

Effective Management of Polyethers through Depolymerization to Symmetric and Unsymmetric Glycol Diesters Using Proton-exchanged Montmorillonite Catalyst

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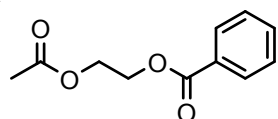
Supporting Information

Product Identification

Products **2**, **13**, and **14** were identified using GC and GC-MS. The CG retention times were identical with those of commercially available authentic samples. Products **11** and **12** were isolated from the reaction mixture of the depolymerization of polyethers **9** and **10**, respectively. After the reaction, H-mont was removed by filtration and washed with CH₂Cl₂, and then the reaction mixture was washed with saturated aq. NaHCO₃ to remove benzoic acid. The organic phase was concentrated by evaporation to afford the crude product. The desired product was obtained by recrystallization, and the solid obtained was washed with diethyl ether. The structure was identified by ¹H and ¹³C NMR and GCMS.

A series of authentic samples of unsymmetric glycol diesters **15–18** were synthesized as follows. A mixture of acyl chloride (33.6 mmol) and THF (20 mL) was added slowly to the THF solution (30 mL) containing 2-hydroxyethyl acetate (5 g, 48 mmol) and trimethylamine (9.7 g, 96 mmol) cooling in an ice bath, and the resulting mixture was stirred for 12 h. The reaction mixture was filtered, washed with THF, and the filtrate concentrated by evaporation. The crude product was purified by column chromatography or Kugelrohr. The structure was confirmed by ¹H and ¹³C NMR measurements and GCMS.

Spectrum data

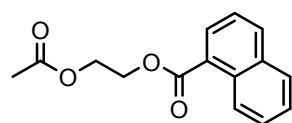


2-(acetoxyl)ethyl benzoate (**15**) [CAS No. 38353-69-4]

¹H NMR: (400 MHz, CDCl₃): 8.14–7.95 (m, 2H, aryl), 7.64–7.45 (m, 3H, aryl), 4.64–4.46 (m, 2H, OCH₂), 4.46–4.28 (m, 2H, OCH₂), 2.09 (s, 3H, CH₃).

¹³C NMR: (100 MHz, CDCl₃): 170.71, 166.22, 133.04, 129.77, 129.60, 128.32, 62.62, 62.10, 20.70.

¹H NMR and ¹³C NMR results were consistent with previously reported values. See ref S1.



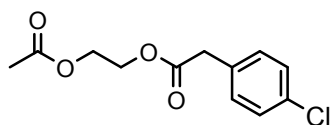
2-acetyloxyethyl naphthalene-1-carboxylate (**16**)

$^1\text{H NMR}$: (400 MHz, CDCl_3): 8.91 (d, 1H, aryl, $J = 8.70$ Hz), 8.21 (dd, 1H, aryl, $J = 7.32$ and 1.37 Hz), 8.03 (d, 1H, aryl, $J = 8.24$ Hz), 7.89 (d, 1H, aryl, $J = 8.24$ Hz), 7.67–7.58 (m, 1H, aryl), 7.58–7.46 (m, 2H, aryl), 4.72–4.58 (m, 2H, OCH_2), 4.58–4.42 (m, 2H, OCH_2), 2.12 (s, 3H, CH_3).

$^{13}\text{C NMR}$: (100 MHz, CDCl_3): 170.8, 167.2, 133.8, 133.6, 131.3, 130.4, 128.6, 127.8, 126.7, 126.2, 125.7, 124.6, 62.7, 62.2, 20.8.

IR (neat, cm^{-1}): 3050 ($\text{C}_{\text{aryl}}\text{-H}$ stretch), 2956 (CH_2 stretch), 1742 (C=O stretch), 1717 (C=O stretch), 1593 (C=C aromatic stretch), 1440 (CH_3 asymmetric stretch), 1373 (CH_3 symmetric stretch), 1231 (C(=O)-O stretch), 1196 (C(=O)-O stretch), 783 ($\text{C}_{\text{aryl}}\text{-H}$ bending).

HRMS (EI): calculated (for $\text{C}_{15}\text{H}_{14}\text{O}_4$) 258.0892, found 258.0892.



