

Electronic Supporting Information

Synthesis of Degradable and Chemically Recyclable Polymers Using 4,4-Disubstituted Five-Membered Cyclic Ketene Hemiacetal Ester (CKHE) Monomers

Xin Yi Oh,^a Yicen Ge^a and Atsushi Goto^{a}*

^aDivision of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences,
Nanyang Technological University, 21 Nanyang Link, 637371 Singapore

Materials

2-Acetoxyisobutyryl chloride (>97%, Tokyo Chemical Industry (TCI)), 2-hydroxyisobutyric acid (>98%, TCI), acetyl chloride ($\geq 99.0\%$, Sigma-Aldrich, USA), oxalyl chloride ($\geq 99.0\%$, Sigma-Aldrich), triethylamine (>99.0%, TCI), anhydrous dichloromethane (DCM) (>99.0%, TCI), hexane (>99%, International Scientific, Singapore), diethyl ether (ACS reagent grade, VWR International, USA), ethanol ($\geq 99.5\%$, absolute, Fisher Scientific, USA), chloroform (>99.2%, VWR Chemicals, USA), tetrahydrofuran (THF) (>99.5%, Kanto Chemical, Japan), *N,N*-dimethylformamide (DMF) (>99.5%, Kanto), 2,2'-azobis(2-methylpropionitrile) (AIBN) (95%, Wako Pure Chemical, Japan), 2,2'-azobis(2,4-dimethylvaleronitrile) (V65) (95%, Wako), ethylene carbonate (EC) (>99%, TCI), toluene (ACS reagent grade, VWR International), methanol (ACS reagent grade, VWR International), *tert*-butyl peroxybenzoate (TBPB) ($\geq 98.0\%$, Sigma-Aldrich), methyl methacrylate (MMA) (>99.8%, TCI), poly(ethylene glycol) methyl ether methacrylate (PEGMA) (average molecular weight = 300) (98%, Sigma-Aldrich), butyl acrylate (BA) (>99%, TCI), acrylonitrile (AN) (>99%, TCI), butyl methacrylate (BMA) (>99.8%, TCI), styrene (St) (>99.8%, TCI), 2-(dimethylamino)ethyl methacrylate (DMAEMA) ($\geq 98.5\%$, TCI), 2-methoxyethyl acrylate (MEA) (>98%, TCI), *N,N*-dimethylacrylamide (DMA) (>99.0%, TCI), vinyl acetate (VAc) (>99.0%, TCI), 1-vinyl-2-pyrrolidinone (NVP) (>99.0%, TCI), lauryl methacrylate (LMA) (>97.0%, TCI), benzyl methacrylate (BzMA) (>98.0%, TCI), 2-ethylhexyl methacrylate (EHMA) (>99.0%, TCI), stearyl methacrylate (SMA) (>97.0%, TCI), potassium hydroxide (KOH) (min. 85%, GCE, Sweden), sodium hydroxide (NaOH) ($\geq 97.0\%$, VWR Chemicals), hydrochloric acid (1M, TCI), trifluoroacetic acid (TFA) (>99.0%, TCI), pentylamine (>98.0%, TCI), and anhydrous magnesium sulfate (>98.0%, TCI) were used as received.

Measurement

The GPC analysis using THF as an eluent was performed on a Shimadzu i-Series Plus liquid chromatograph LC-2030c Plus (Kyoto, Japan) equipped with a Shodex (Japan) KF-804L mixed gel column (300 × 8.0 mm; bead size = 7 μm ; pore size = 1500 Å) and a Shodex LF-804 mixed gel column

(300 × 8.0 mm; bead size = 6 μm; pore size = 3000 Å). The flow rate was 0.7 mL/min (40 °C). The GPC analysis using DMF as an eluent was performed on a Shimadzu LC-2030c Plus equipped with two Shodex LF-804 mixed gel columns (300 × 8.0 mm; bead size = 6 μm; pore size = 3000 Å) and a Shodex KD-802 (300 × 8.0 mm; bead size = 6 μm; pore size = 150 Å). The flow rate was 0.34 mL/min (40 °C). The DMF eluent contained LiBr (10 mM). The sample detection was conducted using a refractive index detector (RID-20A) for THF-GPC and for DMF-GPC. The column system was calibrated with standard poly(methyl methacrylate)s (PMMA)s for both THF-GPC and DMF-GPC systems.

The NMR spectra were recorded on Bruker (Germany) BBFO400 spectrometer (400 MHz) at ambient temperature. CDCl₃, DMSO-*d*₆, THF-*d*₈ and CD₃CN (Cambridge Isotope Laboratories, USA) were used as the solvents for the NMR analysis, and the chemical shift was calibrated using residual undeuterated solvents or tetramethylsilane (TMS) as the internal standard. The monomer conversions and the monomer compositions in the obtained polymers were determined with ¹H NMR.

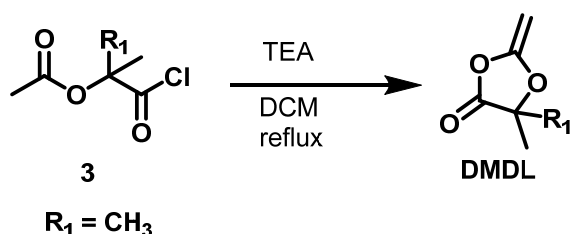
The differential scanning calorimetry (DSC) curves were recorded with QSeries DSC Q50 model device (TA instrument, New Castle, US). The DSC analysis was conducted using an aluminium sample pan under flowing nitrogen at a flow rate of 50 mL/min. The samples were cooled down to -80 °C or -50 °C and heated up to 225–400 °C with a heating rate of 10 °C/min.

The thermal gravimetric analysis (TGA) curves were recorded with TGA Q500 model device (TA instrument). The TGA analysis was carried out in platinum pans under flowing air at a flow rate of 60 mL/min with a heating rate of 10 °C/min at a temperature range of 25–700 °C.

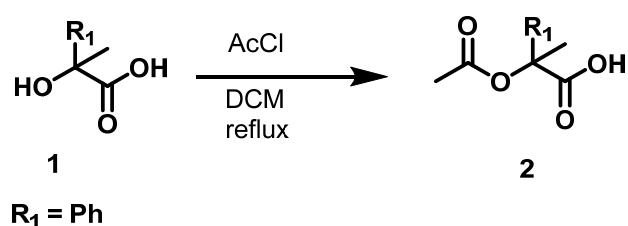
Experimental Part

Synthesis of DMDL. 5,5-Dimethyl-2-methylene-1,3-dioxolan-4-one (DMDL) was synthesized according to reported literature.¹ A mixture of 2-acetoxyisobutyryl chloride (**3** (**R**₁ = **CH**₃), 50.0 g, 0.30 mol), triethylamine (36.8 g, 0.36 mol), and anhydrous DCM (200 mL) was heated under reflux in nitrogen atmosphere. After 5 h, the mixture was cooled down and diluted with 200 mL of

hexane/diethyl ether (1/1 (v/v)). The resulting suspension was filtered, and the solvent was evaporated with a rotary evaporator. The residual liquid was subjected to fractional distillation to give DMDL (30 g, 0.23 mol) at 15 Torr at 40 °C in 80% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.70 (d, $J = 4.0$ Hz, 1H), 3.62 (d, $J = 4.0$ Hz, 1H), 1.54 (s, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 173.3, 157.4, 79.3, 61.5, 23.7.

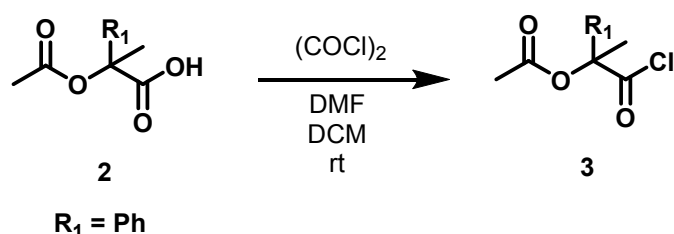


Synthesis of PhDL. 2-Acetoxy-2-phenylpropanoic acid (**2** ($\text{R}_1 = \text{Ph}$))) was synthesized according to the reported literature.² 2-Hydroxy-2-phenylpropanoic acid hydrate (**1** ($\text{R}_1 = \text{Ph}$)), 10.0 g, 60 mmol) was suspended in anhydrous DCM (60 mL) under Ar, followed by the addition of acetyl chloride (12 mL, 2.8 equiv., 168 mmol) dropwise. The mixture gradually became clear and was heated to reflux. After 2 h, the resulting solution was cooled down, and concentrated under vacuum to remove all volatiles. The residue was crystallized to give **2** ($\text{R}_1 = \text{Ph}$) (12.0 g, 57.6 mmol) in 96% yield as a white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.57-7.52 (m, 2H), 7.42-7.32 (m, 3H), 2.20 (s, 3H), 1.96 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 176.3, 170.1, 139.2, 128.9, 128.7, 128.6, 125.1, 124.9, 81.4, 23.6, 21.4.

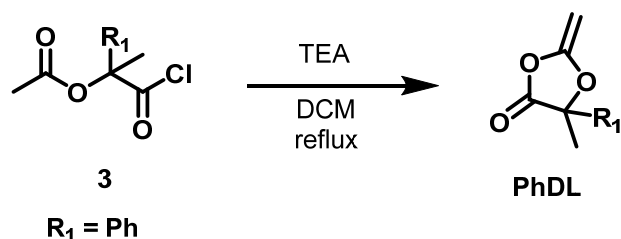


1-Chloro-1-oxo-2-phenylpropan-2-yl acetate (**3** ($\text{R}_1 = \text{Ph}$))) was synthesized using a modified procedure according to the reported literature.³ 2-Acetoxy-2-phenylpropanoic acid (**2** ($\text{R}_1 = \text{Ph}$)), 12.0 g, 57.6 mmol) was dissolved in anhydrous DCM (60 mL) under Ar, followed by the addition of *N,N*-

dimethylformamide (0.45 mL, 10 mol%, 5.8 mmol) and oxalyl chloride (5.4 mL, 1.1 equiv., 63.4 mmol) with caution. The mixture was stirred at room temperature overnight. The resulting solution was concentrated under vacuum to remove all volatiles. The residue was directly used in the following step as **3** ($R_1 = \text{Ph}$) (13.0 g, 57.4 mol, 99% yield) as a yellow sticky semi-solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.59-7.51 (m, 2H), 7.45-7.30 (m, 3H), 2.29-2.19 (m, 3H), 1.99-1.95 (m, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 173.3, 172.9, 169.9, 169.8, 139.9, 136.5, 129.1, 128.9, 128.4, 125.1, 125.0, 86.7, 81.6, 24.2, 23.8, 21.4, 21.1.



