

A Recyclable Vinyl Polymer with a Hemiacetal Ester Skeleton Prepared via the Radical Polymerization of 'Dehydroaspirin'

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Electronic Supplementary Information

Experimental

Instruments

¹H and ¹³C NMR spectra were recorded in CDCl₃ (Across Organics) on an AVANCE NEO (Bruker) and an AVANCE III (Bruker) spectrometers. Chemical shifts in ¹H and ¹³C NMR spectra were referred to the signal of tetramethylsilane (TMS) and solvent (CDCl₃), respectively. Molecular weight and its distributions were determined at 40 °C by size-exclusion chromatography (SEC) on an EXTREMA chromatograph (JASCO) equipped with two SEC columns [PL-gel, Mixed C (300 mm × 7.5 mm), Polymer Laboratories], using tetrahydrofuran (THF, Wako Pure Chemical Industries, for HPLC grade) as an eluent (flow rate = 0.8 mL min⁻¹), and calibrated against standard polystyrene (PS) samples (TSK-gel oligomer kit, Tosoh, *M_n*: 1.03 × 10⁶, 3.89 × 10⁵, 1.82 × 10⁵, 3.68 × 10⁴, 1.36 × 10⁴, 5.32 × 10³, 3.03 × 10³, 8.73 × 10²) and detected with UV (UV-4070, JASCO) and RI (RI-4030, JASCO) detectors. IR spectra were recorded on a Cary 630 FTIR spectrometer equipped with a transmission attachment (single reflection). Thermogravimetric /differential thermal analyses (TG/DTA) was carried out from room temperature to 500 °C at a heating rate of 10 °C with Rigaku Thermo plus II TG8120 under an N₂ atmosphere.

Materials

Phthaloyl chloride and 2-chlorotoluene were a kind gift from Osaka Organic Chemical Industry Ltd. Acetylsalicylic acid, *p*-xylene, *N,N*-dimethylformamide (DMF), triethylamine (Et₃N), vinyl acetate (Vac), formaldehyde aqueous solution (37 wt%), thionyl chloride, concentrated hydrochloric acid (*conc.* HCl aq), Molecular Sieves 4A and solvents were purchased from Wako Pure Chemical Industries, Ltd. Toluene and dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) were purchased from Kanto Chemical Co, Inc. AIBN was purchased from Tokyo Chemical Industry Co., Ltd and recrystallized with MeOH. Chloroform (CHCl₃) was purchased from Yoneyama Yakuin Kogyo Co, Ltd. Other chemicals were purchased from Tokyo Chemical Industry Co., Ltd.

Synthesis of Vilsmeier-Haak reagent

In a three-necked flask, a solution of phthaloyl chloride (64.8 mL, 0.450 mol) in 2-chlorotoluene (30 mL) was added dropwise from a dropping funnel to a mixture of DMF (104 mL, 1.35 mol) and 2-chlorotoluene (200 mL) over 30 min under argon atmosphere. 2-Chlorotoluene (30 mL) was charged to the dropping funnel for washing and added to the reaction mixture. The reaction mixture was stirred at 50 °C for 4 h and cooled to room temperature. The precipitate was collected by filtration and dried *in vacuo* to afford yellowish-white powders (55.5 g, Yield 96.4%). The crude product was used in the next reaction without further purification.

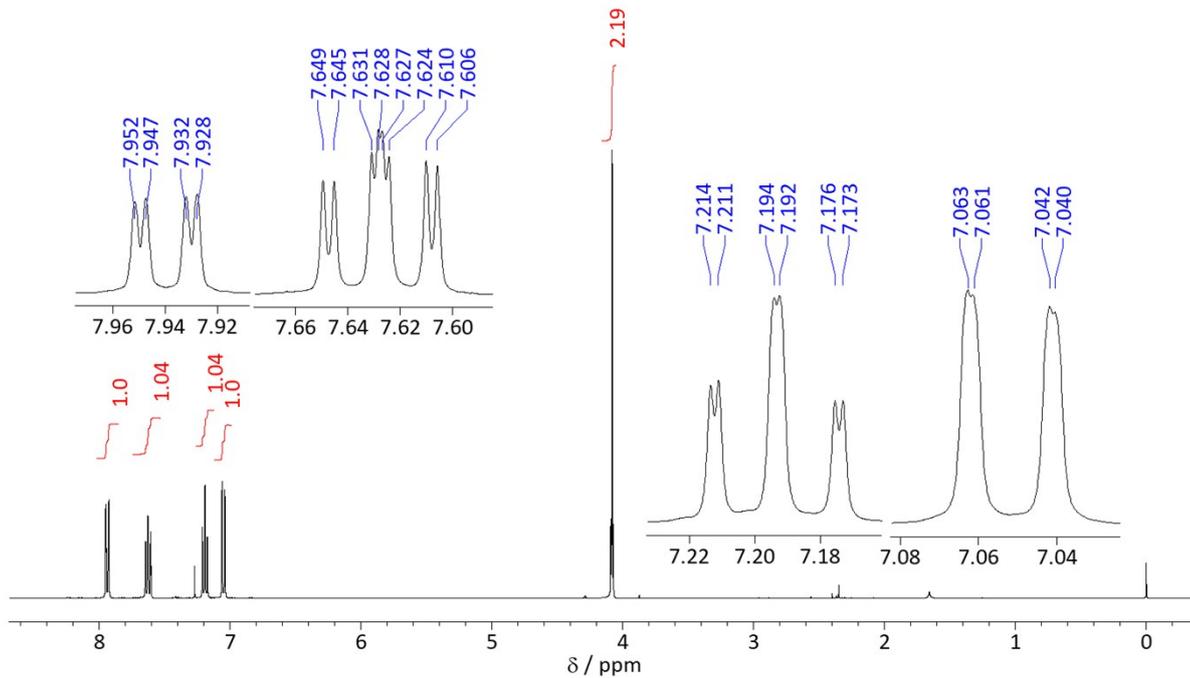
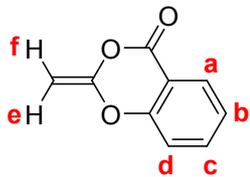
Synthesis of acetylsalicyloyl chloride