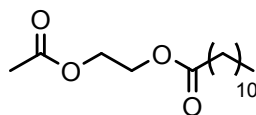
2-acetoxyethyl 2-(4-chlorophenyl)acetate (**17**)

$^1\text{H NMR}$: (400 MHz, $(\text{CD}_3)_2\text{SO}$): 7.41–7.26 (m, 4H, aryl), 4.30–4.16 (m, 4H, C_2H_4), 3.74–3.68 (m, 2H, CH_2), 1.99 (s, 3H, CH_3).

$^{13}\text{C NMR}$: (100 MHz, $(\text{CD}_3)_2\text{SO}$): 171.1, 170.7, 133.5, 131.5, 131.2, 128.5, 62.6, 62.0, 20.8.

IR (neat, cm^{-1}): 3031 ($\text{C}_{\text{aryl}}\text{-H}$ stretch), 2959 (CH_2 stretch), 1741 (C=O stretch), 1960 (C=C aromatic stretch), 1492 (CH_3 asymmetric stretch), 1375 (CH_3 symmetric stretch), 1229 (C(=O)-O bending), 807 ($\text{C}_{\text{aryl}}\text{-H}$ bending).

HRMS (FAB): calculated (for $\text{C}_{12}\text{H}_{14}\text{O}_4\text{Cl}$) 256.0502, found 257.0580 $[\text{M}+\text{H}]^+$.



2-(acetoxy)ethyl laurate (**18**)

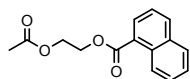
$^1\text{H NMR}$: (400 MHz, CDCl_3): 4.27 (s, 4H, OC_2H_4), 2.33 (t, 2H, CH_2 , $J = 7.78$ Hz), 2.08 (s, 3H, CH_3), 1.67–1.57 (m, 2H, CH_2), 1.37–1.20 (m, 16H, C_8H_{16}), 0.88 (t, 3H, CH_3 , $J = 7.32$ Hz).

$^{13}\text{C NMR}$: (100 MHz, CDCl_3): 173.6, 170.8, 62.3, 61.9, 34.2, 31.9, 29.6, 29.5, 29.3, 29.2, 29.1, 24.9, 22.7, 20.8, 14.1.

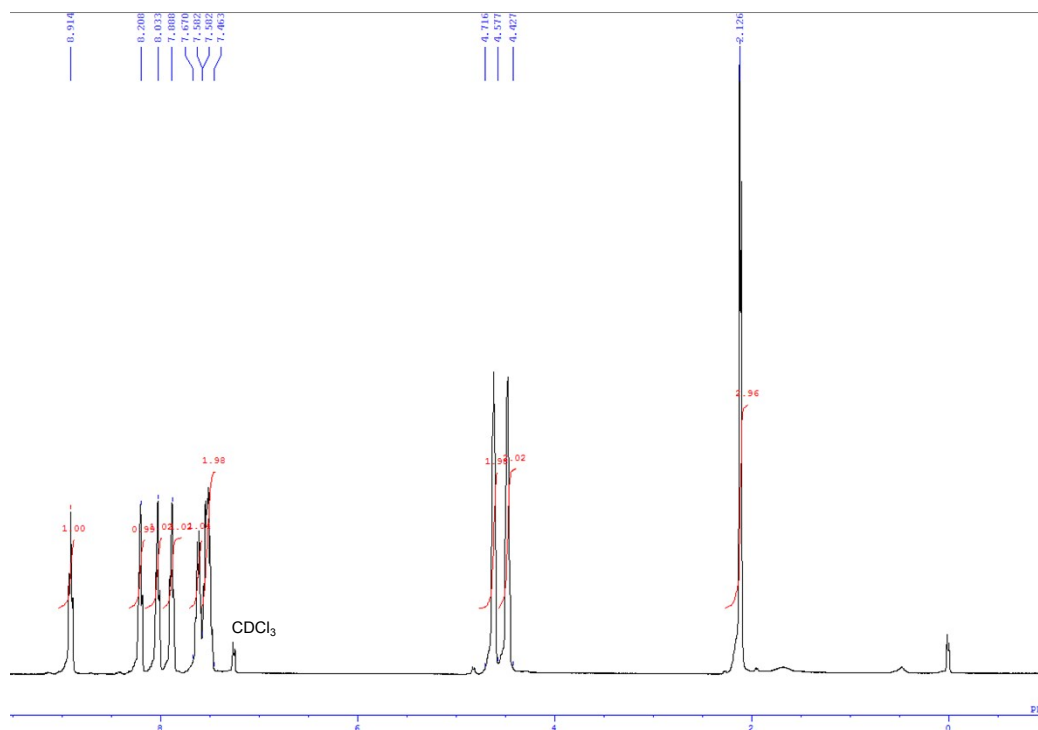
IR (neat, cm^{-1}): 2954 (CH_2 stretch), 2926 (CH_2 stretch), 2858 (CH_2 stretch), 1745 (C=O stretch), 1459 (CH_3 asymmetric stretch), 1376 (CH_3 symmetric stretch), 1229 (C(=O)-O stretch).