5-Methyl-2-methylene-5-phenyl-1,3-dioxolan-4-one (PhDL) was synthesized using a modified procedure according to the reported literature.¹ The 1-chloro-1-oxo-2-phenylpropan-2-yl acetate (**3** ($R_1 = \text{Ph}$), 13.0 g, 57.4 mmol) obtained above was dissolved in anhydrous DCM (100 mL), followed by the addition of triethylamine (37.6 g, 4.7 equiv., 270 mmol) under Ar. The mixture was heated to reflux. After 2 h, the mixture was cooled down, concentrated and precipitated with 100 mL of diethyl ether.



The resulting suspension was filtered, and the solvent was evaporated with a rotary evaporator. The residual liquid was subject to fractional distillation to give PhDL (9.8 g, 51.5 mmol) at 0.1 Torr at 60 °C

in 90% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.59-7.54 (m, 2H), 7.46-7.36 (m, 3H), 3.85 (d, $J = 4.0$ Hz, 1H), 3.83 (d, $J = 4.0$ Hz, 1H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.5, 157.5, 137.2, 129.1, 128.9, 124.6, 81.8, 62.1, 25.1.

Stability of DMDL under Moisture. DMDL (0.05 g, 8.9 wt%) and DMSO-d_6 (0.50 g, 89.3 wt%) were mixed at room temperature in a vial. The mixture was transferred to a NMR tube. Water (0.01 g, 1.8 wt%) was added to the mixture. After a prescribed time t , the mixture was analyzed with NMR. In the presence of moisture, DMDL was hydrolyzed to form compound **2** (Scheme 3). We compared integrals of the vinyl protons (a) of DMDL at 3.62 and 3.70 ppm with and those of the methyl protons (c) of compound **2** and possibly further decomposed species of compound **2** from 1.86 to 2.09 ppm (Fig. S3). The extents of the DMDL hydrolysis were determined to be 5%, 11%, and 64% at 0.5 h (Fig. S3a), 12 h (Fig. S3b), and 4 days (Fig. S3c), respectively.

General Procedure for Polymerization. In a typical run, a mixture (1.2–2.5 mL, typically) of a CKHE monomer, a co-monomer, AIBN or V65 or TBPB (radical initiator), and solvent was heated in a Schlenk flask at 60-120 °C under argon atmosphere with magnetic stirring. After a prescribed time t , an aliquot (0.1 mL) of the solution was taken out by a syringe, cooled to room temperature, and analyzed with GPC and ^1H NMR. At the last date point of the reaction, the polymer solution was diluted with chloroform (acetonitrile for AN and DMA), and the polymer was reprecipitated in a mixture of hexane/diethyl ether (1/1 (v/v)) twice (methanol for BA, St, BMA, LMA, EHMA, and SMA) for purification. The collected polymer was dried in vacuo and analyzed with ^1H NMR.

Synthesis of PDMDL ($M_n = 104000$ and $\mathcal{D} = 2.04$) (Table 1, entry 2) Used for Degradation. A mixture of DMDL (2.50 g, 19.5 mmol) and AIBN (16.0 mg, 0.0975 mmol) was heated in a Schlenk flask at 70 °C under argon atmosphere with magnetic stirring. After 1.5 h, the reaction was cooled to room temperature and analyzed with GPC and ^1H NMR. The polymer solution was diluted with chloroform (5 mL), and the polymer was reprecipitated in a mixture of hexane/diethyl ether (1/1 (v/v))

(50 mL) twice. The collected polymer was dried in vacuo to give a PDMDL ($M_n = 104000$ and $\bar{D} = 2.04$) as a white solid.

Synthesis of PDMDL ($M_n = 39000$ and $\bar{D} = 1.42$) Used for Degradation. A mixture of DMDL (2.50 g, 19.5 mmol), AIBN (16.0 mg, 0.0975 mmol), and toluene (10 wt%) was heated in a Schlenk flask at 70 °C under argon atmosphere with magnetic stirring. After 3 h, the reaction was cooled to room temperature and analyzed with GPC and ^1H NMR. The polymer solution was diluted with chloroform (5 mL), and the polymer was reprecipitated in a mixture of hexane/diethyl ether (1/1 (v/v)) (50 mL) twice. The collected polymer was dried in vacuo to give a PDMDL ($M_n = 39000$ and $\bar{D} = 1.42$) as a white solid.

Synthesis of PPEGMA-*r*-PDMDL ($M_n = 39000$ and $\bar{D} = 2.22$) (Table 1, entry 10) Used for Degradation. A mixture of PEGMA (1.17 g, 3.90 mmol), DMDL monomer (0.50 g, 3.90 mmol), V65 (19.4 mg, 0.0780 mmol), and toluene (50 wt%) was heated in a Schlenk flask at 60 °C under argon atmosphere with magnetic stirring. After 4 h, the reaction was cooled to room temperature and analyzed with GPC and ^1H NMR. The polymer solution was diluted with chloroform (2 mL), and the polymer was reprecipitated in a mixture of hexane/diethyl ether (1/1 (v/v)) (20 mL) twice. The collected polymer was dried in vacuo to give a PPEGMA-*r*-PDMDL ($M_n = 39000$ and $\bar{D} = 2.22$) as a transparent viscous solid.

Synthesis of PPEGMA ($M_n = 72000$ and $\bar{D} = 2.82$) Used for Degradation. A mixture of PEGMA (1.09 g, 3.63 mmol), V65 (9.02 mg, 0.0363 mmol), and toluene (50 wt%) was heated in a Schlenk flask at 60 °C under argon atmosphere with magnetic stirring. After 1.5 h, the reaction was cooled to room temperature and analyzed with GPC and ^1H NMR. The polymer solution was diluted with chloroform (2 mL), and the polymer was reprecipitated in a mixture of hexane/diethyl ether (1/1 (v/v)) (20 mL) twice. The collected polymer was dried in vacuo to give a PPEGMA ($M_n = 72000$ and $\bar{D} = 2.82$) as a transparent viscous solid.

Synthesis of PLMA-*r*-PDMDL ($M_n = 42000$ and $\bar{D} = 1.76$) (Table 1, entry 13) Used for Degradation. A mixture of LMA (1.00 g, 3.93 mmol), DMDL (0.50 g, 3.90 mmol), AIBN (12.8 mg, 0.0780 mmol), and toluene (50 wt%) was heated in a Schlenk flask at 70 °C under argon atmosphere with magnetic stirring. After 3 h, the reaction was cooled to room temperature and analyzed with GPC and ^1H NMR. The polymer solution was diluted with chloroform (2 mL), and the polymer was reprecipitated in methanol (20 mL) twice. The collected polymer was dried in vacuo to give a PLMA-*r*-PDMDL ($M_n = 42000$ and $\bar{D} = 1.76$) as a transparent viscous solid.

Synthesis of PLMA ($M_n = 90000$ and $\bar{D} = 2.32$) Used for Degradation. A mixture of LMA (1.00 g, 3.93 mmol), AIBN (12.8 mg, 0.0393 mmol), and toluene (50 wt%) was heated in a Schlenk flask at 70 °C under argon atmosphere with magnetic stirring. After 3 h, the reaction was cooled to room temperature and analyzed with GPC and ^1H NMR. The polymer solution was diluted with chloroform (2 mL), and the polymer was reprecipitated in methanol (20 mL) twice. The collected polymer was dried in vacuo to give a PLMA ($M_n = 90000$ and $\bar{D} = 2.32$) as a transparent viscous solid.

Determination of Monomer Reactivity Ratios. The monomer reactivity ratio was determined at early stages of polymerization, where the monomer conversions were low, using the Fineman-Ross method. We varied the monomer feed compositions (f) of two monomers and determined the copolymer compositions (F) using ^1H NMR. According to the Fineman-Ross equation, i.e., $G = r_1H - r_2$, where $G = x(y - 1)/y$ and $H = x^2/y$ with $x = f_1/f_2$ and $y = F_1/F_2$, G was plotted against H . From the slope and intercept of the obtained straight line, r_1 and r_2 were determined (Figs. S8–S12).

For the comparison of the monomer reactivity ratios for DMDL and literature CKAs, examples of the monomer reactivity ratios for literature CKAs are summarized in Table S1.⁴⁻⁹

Table S1. Examples of monomer reactivity ratios for CKAs and vinyl co-monomers.

CKA ^a	Vinyl comonomer	r_{CKA}	$r_{\text{co-monomer}}$	Polymerization condition ^b	Method ^c	Reference
MPDL	MMA	0.01	4	NMP, 90 °C, 50 wt % toluene	NLLS	4
MDO	MMA	0.04	3.5	DTBP, 120 °C, bulk	KT	5
MDO	VAc	0.93	1.71	AIBN, 60 °C, bulk	FR	6
BMDO	MMA	0.53	1.96	ATRP, 120 °C, bulk	KT	7
BMDO	BA	0.08	3.7	ATRP, 110 °C, bulk	KT	8
BMDO	St	1.08	8.53	ATRP, 120 °C, bulk	KT	9

^aThe structures of MPDL, MDO, and BMDO are given in Scheme 1. ^bNMP is nitroxide mediated polymerization, DTBP denotes a conventional radical polymerization using di-*tert*-butyl peroxide, AIBN denotes a conventional radical polymerization using azobisisobutyronitrile, and ATRP is atom transfer radical polymerization. ^cNLLS is the nonlinear least-square method, KT is the Kelen-Tüdös method, and FR is the Fineman-Ross method.

Hydroxide-assisted Degradation of PDMDL ($M_n = 104000$ and $\mathcal{D} = 2.04$ (DMF-GPC) and $M_n = 106000$ and $\mathcal{D} = 1.88$ (THF-GPC)). PDMDL ($M_n = 104000$ and $\mathcal{D} = 2.04$ (DMF-GPC)) (0.064 g, 1 equiv of the DMDL monomer unit, 2.4 wt%) was dissolved in DMSO- d_6 (2.08 g, 77.2 wt%) in a vial, and to this solution, 1M NaOH in D₂O (0.55 g, 1 equiv of NaOH, 20.4 wt%) was added. The mixture was stirred at room temperature for 10 min. The mixture was analyzed with NMR and DMF-GPC within 5 h after the start of the reaction.

This experiment was also conducted using a valved NMR tube. PDMDL ($M_n = 104000$ and $\mathcal{D} = 2.04$ (DMF-GPC)) (0.064 g, 1 equiv of the DMDL monomer unit, 2.4 wt%) was dissolved in DMSO- d_6 (2.08 g, 77.2 wt%) in a vial, and to this solution, 1M NaOH in D₂O (0.55 g, 1 equiv of NaOH, 20.4 wt%) was added. The mixture was transferred to a valved NMR tube, and the tube was valved (sealed) within 15 seconds after the addition of NaOH. The mixture was analyzed with NMR after 10 min at room temperature and DMF-GPC within 5 h after the start of the reaction (Fig. S35).