Acetylsalicylic acid (64.3 g, 0.357 mol) was added to a suspension of the crude Vilsmeier-Haak reagent (55.5 g) in toluene (500 mL) dried over Molecular Sieves 4A under argon atmosphere. After 2 h, the reaction mixture became heterogeneous with cloudy two layers. The upper layer was separated and concentrated under reduced pressure to yield yellowish oil (75.0 g, Yield 106%). The crude acetylsalicyloyl chloride was used in the next reaction without further purification.

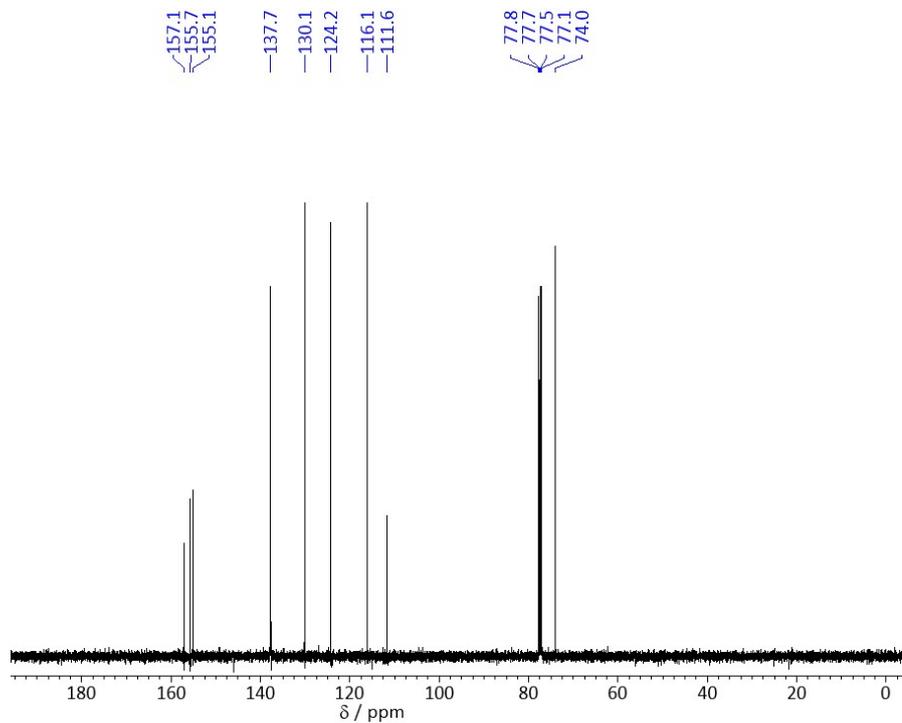
Synthesis of 2-methylene-4H-benzo[d][1,3]dioxin-4-one (MBDO)

Et₃N (60.2 mL, 0.434 mmol) was added dropwise to a solution of crude acetylsalicyloyl chloride (75.0 g) in *p*-xylene (500 mL, anhydrous grade) under argon atmosphere. The reaction mixture was refluxed for 22 h. The precipitate was removed by filtration, and the filtrate was concentrated and distilled under reduced pressure (bp: 72-78.0 °C / 0.28-0.32 mmHg) to yield MBDO as colorless oil (42.2 g, Yield: 72.9%).

¹H NMR spectrum (400 MHz, CDCl₃, 25 °C): δ/ppm 7.94 (dd, *J*₁ = 7.8 Hz, *J*₂ = 1.7 Hz, 1H, a), 7.63 (td, *J*₁ = 8.1 Hz, *J*₂ = 1.7 Hz, 1H, c), 7.19 (td, *J*₁ = 7.8 Hz, *J*₂ = 0.9 Hz, 1H, b), 7.05 (dd, *J*₁ = 8.1 Hz, *J*₂ = 0.9 Hz, 1H, d), 4.08 (d, *J* = 1.1 Hz, 2H, e and f); ¹³C NMR spectrum (100 MHz, CDCl₃, 25 °C) δ/ppm 157.1, 155.7, 155.1, 137.7, 130.1, 124.2, 116.1, 111.6, 74.0. bp 77 °C/0.89 Torr



¹H NMR spectrum of MBDO (400 MHz, CDCl₃, 25 °C).