HRMS (EI): calculated (for $\text{C}_{16}\text{H}_{30}\text{O}_4$) 286.2144, found 286.2145.

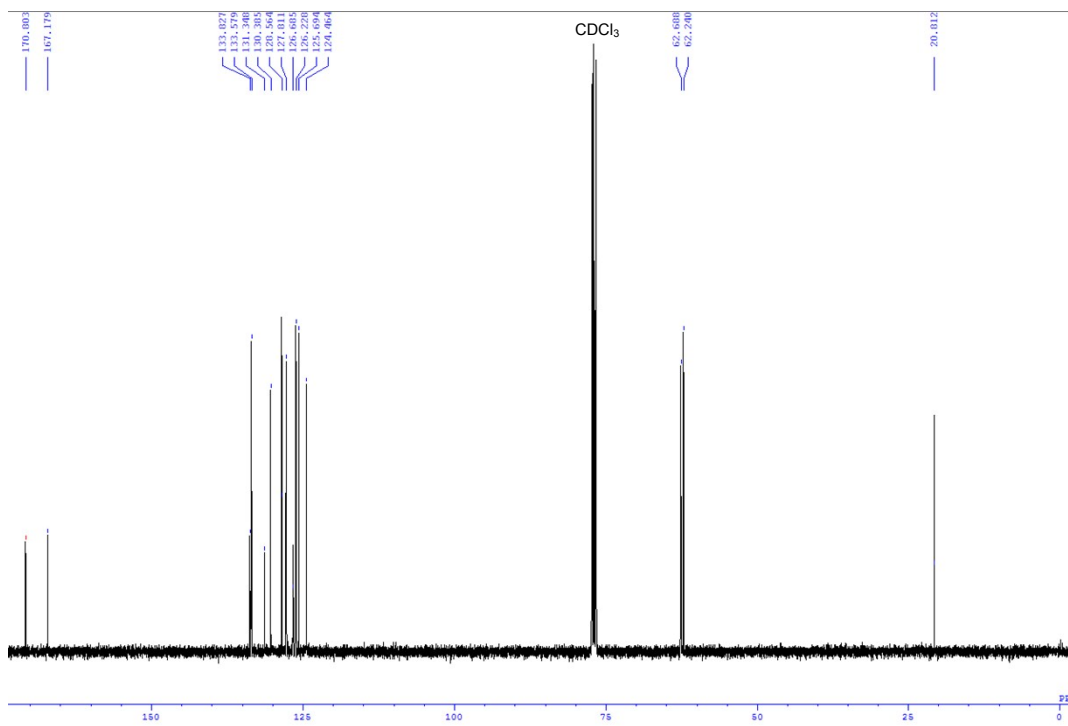
NMR spectra