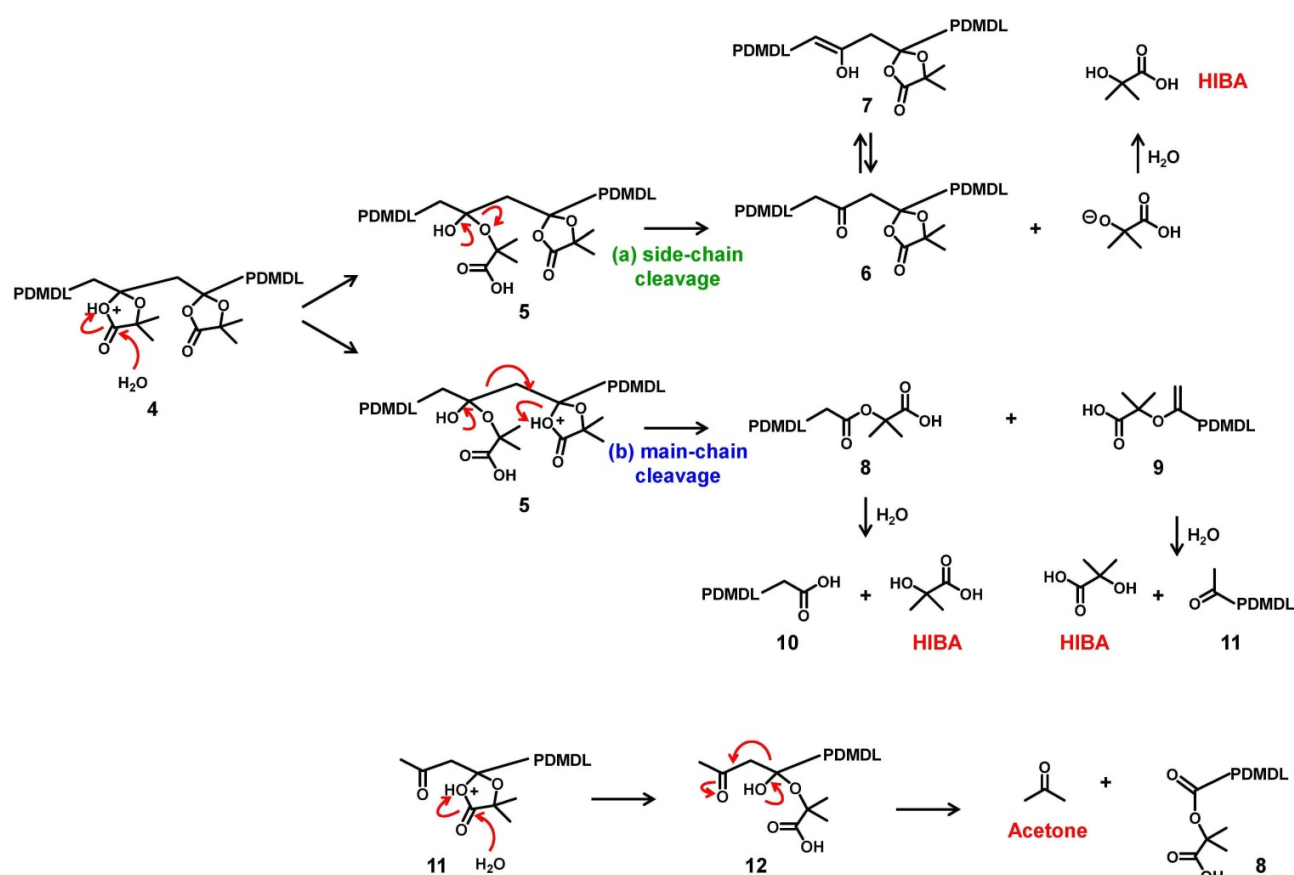
We also studied the degradation of PDMDL in a more hydrophobic solvent (a mixture of THF- d_8 and D₂O instead of a mixture of DMSO- d_6 and D₂O). We dissolved PDMDL ($M_n = 106000$ and $\mathcal{D} = 1.88$

(THF-GPC)) (0.064 g, 3.4 wt%, 1 equiv of the DMDL monomer unit) in a mixture of THF- d_8 (1.4 g, 75.2 wt%) and D₂O (0.20 g, 10.7 wt%), which was a colorless transparent solution. To this solution, NaOH (0.20 g, 10.7 wt%, 10 equiv) was added, and the mixture was heated at 50 °C. We used an excess of NaOH (10 equiv) and heated (50 °C) to accelerate the reaction. The reaction mixture turned to a reddish brown suspension. After the heat treatment for 30 min, no polymer was observed in the GPC chromatogram (THF eluent) of the reaction mixture (Fig. S36a), meaning that PDMDL degraded. Because of the poor solubility of HIBA (carboxylic acid) in THF, the reaction mixture was cloudy. Therefore, the mixture was treated with HCl to adjust the pH to 3 before the analysis with NMR. At pH = 3, the mixture turned homogeneous. The ¹H NMR and ¹³C NMR spectra of the reaction mixture (Figs. S36b and S36c) again showed only HIBA even in this more hydrophobic solvent (THF- d_8 /D₂O mixture). Thus, the reason for no detection of other species is not clear at this moment, and hence the proposed degradation scheme (Scheme 4) is viewed as a tentative mechanism.

HCl-assisted Degradation of PDMDL ($M_n = 104000$ and $\mathcal{D} = 2.04$ (DMF-GPC) and $M_n = 106000$ and $\mathcal{D} = 1.88$ (THF-GPC)). A mixture of PDMDL ($M_n = 106000$ and $\mathcal{D} = 1.88$ (THF-GPC)) (0.064 g, 2.4 wt%, 1 equiv of the DMDL monomer unit), 1M HCl aqueous solution (0.5 g, 18.9 wt%, 1 equiv of HCl), and DMSO- d_6 (2.08 g, 78.7 wt%) was heated at 80 °C with magnetic stirring for 24 h. The mixture was cooled to room temperature. The cloudy mixture was centrifuged to separate the white precipitate from the solution. The precipitate was dried in vacuum and analyzed with THF-GPC (Fig. S37).

Trifluoroacetic acid-assisted degradation of PDMDL ($M_n = 104000$ and $\mathcal{D} = 2.04$ (DMF-GPC) and $M_n = 106000$ and $\mathcal{D} = 1.88$ (THF-GPC)). We dissolved a PDMDL ($M_n = 104000$ and $\mathcal{D} = 2.04$ (DMF-GPC)) (0.064 g, 10.2 wt%, 1 equiv of the DMDL monomer unit) in DMSO (0.5 g, 79.4 wt%), which was a colorless transparent solution. We transferred this mixture to a valved NMR tube. To this solution, trifluoroacetic acid (0.057 g, 9 wt%, 1 equiv) and water (9 mg, 1.4 wt%, 1 equiv) were added, and the mixture was clear and colorless. The mixture was heated at 80 °C for 3 days and analyzed with

NMR and DMF-GPC (Fig. S38). The M_n value decreased from 104000 (original PDMDL) to 73000 after heating at 80 °C for 3 days (Fig. S38a). The ^1H (Fig. S38b) NMR spectrum showed the remained PDMDL signals (2.12-3.55 ppm for the backbone CH_2 protons and 1.00-1.85 ppm for the dimethyl protons), HIBA (1.26 ppm for the dimethyl protons) and acetone (2.06 ppm for the two methyl protons). The ^{13}C (Fig. S38c) NMR spectrum confirmed the presence of acetone in the reaction mixture (207 ppm for the carbonyl carbon and 31 ppm for the methyl carbons). Scheme S1 shows a possible mechanism for the acid-assisted degradation. This scheme is a possible mechanism but is not a definitive one.

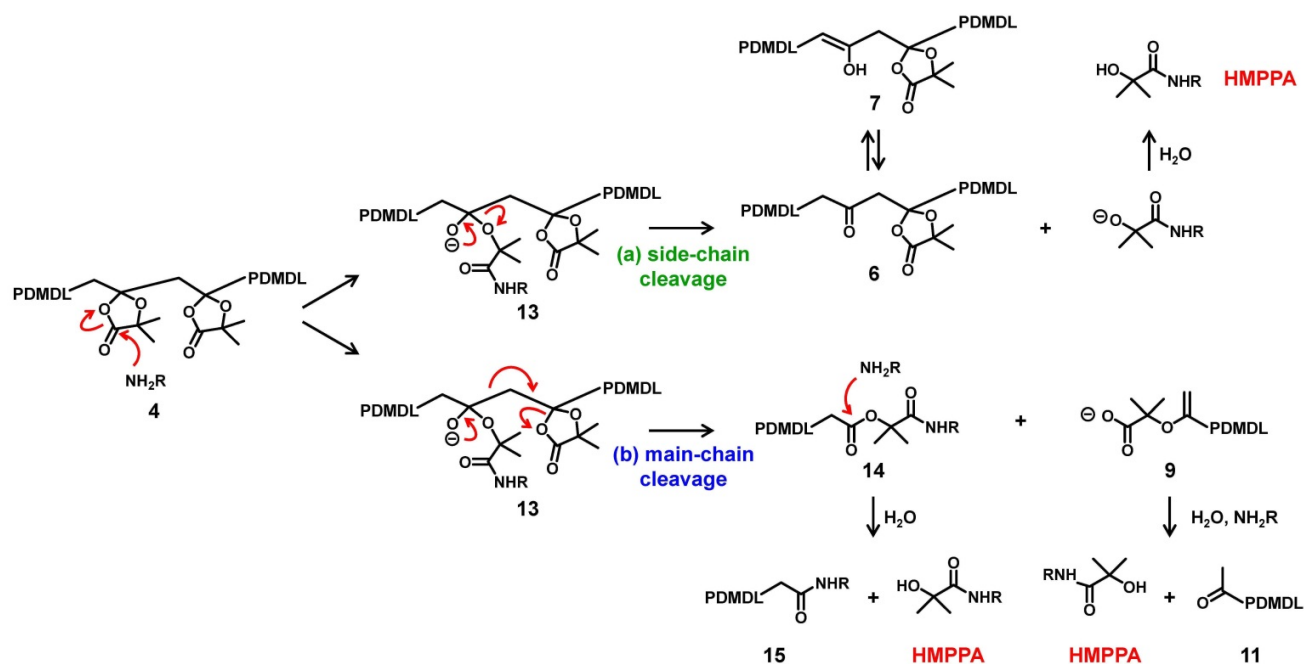


Scheme S1. Possible Mechanisms of Acid-assisted Degradation of PDMDL.

Amine-assisted Degradation of PDMDL ($M_n = 39000$ and $\mathcal{D} = 1.42$ (DMF-GPC)). A mixture of PDMDL ($M_n = 39000$ and $\mathcal{D} = 1.42$ (DMF-GPC)) (0.064 g, 4.0 wt%, 1 equiv of the DMDL monomer

unit), pentylamine (0.065g, 4.0 wt%, 1.5 equiv), and CD₃CN (1.48 g, 92.0 wt%) was heated at 65 °C with magnetic stirring. After a prescribed time *t*, an aliquot (0.1 mL) of the solution was taken out by a syringe, cooled to room temperature, and analyzed with DMF-GPC. At the last date point of the reaction, the mixture was analyzed with NMR.