¹³C NMR spectrum of MBDO (100 MHz, CDCl₃, 25 °C).

Polymerization of MBDO

AIBN (76.9 mg, 0.468 mmol) was added to MBDO (3.79 g, 23.38 mmol) in a 10 mL round-bottom flask and the mixture was heated at 65 °C for 18 h. After cooling to room temperature, CHCl₃ (25 mL) was added to the products. The soluble fraction in CHCl₃ was collected by filtration and poured into toluene (400 mL). The precipitate was collected by centrifugation, dried *in vacuo* at 100 °C for 6 h to afford the polymer (1.47 g, Yield 38.8 %; Table 1, Entry 1, $M_n = 2400$, $D = 2.10$).

Copolymerization of MBDO and Vinyl acetate

A typical procedure (Table 1, Entry 3): AIBN (0.0264 g, 0.161 mmol) was added to a mixture of MBDO (0.655 g, 4.04 mmol) and VAc (0.339 g, 3.93 mmol) in a test tube and the solution was heated at 60 °C for 18 h. After cooling to room temperature, the products were dissolved in CHCl₃ (20.7 mL). The solution was poured into hexane (500 mL). The precipitate was collected by centrifugation and dried *in vacuo* to afford the polymer (0.709 g, Yield 69.5%, $M_n = 37500$, $D = 2.35$).

Determination of the relative reactivity by Kelen- Tüdös methods

Copolymerizations of MBDO and VAc were conducted in toluene as described above, but decamethylcyclpentasiloxane (D5) was added as an internal standard. A small portion of the reaction mixture was sampled before and after the polymerization, and ¹H NMR spectra were measured in CDCl₃ that did not contain tetramethylsilane. For the quantitative evaluation, the relaxation delay time (d1) was set as 40 sec. The exact feed ratios and conversions were determined from the intensity ratio of vinylidene and vinyl signals for MBDO and VAc, respectively, against that for internal standard. The results were shown in **Table S1**.

Table S1. Determination of the relative reactivity between MBDO (M1) and VAc (M2) by Kelen- Tüdös methods.

Entry	Feed [%]			Time [min]	Conversion [%]		Composition [%]		f	η	ξ
	M1	M2	F		M1	M2	M1	M2			
S1	93.1	6.95	13.4	30	17.7	2.94	95.3	4.61	20.7	1.19	0.813
S2	79.0	21.0	3.77	30	14.3	2.64	84.8	15.2	5.58	0.681	0.561
S3	61.7	38.3	1.61	150	14.6	10.3	71.8	28.2	2.54	0.324	0.338
S4	42.9	57.1	0.747	120	12.0	5.26	54.8	45.2	1.21	0.053	0.187

$$\eta = 1.805 \times \xi - 0.2938$$

$$\alpha = 1.998$$

$$r_1 = 1.805 \times 1 - 0.294 \approx 1.51$$

$$r_2 = -0.2938 \times 2.00 \times (-1) \approx 0.587$$

Degradation of poly(MBDO)

1 M HCl aqueous solution (1.82 mL, 1.82 mmol) was added to a solution of poly(MBDO) (0.295 g, 1.82 mmol for the repeating unit) in DMSO-*d*₆ (7.76 mL). The solution was heated at 80 °C. The mixture was sampled at the planned time and the ¹H NMR spectrum was measured.

Degradation of poly(MBDO-*r*-VAc)

1 M HCl aqueous solution (2.09 mL, 2.09 mmol) was added to the solution of the copolymer obtained in Entry 3 (0.605 g, 2.09 mmol for MBDO unit) in DMSO-*d*₆ (21.1 mL). The solution was heated at 80 °C. The mixture was sampled and at the planned time and the ¹H NMR spectrum was measured. The reaction mixture was also sampled for SEC, added to CHCl₃ (10 mL) and washed with *sat.* NaHCO₃ solution for neutralization. The organic layer was concentrated by bubbling with argon gas. The sample (10 mg) was dissolved in THF (1.0 mL) and filtered through a membrane filter (SHIMADZU GLC, TORAST Disc, hydrophobic PTFE, pore size 0.22 μm) to measure SEC.

