Electronic Supplementary Information for

Exceptional Copolymerizability of o-Phthalaldehyde in Cationic Copolymerization with Vinyl Monomers

Keisuke Hayashi, Arihiro Kanazawa, and Sadahito Aoshima*  

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan.

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Experimental Section

Materials. Isobutyl vinyl ether (IBVE; TCI; >99.0%) was washed with 10% aqueous sodium hydroxide solution and then with water, dried overnight over potassium hydroxide, and distilled twice over calcium hydride. 2,3-Dihydrofuran (DHF; TCI; >98.0%) and 3,4-dihydro-2H-pyran (DHP; TCI; >97.0%) were distilled twice over calcium hydride. 1,4-Dioxane (Nacalai Tesque; >99.5%), and tetrahydrofuran (THF; Nacalai Tesque; >99.5%) were distilled over calcium hydride and then lithium aluminum hydride. Ethyl 2-methyl-1-propenyl ether (EMPE) was prepared from isobutyraldehyde diethyl acetal (TCI; >96.0%) according to a previous report and then distilled twice over calcium hydride. 1,1-Diphenylethylene (DPE; TCI; >98.0%) was distilled twice over calcium hydride under reduced pressure. o-Pthalaldehyde (OPA; TCI; >99.0%) was recrystallized twice from n-hexane before use. Ethanesulfonic acid (EtSO_3H; Sigma-Aldrich; 95%) was used as received. 1-(Isobutoxy)ethyl chloride (IBVE–HCl) was prepared from addition reaction of IBVE with HCl. For GaCl_3, a stock solution in n-hexane was prepared from commercial anhydrous GaCl_3 (Sigma-Aldrich, 99.999%). SnCl_4 (Sigma-Aldrich, 1.0 M solution in heptane) and TiCl_4 (Sigma-Aldrich, 1.0 M solution in toluene) were used as received. Toluene (Wako) and dichloromethane (Wako) were dried by passage through solvent purification columns (Glass Contour). Diethyl malonate (Nacalai Tesque; >99.0%) and sodium hydride (NaH; Nacalai Tesque; 60% dispersion in paraffin) were used as received.

Polymerization procedures. Polymerization was conducted under dry nitrogen atmosphere in a glass tube equipped with a three-way stopcock. Toluene, 1,4-dioxane, and monomers were first added into the tube using different dry syringes. To this solution, cooled at 0°C in advance, a prechilled 40 mM EtSO_3H solution (0.3 mL) in toluene was added using a dry syringe. The tube was then placed into a cooling bath set at −78°C, 2 min after the EtSO_3H addition. The reaction was started by the addition of a prechilled Lewis acid solution (0.3 mL). The reaction mixture was terminated with methanol containing a small amount of aqueous sodium hydroxide or ammonia solution, or the solution of sodium diethylmalonate prepared according to a previous report. The quenched reaction mixture was diluted with dichloromethane and then washed with water. The solvents and other volatiles were evaporated under reduced pressure. The residual OPA monomer was removed by reprecipitation into methanol. The monomer conversion was determined by a gravimetric method and 1H NMR analysis.

Acid hydrolysis of product copolymers. The purified copolymer (30 mg) was dissolved in 1,2-dimethoxyethane (DME; 3.4 mL) and then the hydrolysis reaction was started by the addition of an aqueous HCl-DME solution (1.0 M, 3.4 mL) at 30°C. After predetermined reaction time, the reaction was quenched with aqueous sodium hydroxide (1.0 M, 3.4 mL). The quenched reaction mixture was diluted with dichloromethane and then washed with distilled water 5 times to remove the resulting salt. The volatiles were evaporated under reduced pressure to yield hydrolysis products.

Characterization. The molecular weight distribution (MWD) of the polymers was measured by gel permeation chromatography (GPC) in chloroform at 40°C with polystyrene columns [TSKgel GMHHR-M × 2; flow rate = 1.0 mL/min] connected to a Tosoh DP-8020 pump, a CO-8020 column oven, a UV-8020 ultraviolet detector, and an RI-8020 refractive-index detector. The number-average molecular weight (M_n) and polydispersity ratio [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were calculated from the chromatographs with respect to 16 polystyrene standards (Tosoh; M_n = 577—1.09 × 10^6, M_w/M_n < 1.1). NMR spectra of the products were recorded using a JEOL JNM-ECA 500 spectrometer (500.16 MHz for 1H and 125.77 MHz for 13C). ESI-MS data were recorded on LTQ Orbitrap XL (Thermo Scientific).

References
**Figure S1.** MWD curves of the products before and after IBVE addition ([IBVE]₀ = [IBVE]_{added} = 0.40 M, [OPA]₀ = 0.40 M, [EtSO₃H]₀ = 4.0 mM, [GaCl₃]₀ = 4.0 mM, [1,4-dioxane]₀ = 0.50 M in toluene at −78 °C).

**Figure S2.** ^{13}C NMR spectrum of poly(IBVE-co-OPA) (\(M_n = 9.1 \times 10^3\), \(M_w/M_n = 1.49\)) recorded in CDCl₃ at 30 °C. * TMS, grease, CHCl₃, residual monomer.