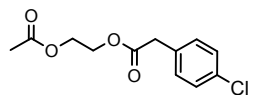


¹H NMR

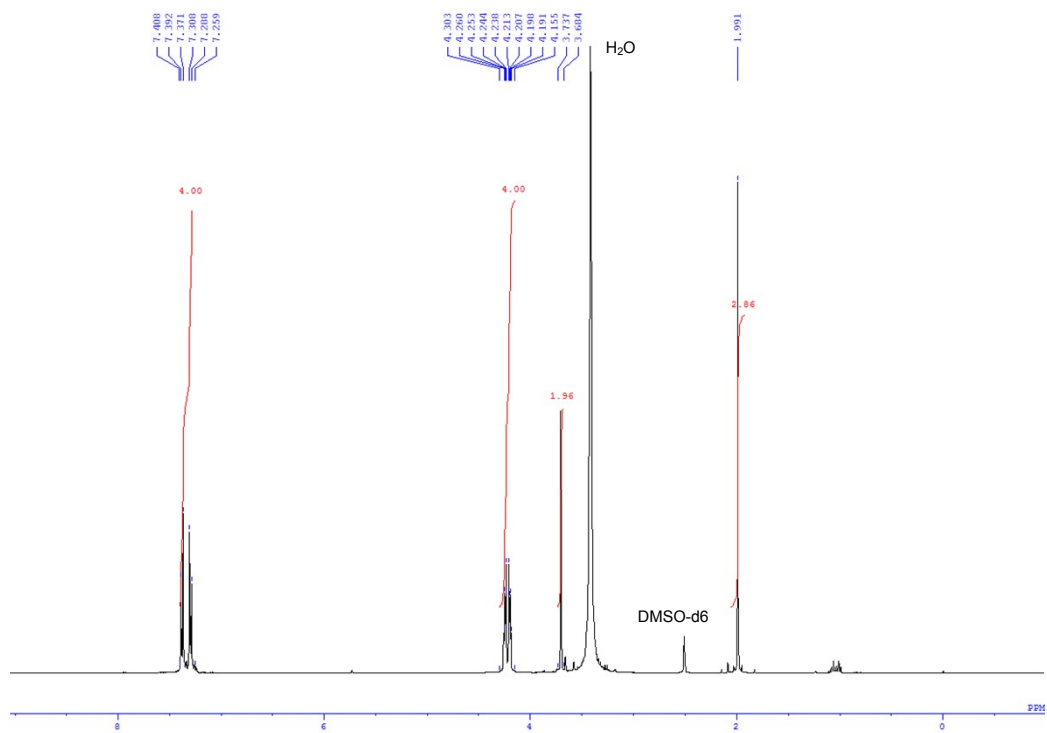


¹³C NMR

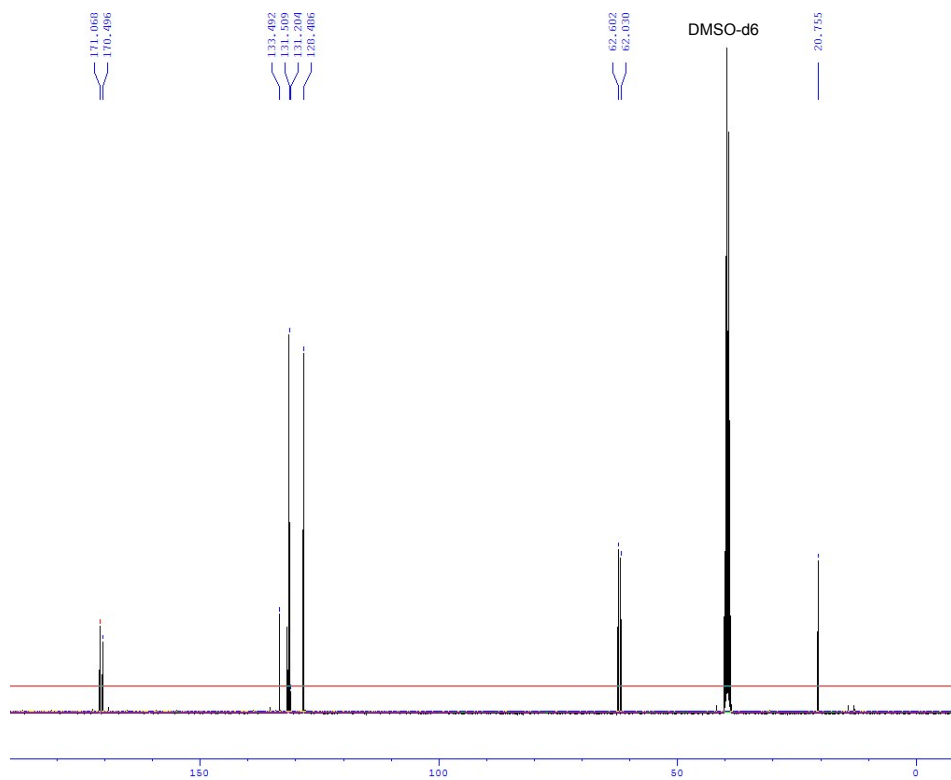


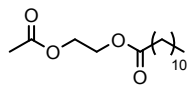