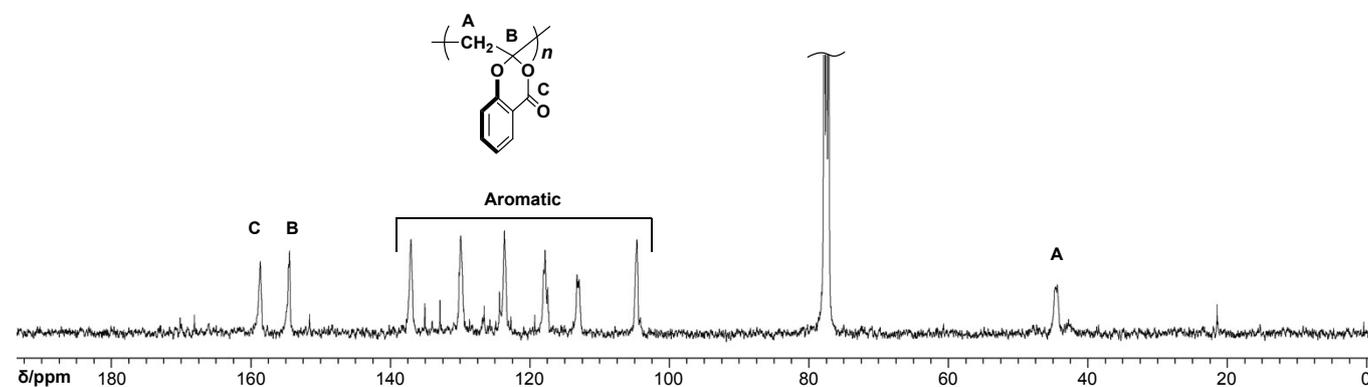


Figure S1. ¹³C NMR spectrum of poly(MBDO) (100 MHz, CDCl₃, 25 °C).

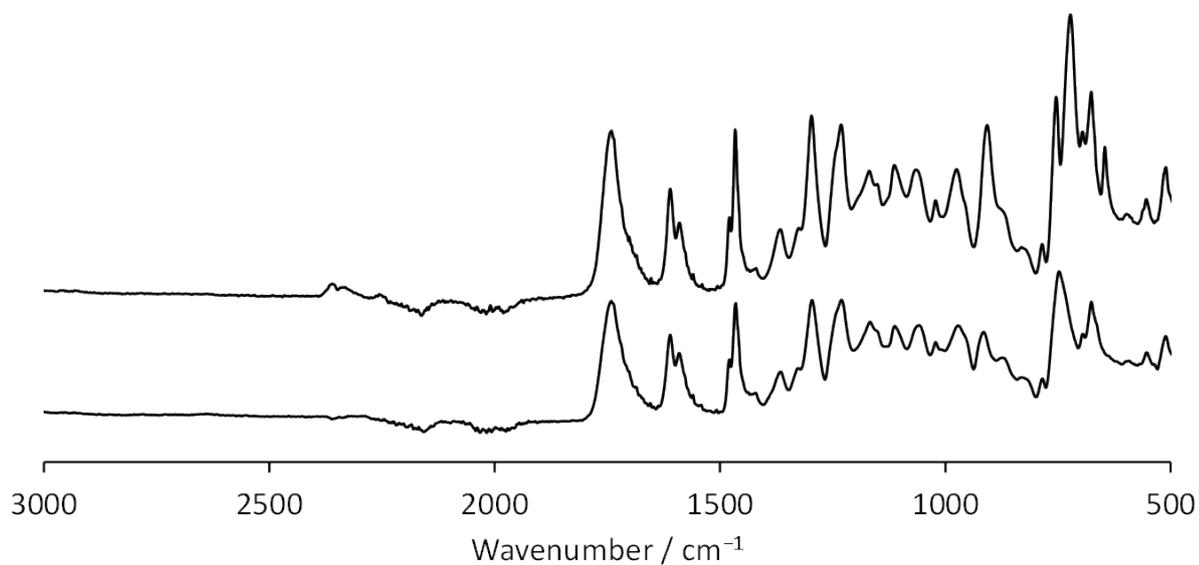


Figure S2. IR spectra of soluble (upper) and insoluble (below) fraction of poly(MBDO) for CHCl_3 .