**Figure S3.** ESI–MS spectrum of the hydrolysis product of poly(IBVE-co-OPA) quenched by sodium diethylmalonate solution. * contamination.
Figure S4. Copolymer compositions in the copolymerization of IBVE and OPA ([IBVE]₀ + [OPA]₀ = 1.20 M, [EtSO₃H]₀/[GaCl₃]₀ = 4.0/4.0 mM, [1,4-dioxane]₀ = 0.50 M in toluene at −78 °C). Solid line: drawn using the $r$ values obtained by the Kelen–Tüdös method; dashed-line: azeotropic line. See Table S1 for the polymerization data.

<table>
<thead>
<tr>
<th>Entry</th>
<th>IBVE conc. [M]</th>
<th>OPA conc. [M]</th>
<th>Time</th>
<th>Total conv. (%) b</th>
<th>$M_n \times 10^{-3}$ c</th>
<th>$M_w/M_n$ c</th>
<th>IBVE in copolymer d</th>
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</thead>
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<td>0.40</td>
<td>10 min</td>
<td>15</td>
<td>5.8</td>
<td>1.70</td>
<td>0.65</td>
</tr>
<tr>
<td>2</td>
<td>0.60</td>
<td>0.60</td>
<td>10 min</td>
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<td>3.2</td>
<td>1.14</td>
<td>0.57</td>
</tr>
<tr>
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<td>0.80</td>
<td>10 min</td>
<td>6</td>
<td>3.2</td>
<td>1.73</td>
<td>0.54</td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>0.90</td>
<td>10 min</td>
<td>10</td>
<td>1.4</td>
<td>2.22</td>
<td>0.49</td>
</tr>
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</table>

* [EtSO₃H]₀ = 4.0 mM, [GaCl₃]₀ = 4.0 mM, [1,4-dioxane]₀ = 0.50 M in toluene at −78 °C. b By gravimetry. c By GPC (polystyrene calibration). d By $^1$H NMR.

Scheme S1. Cationic alternating copolymerization of IBVE and BzAs.
Figure S5. $^1$H NMR spectrum of the hydrolysis products of poly(IBVE-co-OPA) (a sample prepared under the same conditions to those for Figure 1B). * TMS, grease, water, acetone, methanol, CHCl$_3$.

Note for Figure S5: A main compound in the hydrolysis product most likely has a structure shown in Figure S5, which was suggested by the comparison with the compounds reported in reference S3. However, the mechanism of the generation of this compound is unclear.

Reference

Table S2. The number of each sequence per chain$^a$

<table>
<thead>
<tr>
<th>$M_n \times 10^{-3}$</th>
<th>$M_w/M_n$</th>
<th>OPA content in copolymer (%)</th>
<th>IBVE–IBVE</th>
<th>IBVE–OPA</th>
<th>OPA–IBVE</th>
<th>OPA–OPA</th>
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<td>13.0</td>
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<td>14</td>
<td>45</td>
<td>46</td>
<td>12</td>
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$^a$The data of the same sample in Fig. 2A.

Figure S6. $^1$H NMR spectrum of the acid alcoholysis product of poly(IBVE-co-OPA) (0.5 M HCl in MeOH/CH$_2$Cl$_2$ (1/1 v/v) solution for 24 h at r.t., 0.5 wt%). * TMS, water, CHCl$_3$. † References S4 and S5. Number written in green; integral ratio.
Figure S7. MWD curves of the products obtained by the cationic copolymerization of OPA with (A) DHF, (B) DHP, and (C) DPE. See Table 1 for the polymerization conditions.

Figure S8. $^1$H NMR spectrum of poly(DHF-co-OPA) ($M_n = 5.4 \times 10^3$, $M_w/M_n = 2.12$); recorded in CDCl$_3$ at 30 °C. * TMS, grease, water, acetone, CHCl$_3$. 

References
Figure S9. $^1$H NMR spectrum of (A) poly(DHP-co-OPA) ($M_n = 9.0 \times 10^3$, $M_w/M_n = 2.06$) and (B) its hydrolysis product; recorded in CDCl$_3$ at 30 ºC. * TMS, grease, water, acetone, CHCl$_3$.

**Note for Figure S9:** The hydrolysis product had a much lower MW than the original copolymer, which indicates that the hydrolysis reaction successfully proceeded. However, the $^1$H NMR spectrum had negligible peaks assigned to formyl protons at 10–11 ppm. In addition, peaks remained at 4.5–5.5 ppm. We are currently examining the structure of the hydrolysis product.

Figure S10. $^1$H NMR spectrum of the acid hydrolysis product of poly(EMPE-co-OPA); recorded in CDCl$_3$ at 30 ºC. * TMS, grease, water, CHCl$_3$.

**Note for Figure S10:** Approximately 50% of the hydrolysis products consist of a compound above, which was suggested by the comparison with the compounds reported in references S3 and S4. However, the structure of another 50% of the hydrolysis products are unclear.

**References**
Figure S11. $^1$H NMR spectrum of poly(DPE-co-OPA) ($M_n = 7.1 \times 10^3$, $M_w/M_n = 1.75$); recorded in CDCl$_3$ at 30 $^\circ$C. * TMS, grease, water, acetone, methanol.