¹H NMR

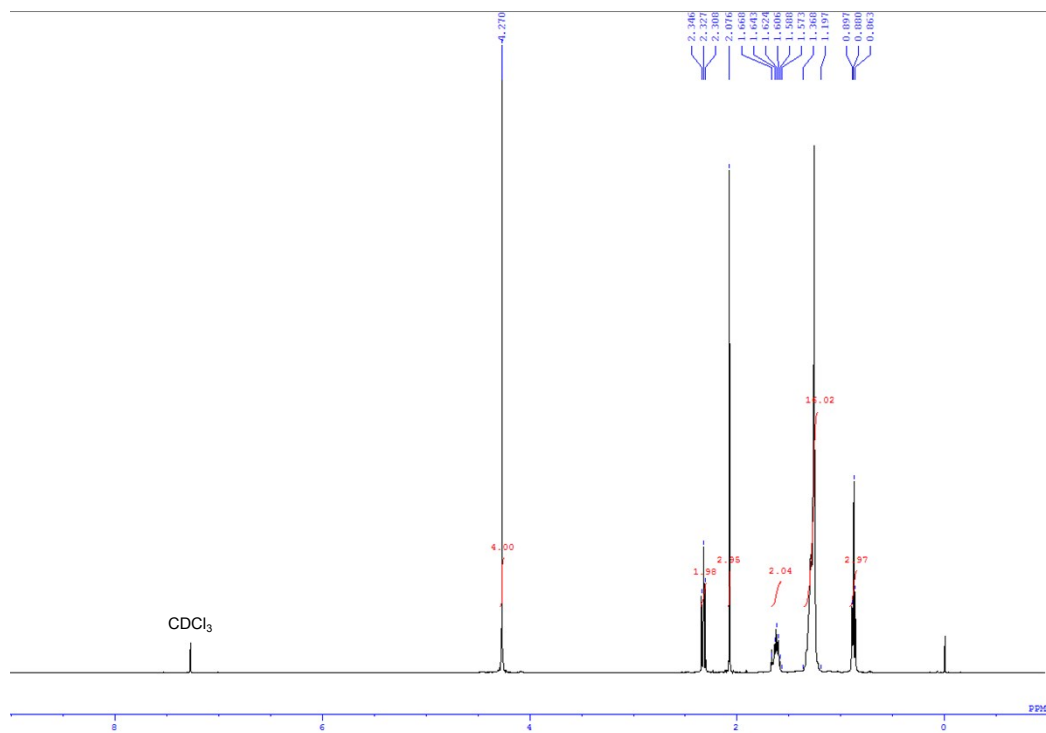


¹³C NMR





¹H NMR



¹³C NMR

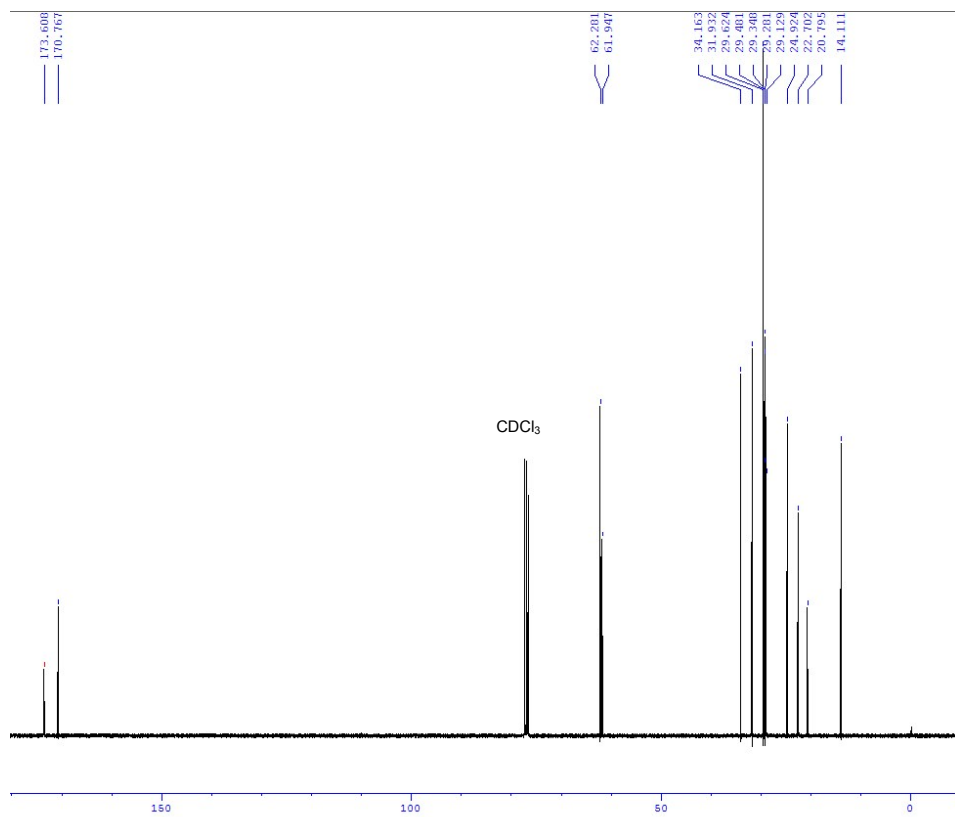
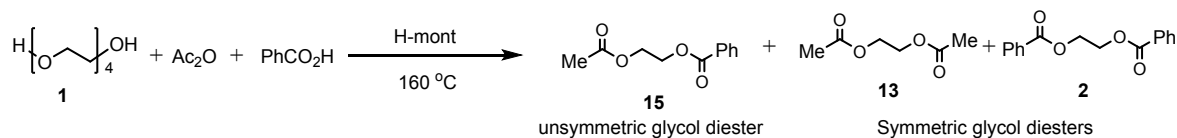


