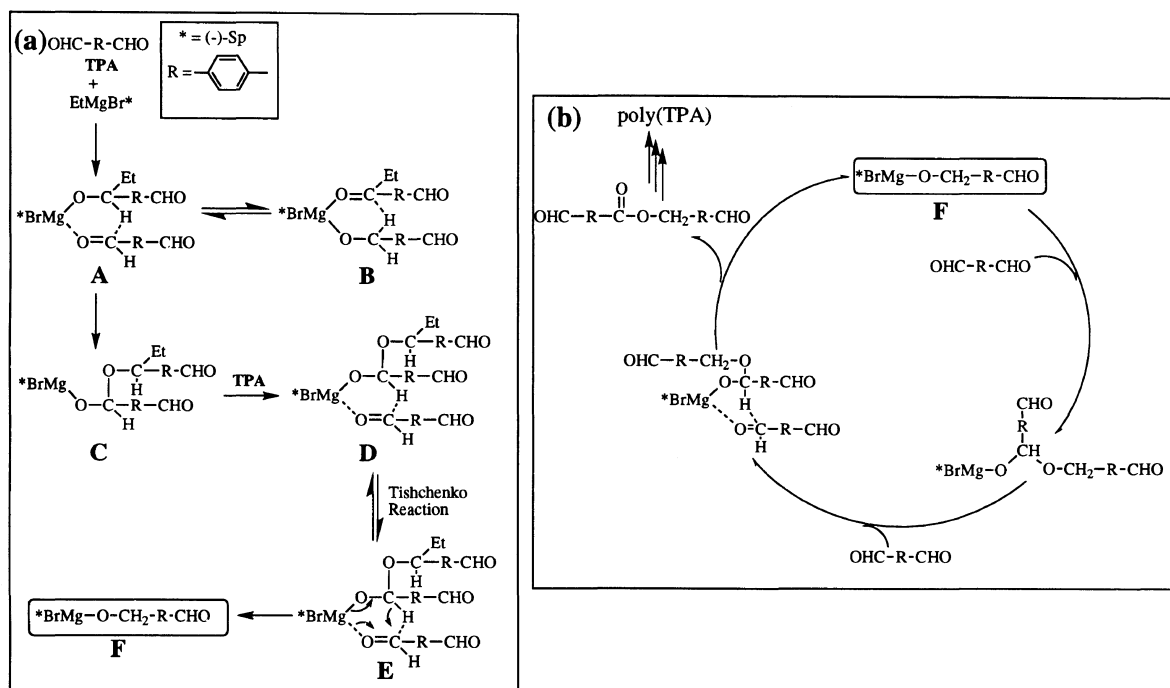
Scheme 1. Mechanism for the polymerization of TPA with the EtMgBr–Sp complex through the Tishchenko reaction: (a) initiation; (b) propagation.
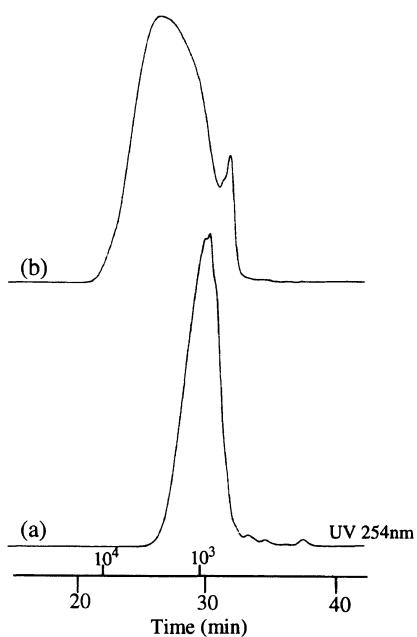

Figure 7. GPC curves of poly(TPA) (a) (run 7 in Table I) obtained with the EtMgBr–Sp complex and polymerized poly(TPA) (b) with the EtMgBr–Sp complex in dichloromethane at 30°C for 18 h.
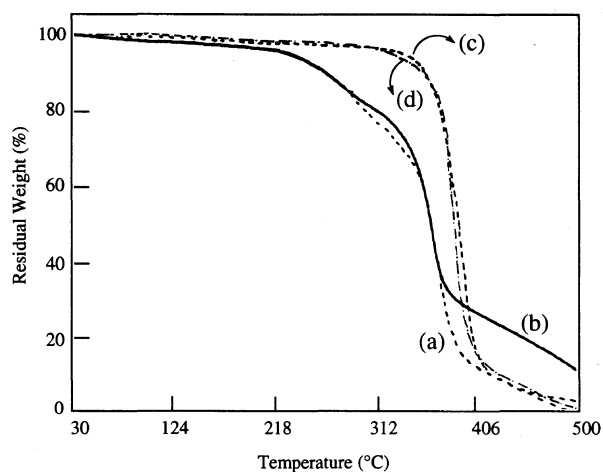

Figure 8. TG curves of poly(TPA) (a) (run 7 in Table I) obtained with the EtMgBr–Sp complex, polymerized poly(TPA) (b), poly(TPP) (c), and poly(oxycarbonyl-1,4-phenylenemethylene) (1) (d).

of m/z 133.1, 267.2, 401.3, 535.4, and 669.0 corresponding to 1—5 mers. However, other peaks corresponding to the molecular weight of the ketones in B and E in Scheme 1 could not be detected probably due to very low concentration.