Scheme S2 shows a possible mechanism for the amine-assisted degradation of PDMDL. Scheme S2 is a possible mechanism but is not a definitive one. R-NH₂ attacks the carbonyl carbon of the hemiacetal ester, generating an alkoxide anion (Scheme S2, compound **13**). Then, either the side-chain or main-chain cleavage can occur. The side-chain cleavage can generate a ketone in the backbone (compound **6**) and 2-hydroxy-2-methyl-*N*-pentylpropanamide (HMPPA). The main-chain cleavage can generate amide (compounds **14** and **15**), carboxylate (compound **9**), and ketone (compound **11**) chain-end PDMDLs as well as HMPPA.



Scheme S2. Possible Mechanisms of Amine-assisted Degradation of PDMDL.

Degradation of PPEGMA-*r*-PDMDL ($M_n = 39000$ and $\bar{D} = 2.22$). A mixture of PPEGMA-*r*-PDMDL ($M_n = 39000$, $\bar{D} = 2.22$, and $F_{\text{DMDL}}=17\%$) (0.06 g, 1 wt%, 1 equiv of the DMDL monomer unit) and 0.9M KOH aqueous solution (6.0 g, 99 wt%, 67 equiv of KOH) was stirred at room temperature. After a prescribed time t , an aliquot (0.1 mL) of the solution was taken out by a syringe and analyzed with DMF-GPC.

Degradation of PPEGMA ($M_n = 72000$ and $\bar{D} = 2.82$). A mixture of PPEGMA ($M_n = 72000$ and $\bar{D} = 2.82$) (0.06 g, 1 wt%) and 0.9M KOH aqueous solution (6.0 g, 99 wt%) was stirred at room temperature. After 24 h, an aliquot (0.1 mL) of the solution was analyzed with DMF-GPC. The M_n decreased (from 72000) to only 70000 and hence did not change significantly (Fig. S43). Thus, the degradation (decrease in the M_n value) of the PPEGMA-*r*-PDMDL (Fig. 5a) was ascribed to the main-chain cleavage of the DMDL units in the polymer.

Degradation of PLMA-*r*-PDMDL ($M_n = 42000$ and $\bar{D} = 1.76$). A mixture PLMA-*r*-PDMDL ($M_n = 42000$, $\bar{D} = 1.76$, and $F_{\text{DMDL}} = 16\%$) (0.04 g, 2.0 wt%, 1 equiv of the DMDL monomer unit), 0.9M KOH in methanol (0.16 g, 3.5 equiv to the DMDL unit, 8.1 wt%), and THF (1.78 g, 89.9 wt%) was stirred at room temperature. After a prescribed time t , an aliquot (0.1 mL) of the solution was taken out by a syringe and analyzed with THF-GPC.

Degradation of PLMA ($M_n = 90000$ and $\bar{D} = 2.32$). A mixture PLMA ($M_n = 90000$ and $\bar{D} = 2.32$) (0.04 g, 2.0 wt%), 0.9M KOH in methanol (0.16 g, 8.1 wt%), and THF (1.78 g, 89.9 wt%) was stirred at room temperature. After 24 h, an aliquot (0.1 mL) of the solution was analyzed with THF-GPC. The M_n changed from 90000 to 91000 and hence did not change significantly (Fig. S44). Thus, the observed degradation (decrease in the M_n value) of the PLMA-*r*-PDMDL (Fig. 5b) was ascribed to the main-chain cleavage of the DMDL units in the polymer.

Recovery of HIBA via NaOH-assisted Degradation of PDMDL. A mixture of PDMDL ($M_n = 56000$ and $\bar{D} = 2.47$) (1.0 g, 1 equiv of the DMDL monomer unit), 0.9M KOH in methanol (28 g, 4

equiv of KOH), and THF (300 g) was stirred at room temperature for 1 h. The mixture was acidified using an aqueous HCl (1M) solution to pH = 3. The mixture was extracted with diethyl ether (100ml) for three times. The collected organic layer was dried with anhydrous magnesium sulfate. The mixture was filtered and dried with rotary evaporator. HIBA (0.39g) (white solid) was obtained and analyzed with NMR.

Synthesis of PDMDL Using Recovered HIBA. The HIBA (1 equiv) recovered above was reacted with acetyl chloride (1.8 equiv) under room temperature for 2 h, according to Scheme 3. The mixture was evaporated under vacuum, extracted with dichloromethane, dried with sodium sulfate, and then evaporated under vacuum, giving compound **2** ($R_1 = CH_3$) (Figs. S45 and S46) in an 80% yield. The purified compound **2** ($R_1 = CH_3$) (1 equiv) was subsequently reacted with oxalyl chloride (1.1 equiv) in a mixture of dichloromethane (99%) and dimethyl formamide (1%) at room temperature overnight, giving compound **3** ($R_1 = CH_3$) (Figs. S47 and S48) in a 70% conversion (as determined with 1H NMR) after the evaporation under vacuum. The crude compound **3** ($R_1 = CH_3$) (1 equiv) was directly reacted in the presence of triethylamine (1.5 equiv) in dichloromethane under reflux for 5 h, yielding DMDL. DMDL was purified by distillation and obtained in a 75% yield (based on the amount of compound **3** ($R_1 = CH_3$)) after distillation (Fig. S49).

PDMDL (Table 1, entry 1). 1H NMR (400 MHz, $CDCl_3$) δ 3.25-2.17 (m, 2H), 1.54 (br s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 106.3, 77.4, 49.6, 26.0.

PDMDL (Table 1, entry 2). 1H NMR (400 MHz, $CDCl_3$) δ 3.25-2.17 (m, 2H), 1.54 (br s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 106.3, 77.4, 49.6, 26.0. The T_g , T_c , T_m , and T_d values were 41 °C, 117 °C, 186 °C, and 269 °C, respectively (Fig. S4).

PMMA-*r*-PDMDL (Table 1, entry 3). 1H NMR (400 MHz, $CDCl_3$) δ 3.71-3.47 (m), 2.47-1.97 (m), 1.97-1.57 (m), 1.52-1.37 (m), 1.28-0.61 (m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 178.0, 177.8, 177.1,

176.8, 176.5, 174.7, 109.5, 77.7, 77.3, 54.4, 51.7, 44.8, 44.4, 43.7, 43.5, 43.3, 43.0, 25.9, 25.5, 21.2, 18.7, 18.3, 16.3. The T_g and T_d values were $104 (\pm 5) ^\circ\text{C}$ and $366 ^\circ\text{C}$, respectively (Fig. S17).

PBA-*r*-PDMDL (Table 1, entry 4). $^1\text{H NMR (400 MHz, CDCl}_3)$ δ 4.07 (br s), 2.70-2.01 (m), 2.01-1.27 (m), 1.00-0.87 (m).

PSt-*r*-PDMDL (Table 1, entry 5). $^1\text{H NMR (400 MHz, CDCl}_3)$ δ 7.85-6.90 (m), 6.90-6.18 (m), 2.75-1.68 (m), 1.68-0.81 (m). The T_g and T_d values were $90 (\pm 5) ^\circ\text{C}$ and $391 ^\circ\text{C}$, respectively (Fig. S18).

PAN-*r*-PDMDL (Table 1, entry 6). $^1\text{H NMR (400 MHz, CDCl}_3)$ δ 3.21-2.87 (m), 2.59-2.35 (m), 2.32-1.99 (m), 1.64-1.54 (m). The T_g and T_d values were $76 (\pm 5) ^\circ\text{C}$ and $350 ^\circ\text{C}$, respectively (Fig. S19).

PVAc-*r*-PDMDL (Table 1, entry 7). $^1\text{H NMR (400 MHz, CDCl}_3)$ δ 5.42-4.73 (m), 2.85-2.08 (m), 2.08-1.66 (m), 1.59-1.40 (m). The T_g and T_d values were $38 (33\text{--}46) ^\circ\text{C}$ and $272 ^\circ\text{C}$, respectively (Fig. S20).

PNVP-*r*-PDMDL (Table 1, entry 8). $^1\text{H NMR (400 MHz, CDCl}_3)$ δ 4.53-3.51 (m), 3.51-2.94 (m), 2.70-1.62 (m), 1.62-1.25 (m).

PDMA-*r*-PDMDL (Table 1, entry 9). $^1\text{H NMR (400 MHz, CDCl}_3)$ δ 3.19-2.64 (m), 2.64-1.18 (m).

PPEGMA-*r*-PDMDL (Table 1, entry 10). $^1\text{H NMR (400 MHz, CDCl}_3)$ δ 4.04 (br s), 3.78-3.49 (m), 3.37 (br s), 2.58-1.59 (m), 1.47 (br s), 1.31-0.64 (m).

PDMAEMA-*r*-PDMDL (Table 1, entry 11). $^1\text{H NMR (400 MHz, CDCl}_3)$ δ 4.04 (br s), 2.81-2.47 (m), 2.26 (br s), 2.46-1.57 (m), 1.57-1.38 (m), 1.37-0.75 (m).

PBMA-*r*-PDMDL (Table 1, entry 12). $^1\text{H NMR (400 MHz, CDCl}_3)$ δ 3.99 (br s), 2.54-1.75 (m), 1.75-1.59 (m), 1.59-1.36 (m), 1.20-0.73 (m).

PLMA-*r*-PDMDL (Table 1, entry 13). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.97 (br s), 2.53-1.76 (m), 1.76-1.47 (m), 1.47-1.21 (m), 1.21-0.81 (m).

PBzMA-*r*-PDMDL (Table 1, entry 14). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43-7.17 (m), 5.12-4.76 (m), 2.54-1.66 (m), 1.50-0.49 (m).

PEHMA-*r*-PDMDL (Table 1, entry 15). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.13-3.59 (m), 2.51-1.70 (m), 1.60-1.18 (m), 1.18-0.66 (m).

PSMA-*r*-PDMDL (Table 1, entry 16). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.92 (br s), 2.46-1.70 (m), 1.70-1.52 (m), 1.52-1.39 (m), 1.39-1.15 (m), 1.15-0.75 (m).

PMEA-*r*-PDMDL (Table 1, entry 17). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.39-3.97 (m), 3.59 (br s), 3.36 (br s), 2.85-2.08 (m), 2.08-1.62 (m), 1.62-1.40 (m).

PPhDL (Table 2, entry 1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.77-6.73 (m, 6H), 2.29-1.56 (m, 5H).

PMMA-*r*-PPhDL (Table 2, entry 2). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.61-7.46 (m), 7.46-7.24 (m), 3.76-3.47 (m), 2.34-1.36 (m), 1.35-0.66 (m).