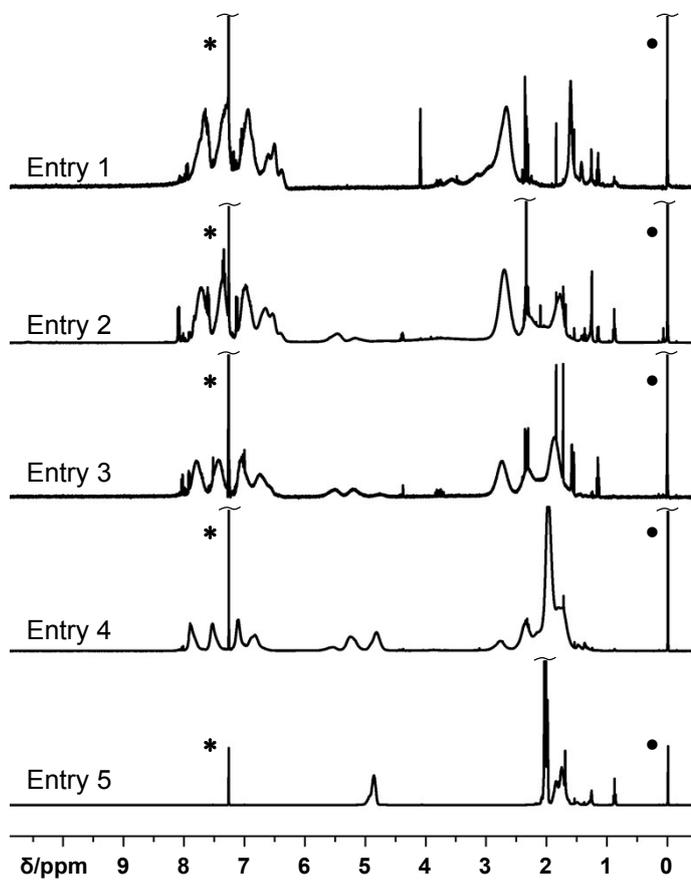


Figure S3. ^1H NMR spectra of poly(MBDO) and poly(MBDO-*r*-VAc) in **Table 1** (400 MHz, CDCl_3 , 25 °C)..

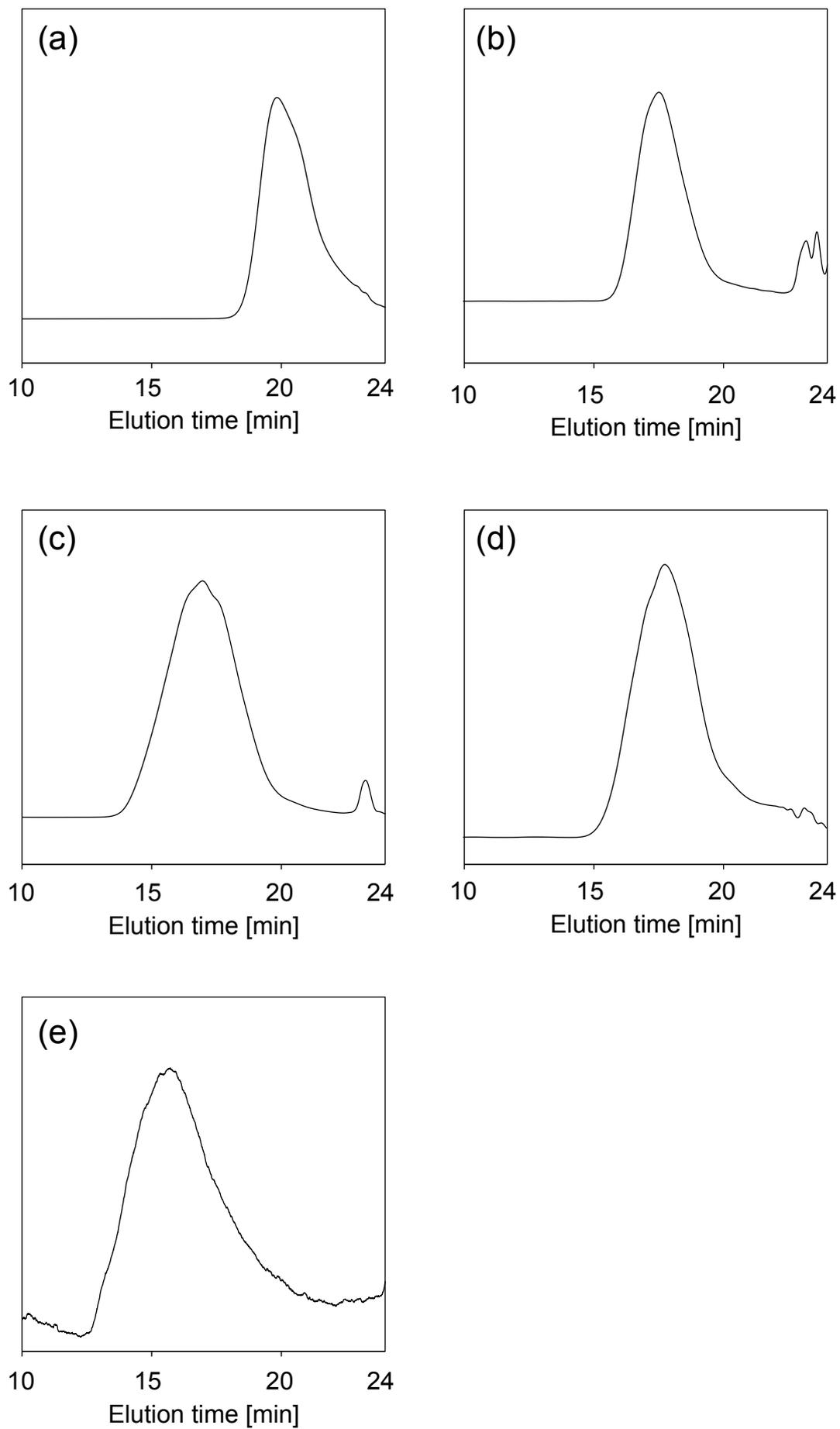


Figure S4. SEC curves of poly(MBDO) and poly(MBDO-*r*-VAc) in **Table 1**. (a) Entry 1, (b) Entry 2, (c) Entry 3, (d) Entry 4, and (e) Entry 5.