Table S1. Effect of Ac₂O and benzoic acid amounts on catalytic depolymerization of **1** to unsymmetric glycol diester **15**.



Catalyst	Ac ₂ O [mmol]	PhCO ₂ H [mmol]	Time [min]	Yield [%] ^a		
				15	13	2
H-mont	6	3	180	40	57	3
H-mont	6	6	180	57	34	7
H-mont	6	9	180	62	28	10
H-mont	6	12	180	60	23	16
H-mont	6	9	60	59	22	11
H-mont	6	9	90	64	24	11
ZnBr ₂ ^b	6	9	90	0	0	0
Zn(OTf) ₂ ^b	6	9	90	12	21	0

Reaction conditions: polyether (2.4 mmol per oxyethylene unit), Ac₂O (6 mmol), PhCO₂H (3-12 mmol), H-mont (0.2 g), dodecane (2 mL) 160 °C. ^a Determined by GC and GCMS using an internal standard method. ^b 0.172 mmol of Zn complex was used instead of H-mont.

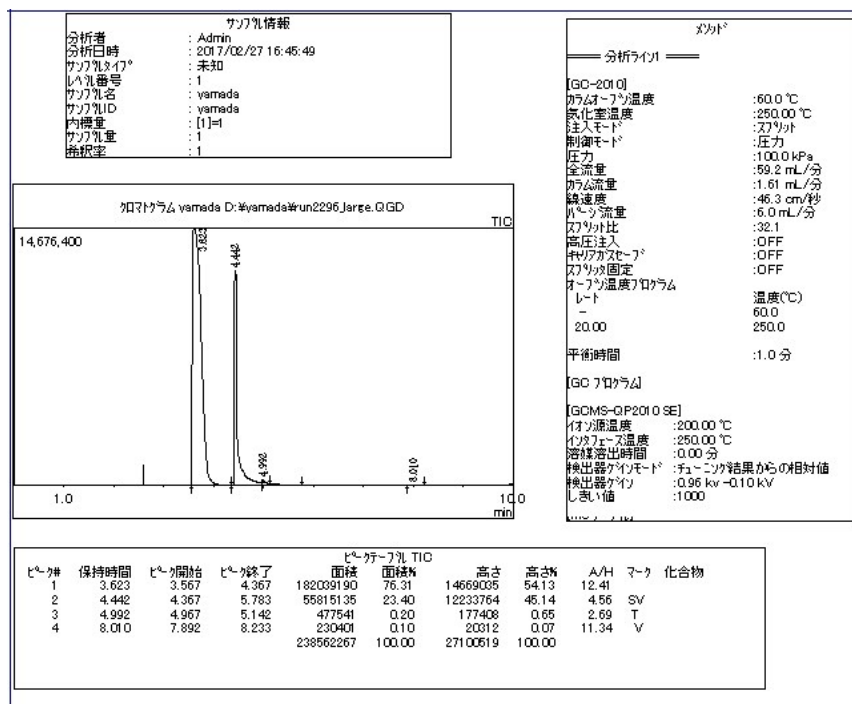


Figure S1. GCMS spectrum of crude solution of the multigram-scale reaction. Retention time, 4.4 min: ethylene glycol diacetate, 3.6 min: AcOH, 5.0 min ethylene glycol monoacetate.