PBA-*r*-PPhDL (Table 2, entry 4). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.67-7.44 (m), 7.44-7.18 (m), 4.03 (br s), 2.82-2.04 (m), 2.04-1.48 (m), 1.47-1.13 (m), 0.93 (br s).

Spectral Data and Plots

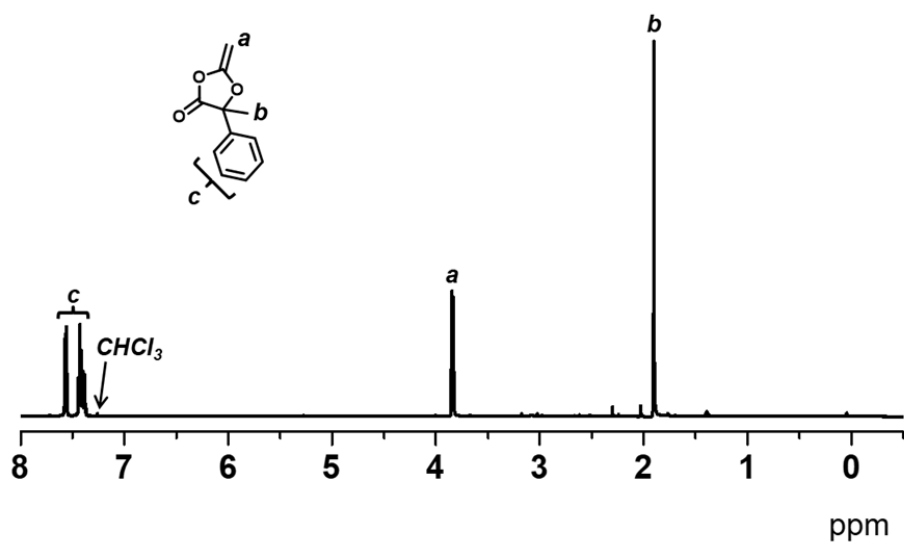


Fig. S1. ¹H NMR spectrum of PhDL (400 MHz, 298 K, CDCl₃).

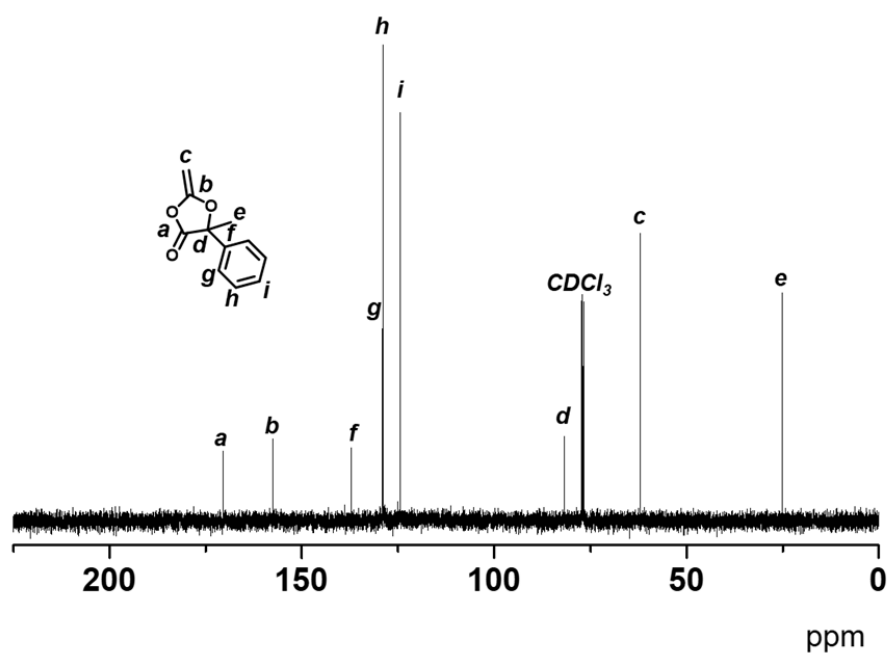


Fig. S2. ¹³C NMR spectrum of PhDL (100 MHz, 298 K, CDCl₃).

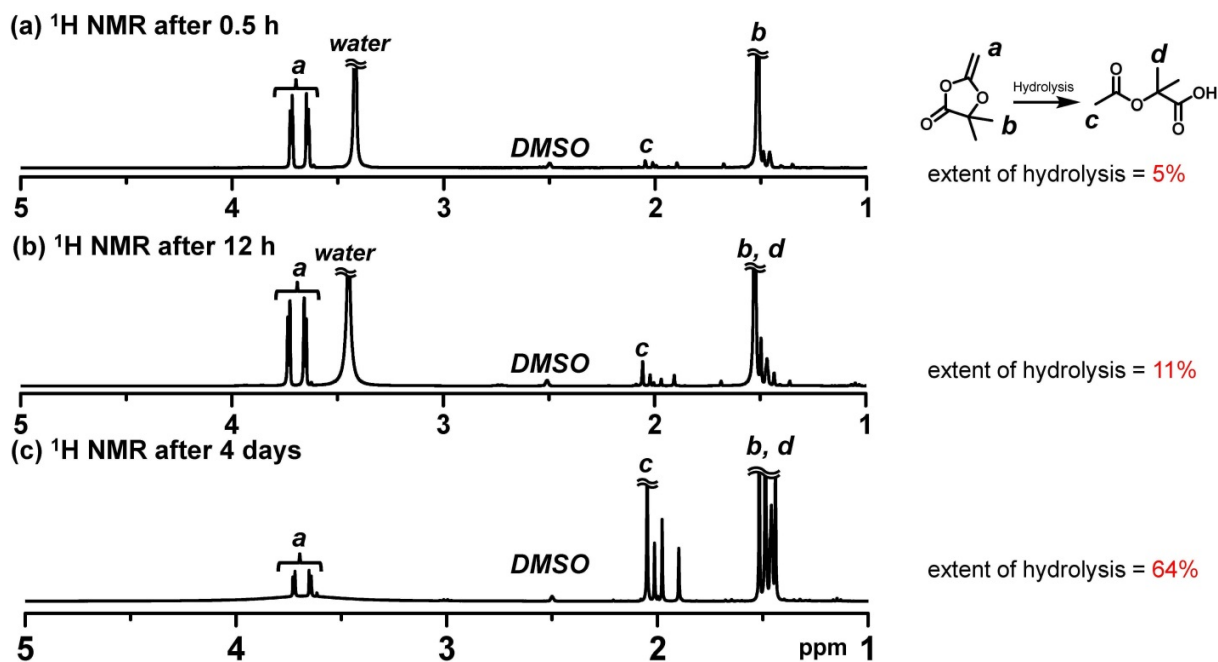


Fig. S3. ^1H NMR spectra of DMDL and water mixture at (a) 0.5 h, (b) 12 h, and (c) 4 days (400 MHz, 298 K, $\text{DMSO-}d_6$).

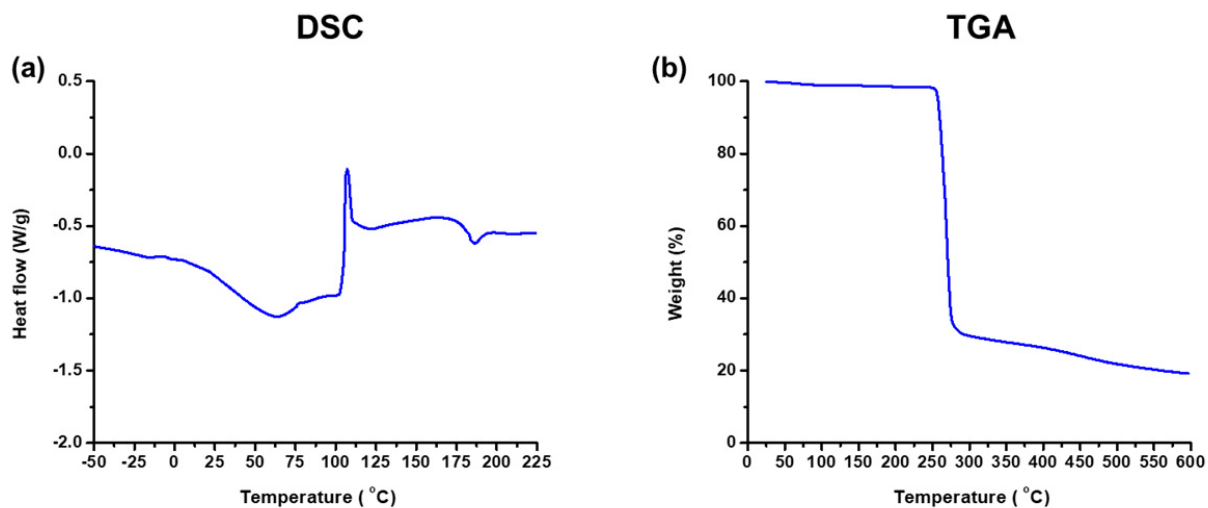


Fig. S4. (a) DSC and (b) TGA curves of PDMDL (Table 1, entry 2) ($M_n = 104000$ and $D = 2.04$).

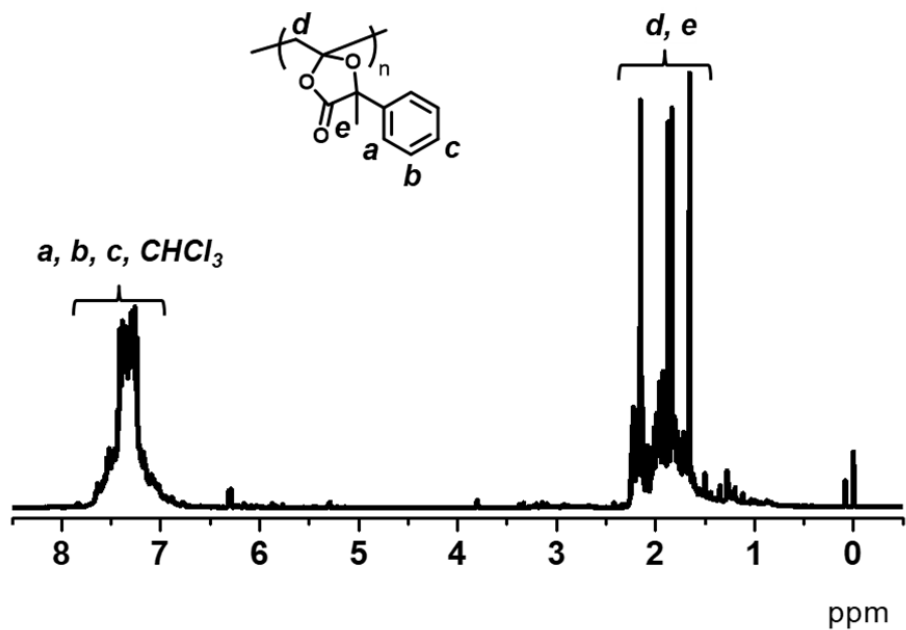


Fig. S5. ¹H NMR spectrum of PPhDL (Table 2, entry 1) (400 MHz, 298 K, CDCl₃).