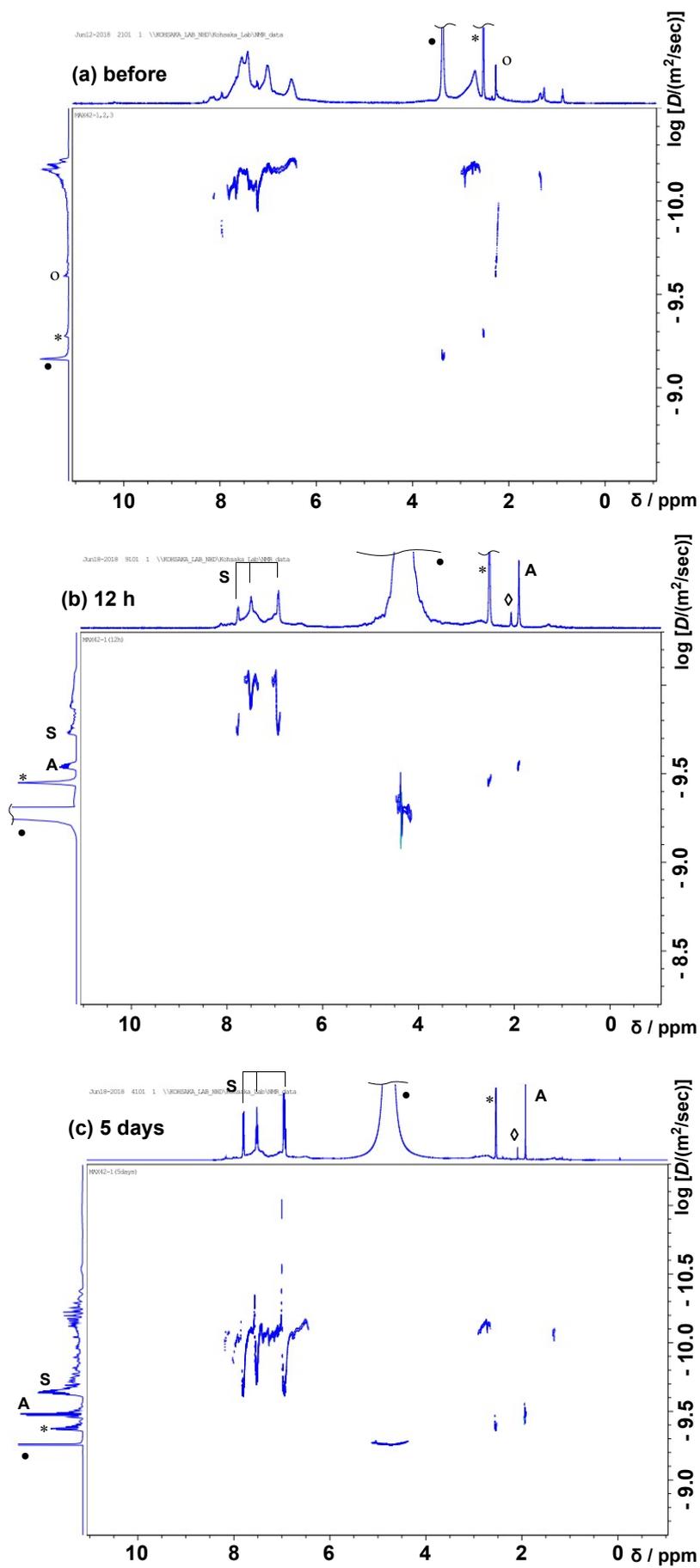


Figure S5. DOSY NMR spectra of degrading poly(MBDO) (400 MHz, DMSO- d_6 , 25 °C).