The complex of bismagnesium alkoxide with (−)-sparteine prepared by the reaction of EtMgBr and 1,4-bis(hydroxymethyl)benzene (7) (molar ratio = 2 : 1) was used as the catalyst (2 mol%) for the polymerization of TPA in chloroform at 30°C. The obtained polymer had a similar molecular weigh ($M_n = 1600$) and showed IR and ^1H NMR spectral patterns similar to Figures 1 and 2(a). This suggests that the alkoxide–Sp complex (F in

Scheme 1) is an active specie for ester formation.

According to the mechanism, most poly(TPA) should have formyl terminals at both ends because only a catalytic amount of the compound F is enough for the Tishchenko reaction in a cyclic mechanism. This indicates that the polymers may be further polymerized with the EtMgBr–Sp complex. To confirm this, the poly(TPA) ($M_n = 2100$, run 7 in Table I) was polymerized with the complex in dichloromethane at 30°C for 18 h. Figure 7 demonstrates GPC curves of the original poly(TPA) (a) and the polymer (b) obtained from the polymerization of the original poly(TPA) with the EtMgBr–Sp complex. The top peak moved to higher molecular weight region and M_n of the polymer increased to 3900. These results indicate that poly(TPA)s prepared with the EtMgBr–Sp have reactive formyl groups and can be used as a monomer again.

Figure 8 shows the TGA thermograms of the original

Table II. Polymerization of TPA with (R)-BÍN-Al or Al[OCH(CH$_3$)$_2$]$_3$ in CH$_2$Cl$_2$ for 18 h[a]

Run	Catalyst	Temp/°C	Yield/%[b]	$\bar{M}_n \times 10^{-3}$[c]	$\bar{M}_w/\bar{M}_n$[c]
1	(R)-BIN-Al	30	83.3	3.9	1.42
2		0	0	—	—
3	Al[OCH(CH$_3$)$_2$]$_3$	30	68.1	1.6	1.28
4		0	0	—	—

[a] TPA (1.0 g, 7.5 mmol), CH$_2$Cl$_2$ 10 ml, [TPA]/[catalyst] = 50. [b] MeOH-insoluble fraction. [c] Estimated by GPC (polystyrene standards).

poly(TPA) (run 7 in Table I) and polymerized poly(TPA) with the EtMgBr–Sp complex and model polyesters, poly(terephthaloyloxymethylene-1,4-phenylenemethyleneoxy) (poly(TPP)) and poly(oxycarbonyl-1,4-phenylenemethylene) (**1**). The thermal properties including thermal decomposition temperatures were dependent on the main chain structures of the polyesters. Poly(TPP) and **1** were more thermally stable than poly(TPA) and weight loss of the polyesters occurred at around 350°C in air. On the other hand, the weight loss of the original poly(TPA) began at around 210°C and the TGA thermogram of the polymerized poly(TPA) showed a slightly different curve.

Polymerization of TPA with Aluminum Alkoxides

Table II shows the results of polymerization of TPA with aluminum isopropoxide and (R)-(+)-1,1'-bi-naphthoxymethylaluminum $((R)$-BIN-Al) in dichloromethane at 0 or 30°C. Mitin *et al.*[6] and later, Sweeny[7] reported that aluminum isopropoxide did not polymerize TPA, although aluminum ethoxide and triisopropylaluminum were effective catalysts for the polymerization of TPA through the Tishchenko reaction. However, the present results clearly show that aluminum isopropoxide is also an effective catalyst as well as (R)-BIN-Al as shown in Table II, though at 0°C no polymer was obtained with the catalysts. The poly(TPA)s obtained with the catalysts showed IR and ^{1}H NMR spectra similar to those of poly(TPA)s prepared with the EtMgBr–Sp complex, indicating that the polyesters consisted of oxycarbonyl-1,4-phenylenemethylene (**1**) and terephthaloyloxymethylene-1,4-phenylenemethyleneoxy (4-xylyleneterephthalate) units (**2**) in analogy with poly(TPA)s prepared with the EtMgBr–Sp complex.

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