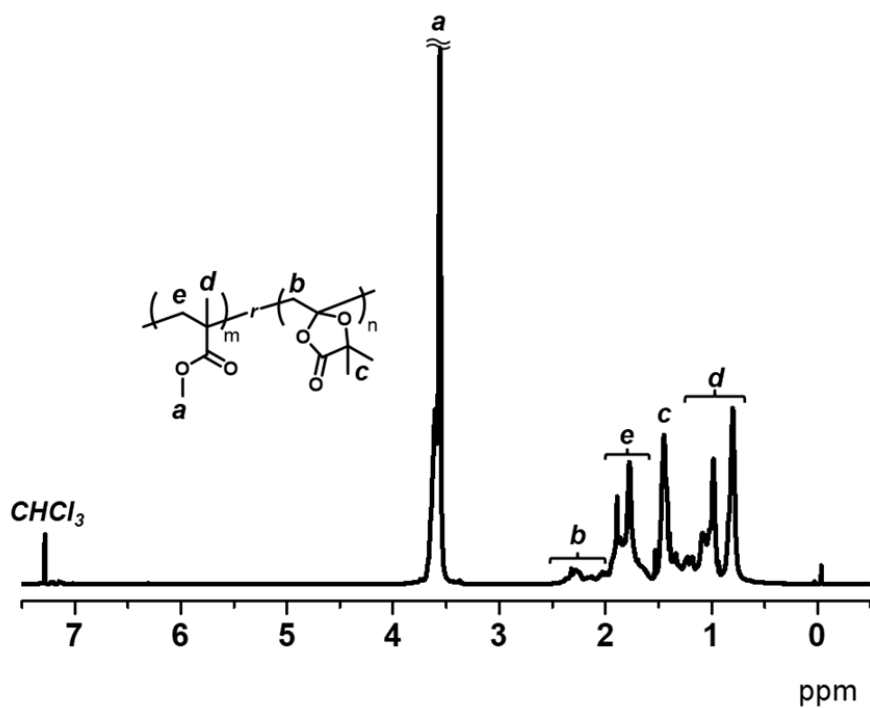


Fig. S6. ¹H NMR spectrum of PMMA-*r*-PDMDL (Table 1, entry 3) (400 MHz, 298 K, CDCl₃).

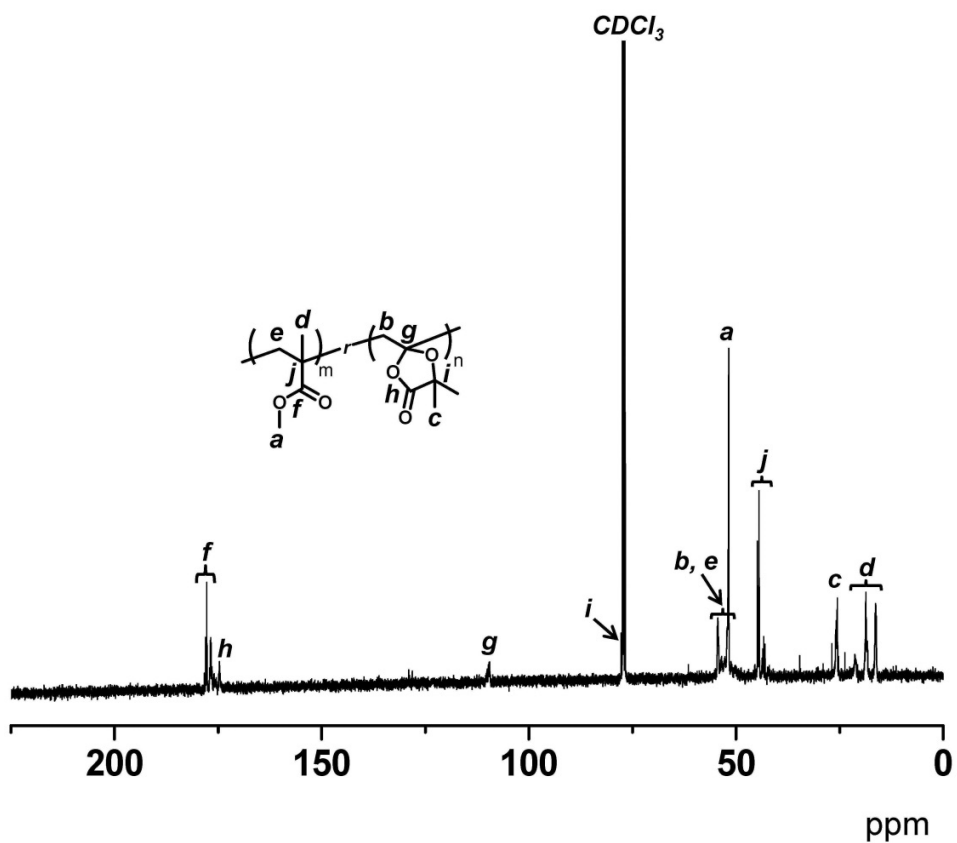


Fig. S7. ^{13}C NMR spectrum of PMMA-*r*-PDMDL (Table 1, entry 3) (100 MHz, 298 K, CDCl_3).

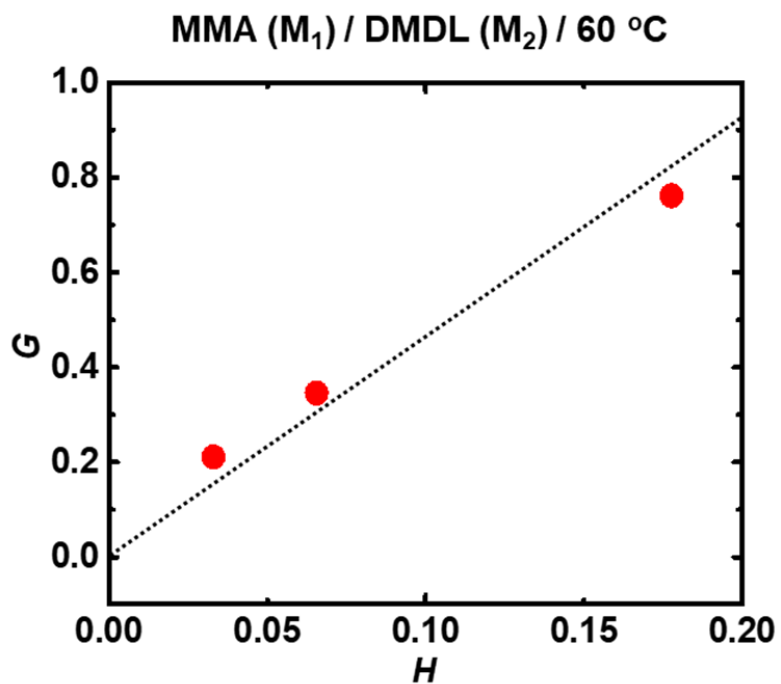


Fig. S8. Fineman-Ross plot of MMA (M_1) and DMDL (M_2) (Table 3, entry 1).

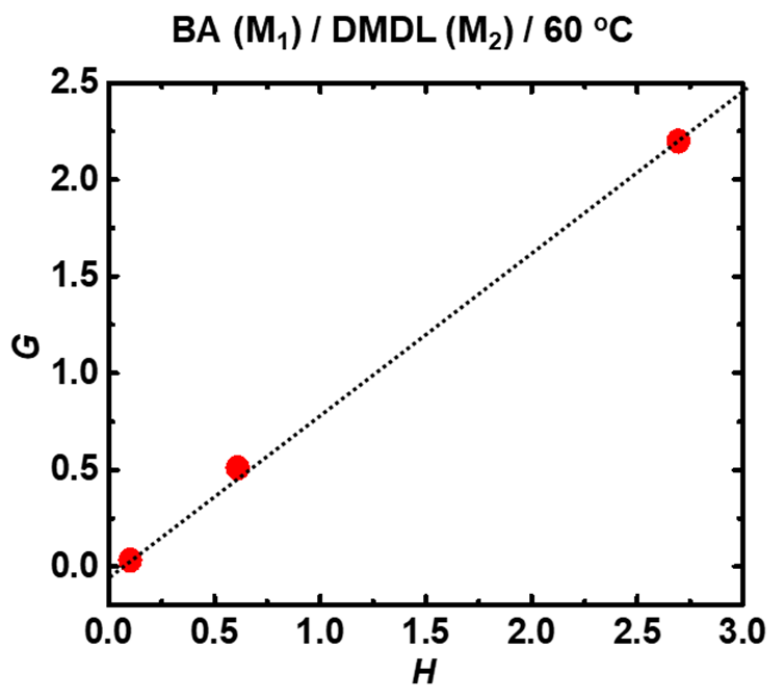


Fig. S9. Fineman-Ross plot of BA (M_1) and DMDL (M_2) (Table 3, entry 2).

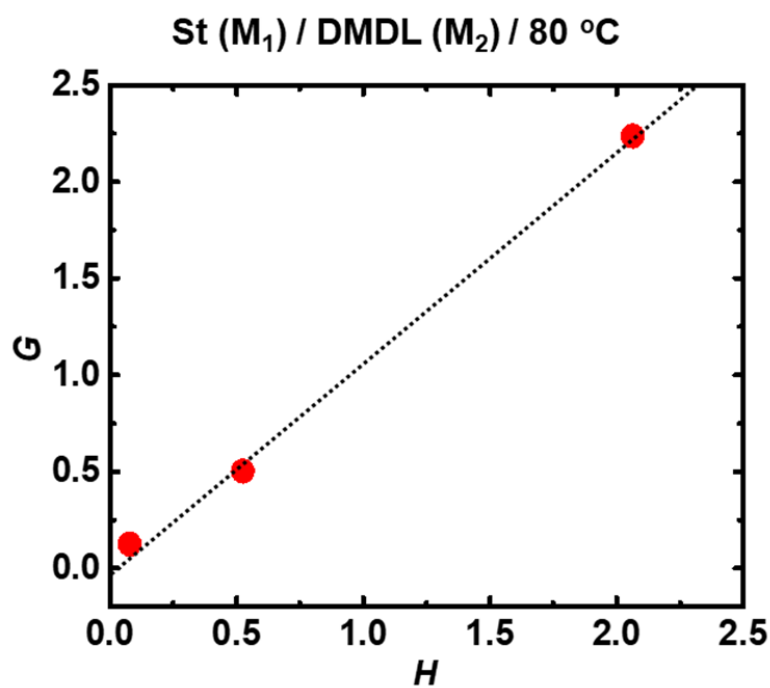


Fig. S10. Fineman-Ross plot of St (M_1) and DMDL (M_2) (Table 3, entry 3).