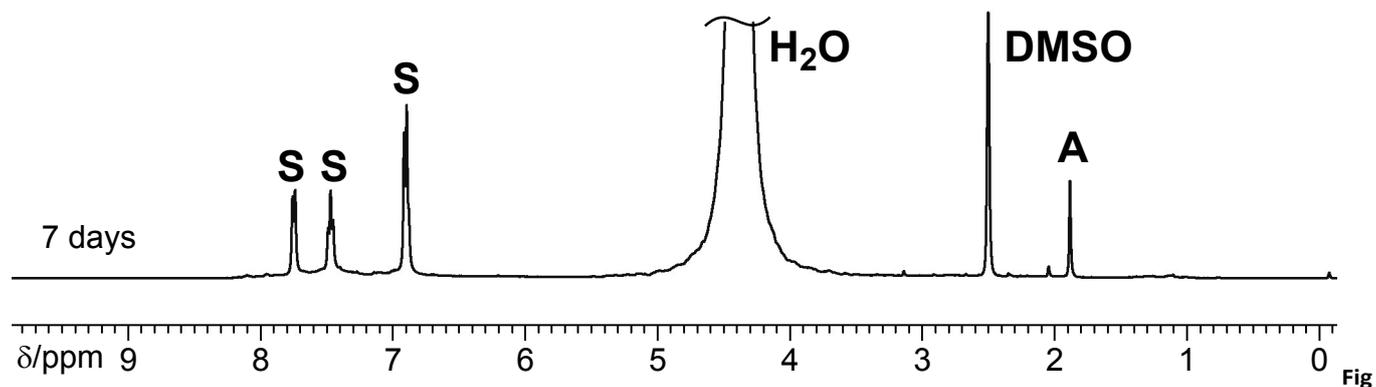


Figure S6. ^1H NMR spectrum (Zoomed-up) of the reaction mixture of acid hydrolysis of poly(MBDO) in DMSO after 7 days (400 MHz, DMSO- d_6 , 25 °C). This experiment was conducted after our first submission in order to corroborate our claims. Therefore, this is a different lot from that for Figure 4(a).

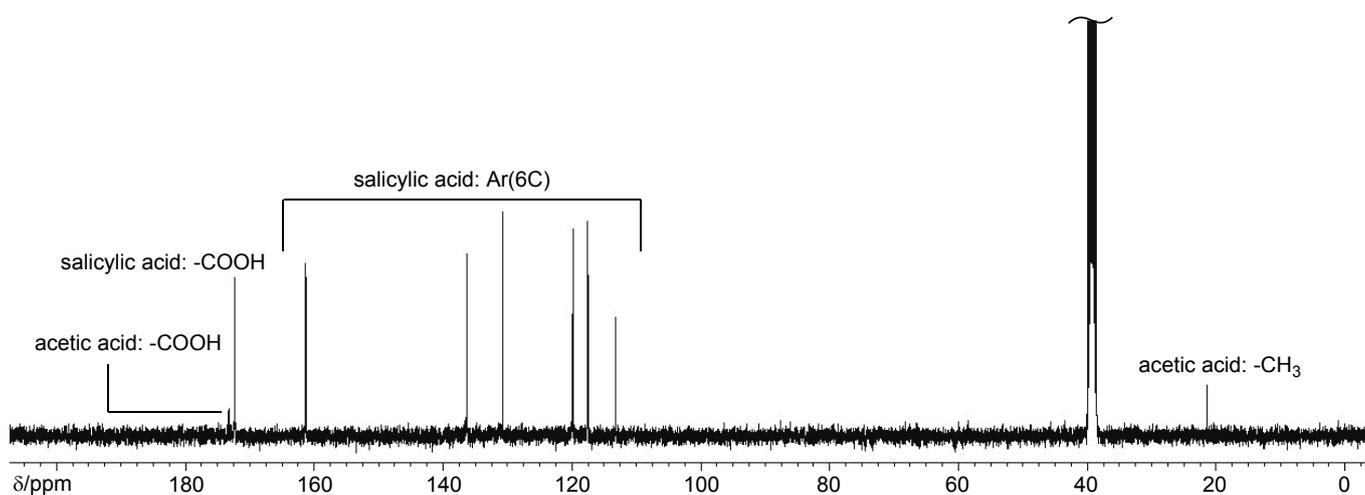


Figure S7. ^{13}C NMR spectrum of the reaction mixture of acid hydrolysis of poly(MBDO) in DMSO after 7 days (100 MHz, DMSO- d_6 , 25 °C). This experiment was conducted after our first submission in order to corroborate our claims. Therefore, this is a different lot from that for Figure 4(a).