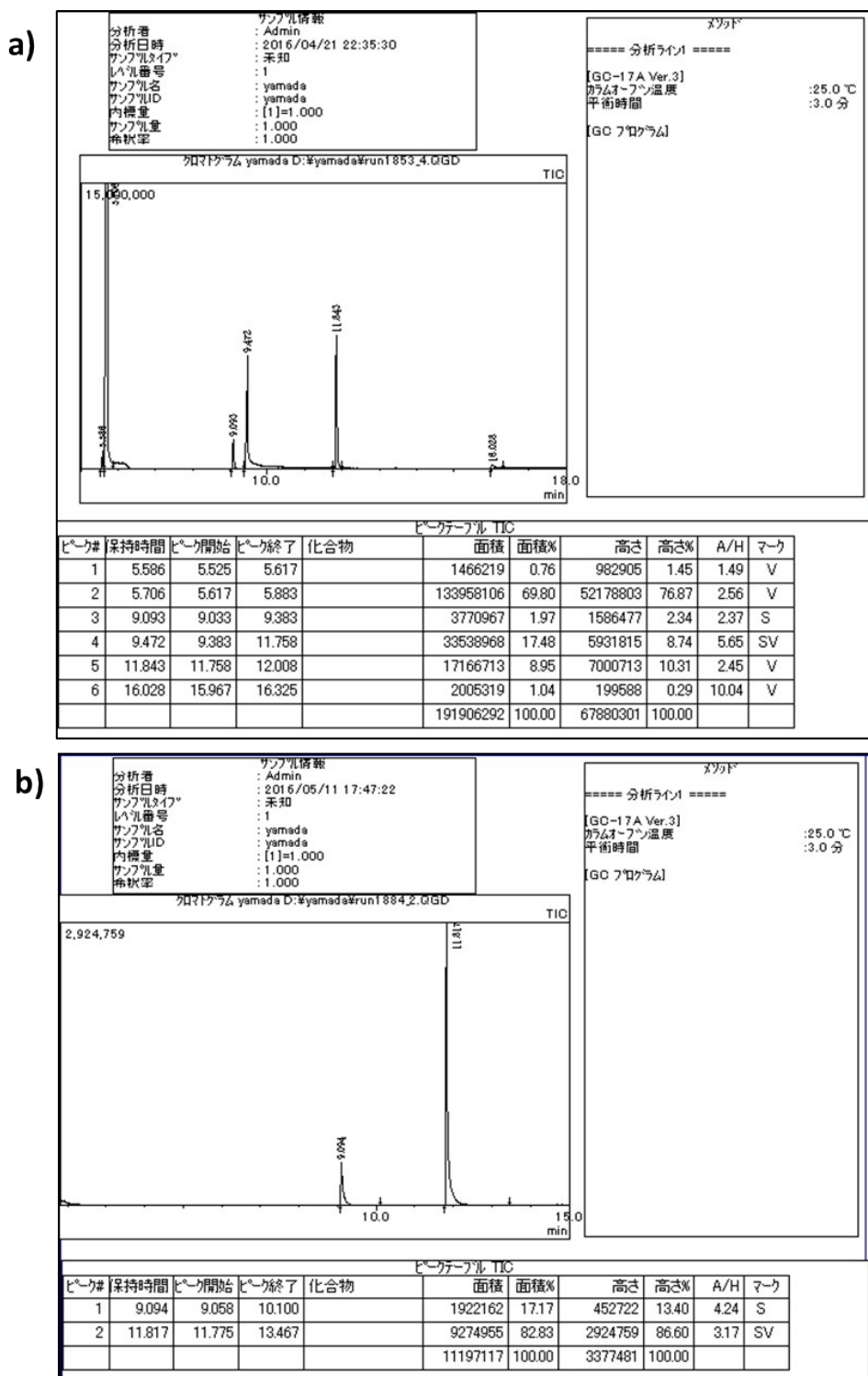


Figure S2. GCMS spectrum of a) crude solution of the depolymerization of polyether **1** with Ac₂O/lauric acid and b) mixture of 2-(acetoxyl)ethyl laurate (**18**) and biphenyl. Retention time, 5.6 min: ethylene glycol diacetate (**13**), 5.7 min: dodecan (solvent), 9.0 min: biphenyl (internal standard), 9.5 min: lauric acid, 11.8 min: 2-(acetoxyl)ethyl laurate (**18**), 16.0 min: ethylene glycol dilaurate.