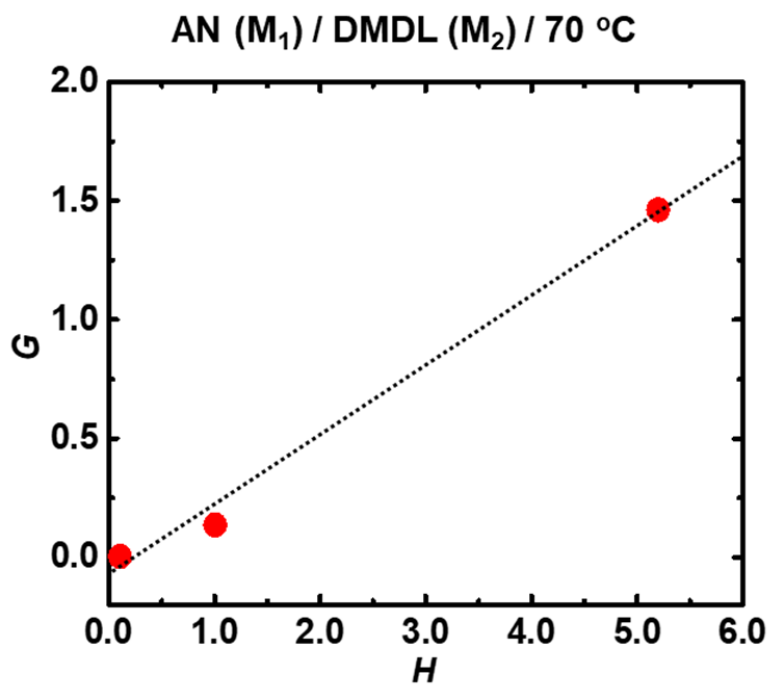


Fig. S11. Fineman-Ross plot of AN (M_1) and DMDL (M_2) (Table 3, entry 4).

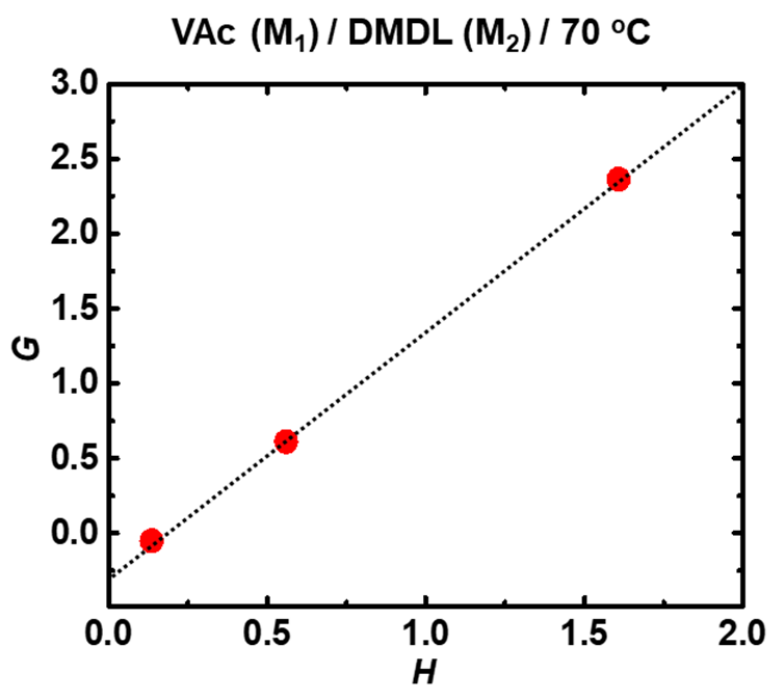


Fig. S12. Fineman-Ross plot of VAc (M_1) and DMDL (M_2) (Table 3, entry 5).

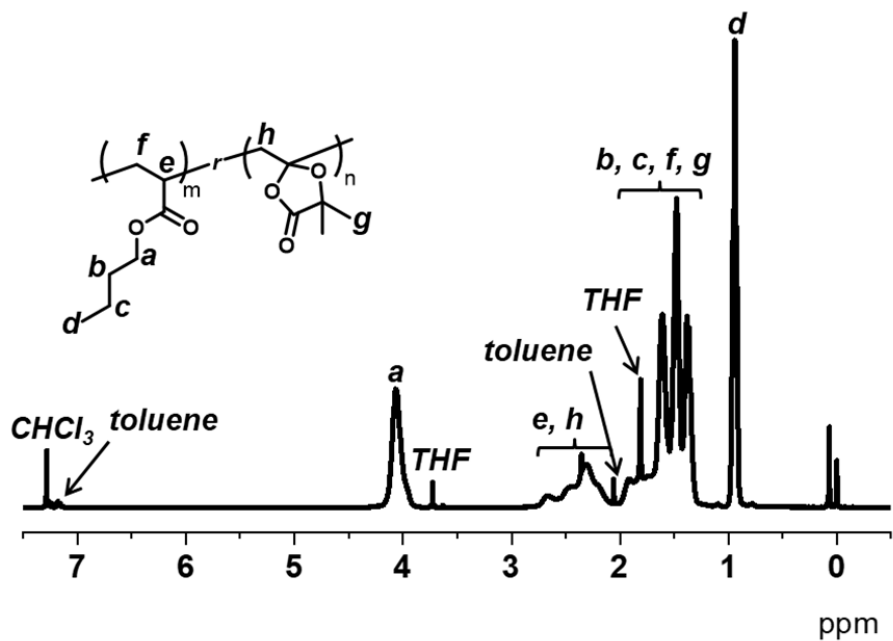


Fig. S13. ¹H NMR spectrum of PBA-*r*-PDMDL (Table 1, entry 4) (400 MHz, 298 K, CDCl₃).

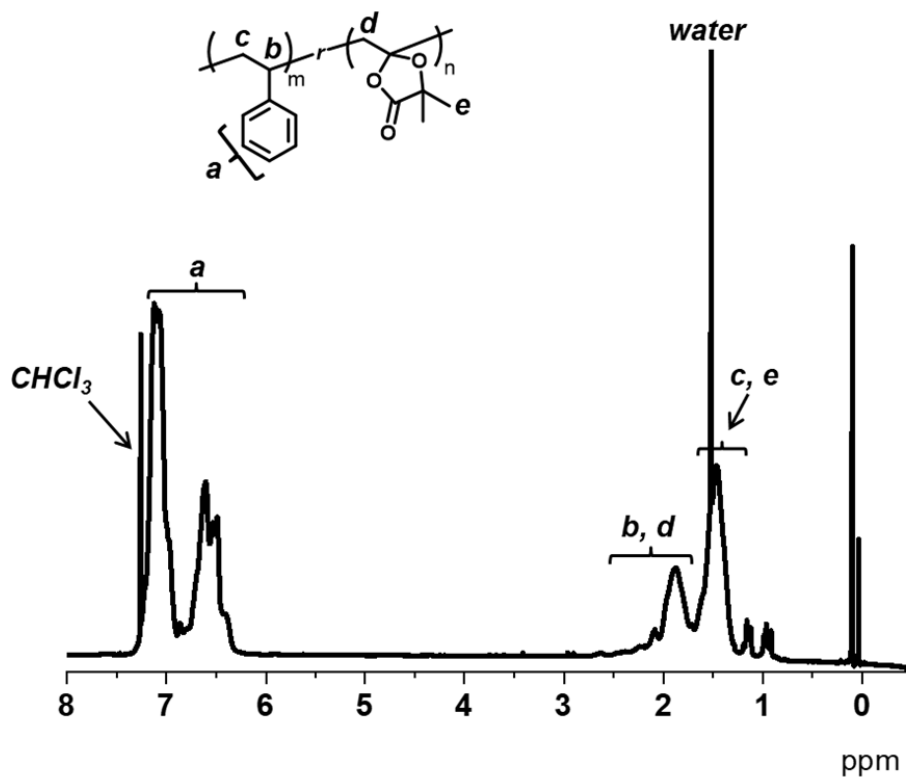


Fig. S14. ¹H NMR spectrum of PSt-*r*-PDMDL (Table 1, entry 5) (400 MHz, 298 K, CDCl₃).

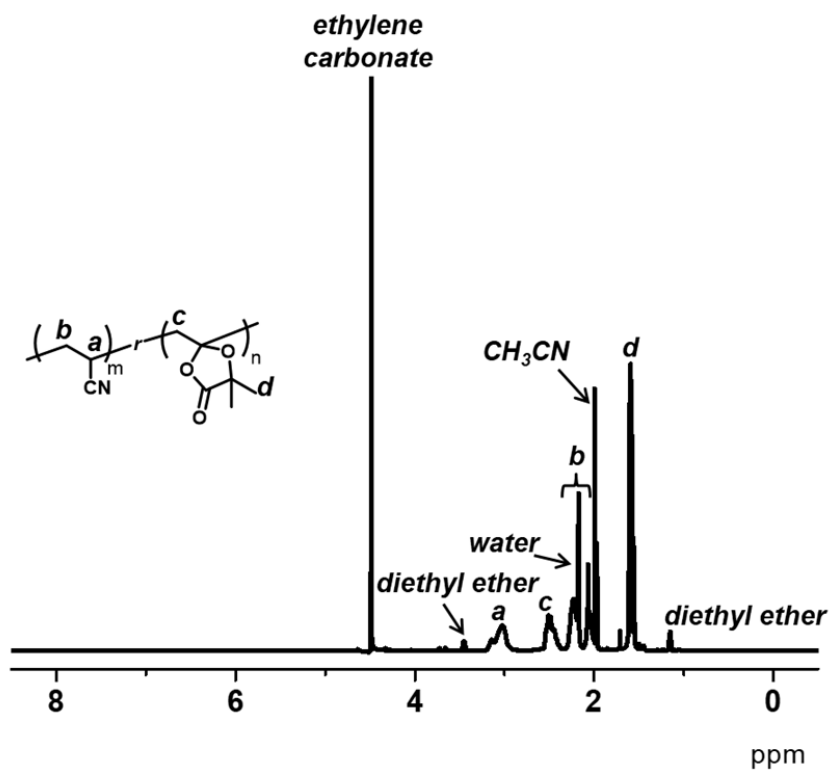


Fig. S15. ^1H NMR spectrum of PAN-*r*-PDMDL (Table 1, entry 6) (400 MHz, 298 K, CD_3CN).