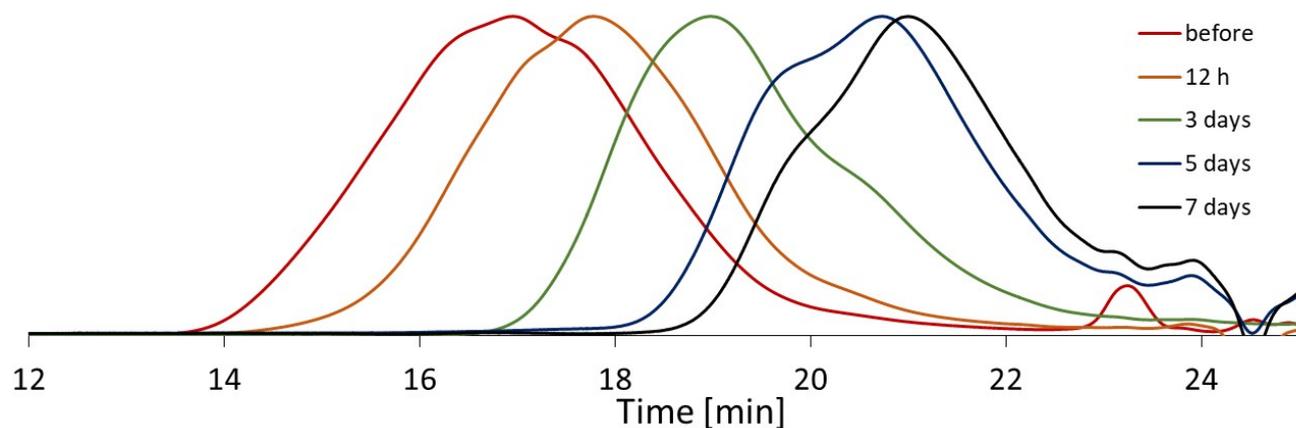
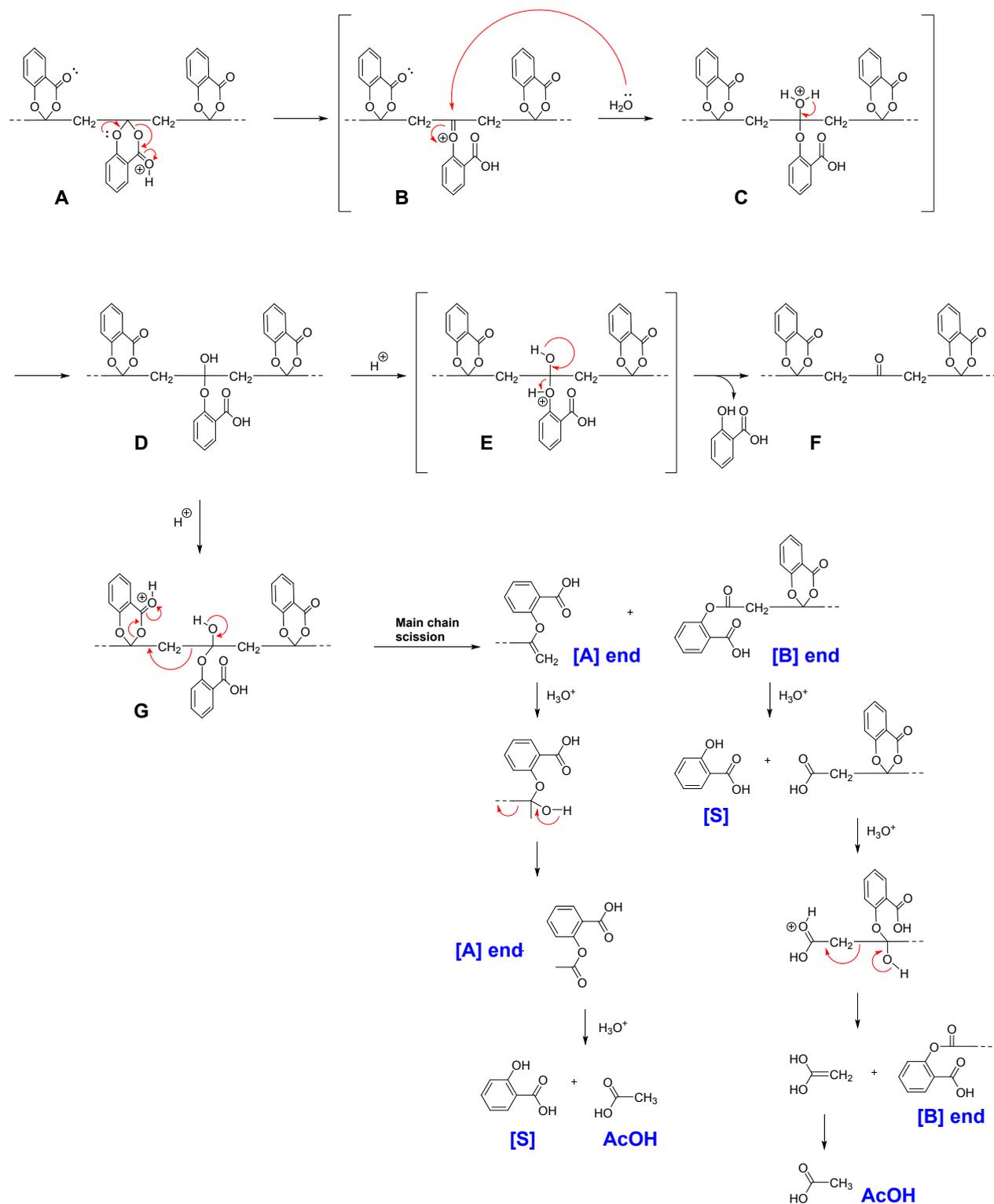


Figure S8. The changes of SEC curves during the hydrolysis of poly(MBDO-*r*-VAc).



Scheme S1. Proposed reaction mechanism of the hydrolysis and main chain scission of poly(MBDO).

From **A** to **D**: A typical hydrolysis reaction of hemiacetal ester **A** via oxonium cation **B**. The hemiacetal **D** should undergo further hydrolysis to form ketone skeleton **F**. However, the investigation with DOSY NMR spectrometry and other experiments implied another path toward acetic acid and salicylic acid. We interpret that the carbonyl group in the neighbouring units of hemiacetal unit would be protonated, as the carbonyl group has higher basicity than phenol ether. Hence, **G** would be formed instead of **E**. Then, the decomposition of hemiacetal would follow, resulting in the main chain scission. After this, the formed [A]- and [B]-ends would be decomposed via acid hydrolysis to form salicylic acid and acetic acid.