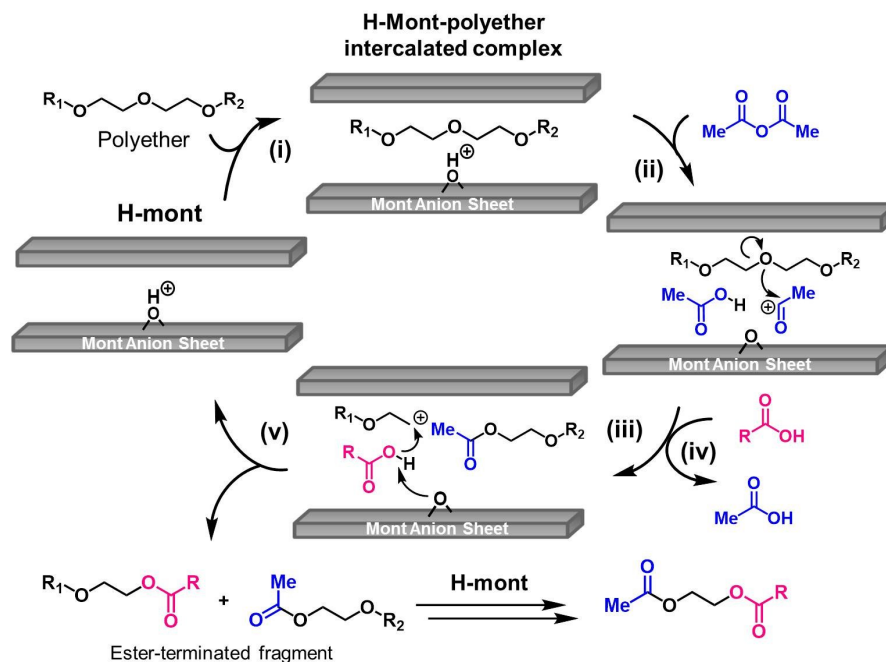
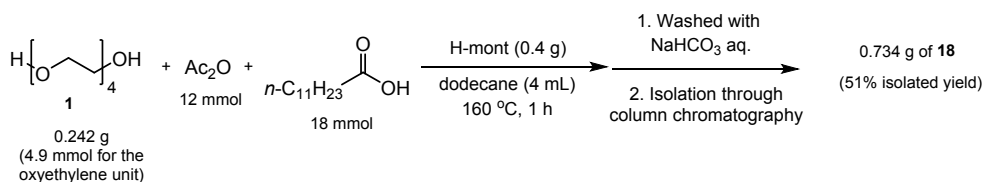


Figure S3. A possible reaction mechanism of depolymerization of polyethers with $\text{Ac}_2\text{O}/\text{RCO}_2\text{H}$ to unsymmetric glycol diester.

The reaction might proceed as follows: (i) polyether is intercalated into the interlayer space of H-mont; (ii) Ac_2O is activated at the Brønsted acid site to form acetyl cations and AcOH ; (iii) the C–O bond of polyether is cleaved by attack of the acetyl cation to give an acetate-terminated fragment and carbocation-terminated fragment; (iv) the resulting AcOH is exchanged with RCO_2H ; (v) the reaction of RCO_2H with the remaining carbocation-terminated fragment results in other ester-terminated fragment. These ester-terminated fragments are further depolymerized by H-mont to afford an unsymmetric glycol diester. The occurrence of step (iv) was supported by the adsorption experiment of H-mont where the addition of an excess amount of PhCO_2H promoted the desorption of the adsorbed AcOH .



Scheme S1. Depolymerization of polyether **1** with Ac_2O /lauric acid

References

[S1] A. Cosxkun, M. Güney, A. Dasxtan, M. Balci, *Tetrahedron*, **2007**, *63*, 4944–4950.