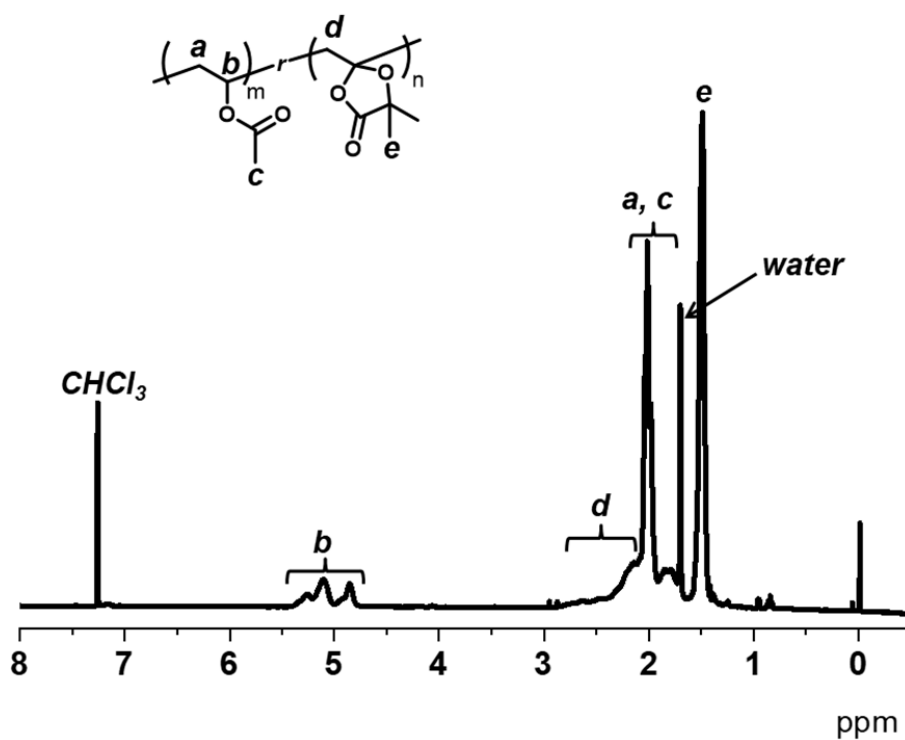


Fig. S16. ^1H NMR spectrum of PVAc-*r*-PDMDL (Table 1, entry 7) (400 MHz, 298 K, CDCl_3).

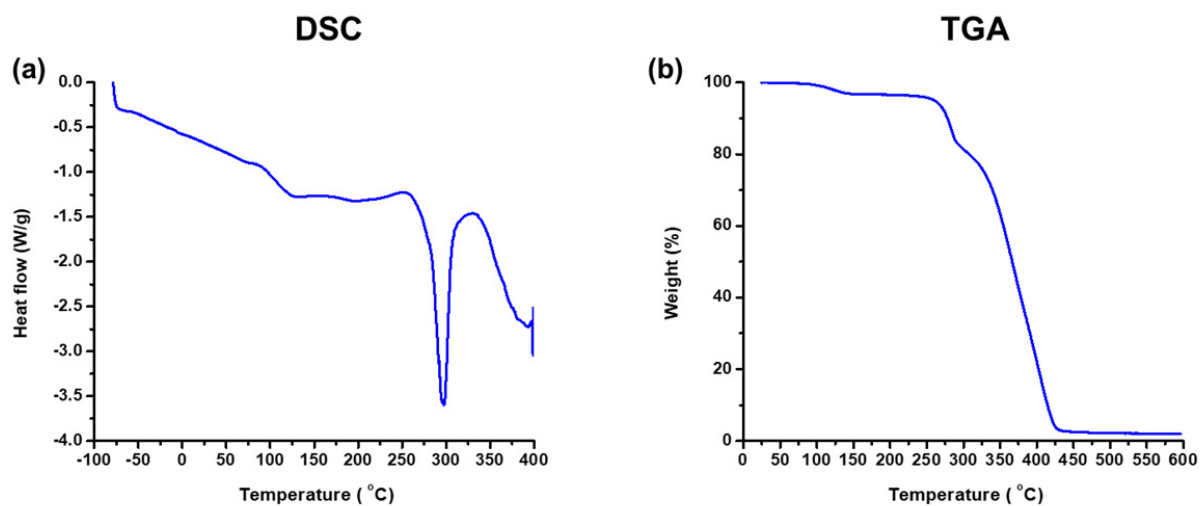


Fig. S17. (a) DSC and (b) TGA of PMMA-*r*-PDMDL (Table 1, entry 3) ($M_n = 19000$ and $\bar{D} = 1.78$). The T_g and T_d values were $104 (\pm 5) ^\circ\text{C}$ and $366 ^\circ\text{C}$, respectively.

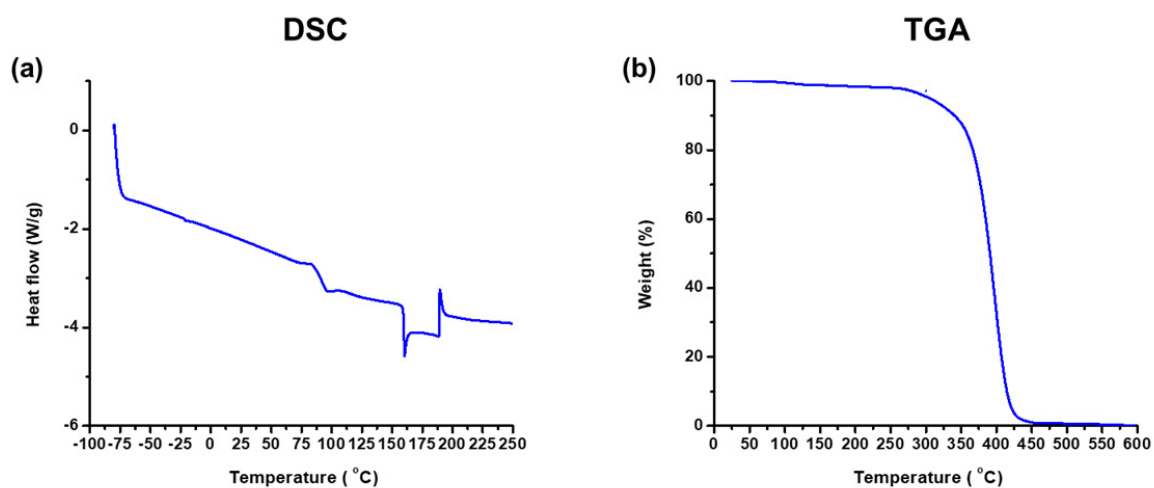


Fig. S18. (a) DSC and (b) TGA of PSt-*r*-PDMDL (Table 1, entry 5) ($M_n = 5100$ and $\bar{D} = 1.46$). The T_g and T_d values were $90 (\pm 5) ^\circ\text{C}$ and $391 ^\circ\text{C}$, respectively.

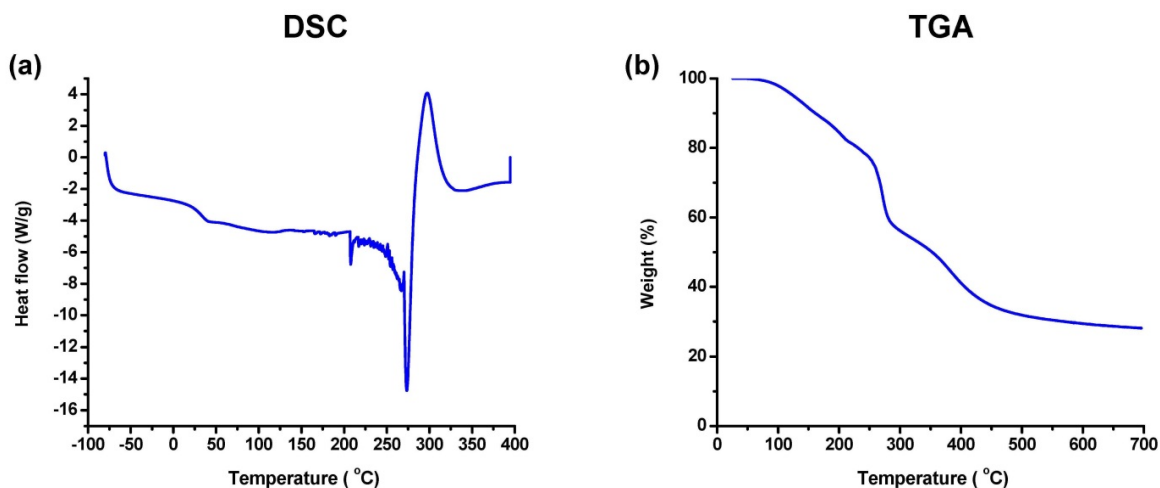


Fig. S19. (a) DSC and (b) TGA of PAN-*r*-PDMDL (Table 1, entry 6) ($M_n = 77000$ and $D = 1.54$). The T_g and T_d values were $76 (\pm 5) ^\circ\text{C}$ and $350 ^\circ\text{C}$, respectively. (The decay in the 20–40 °C region in the DSC curve would be ascribed to the ethylene carbonate (EC) remaining in the polymer (melting point of EC = 36 °C).)

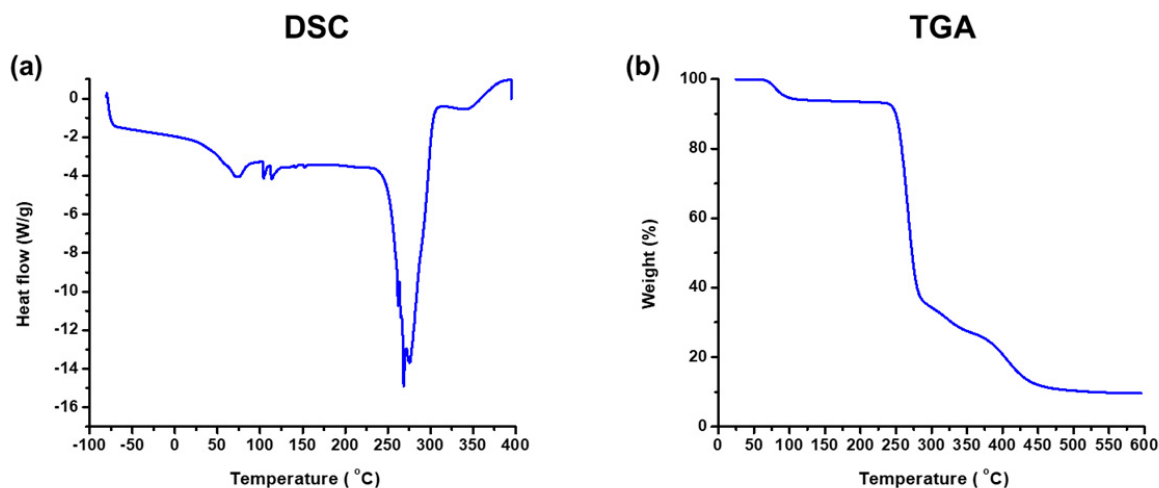


Fig. S20. (a) DSC and (b) TGA of PVAc-*r*-PDMDL (Table 1, entry 7) ($M_n = 11000$ and $D = 1.60$). The T_g and T_d values were 38 (33–46) °C and 272 °C, respectively.

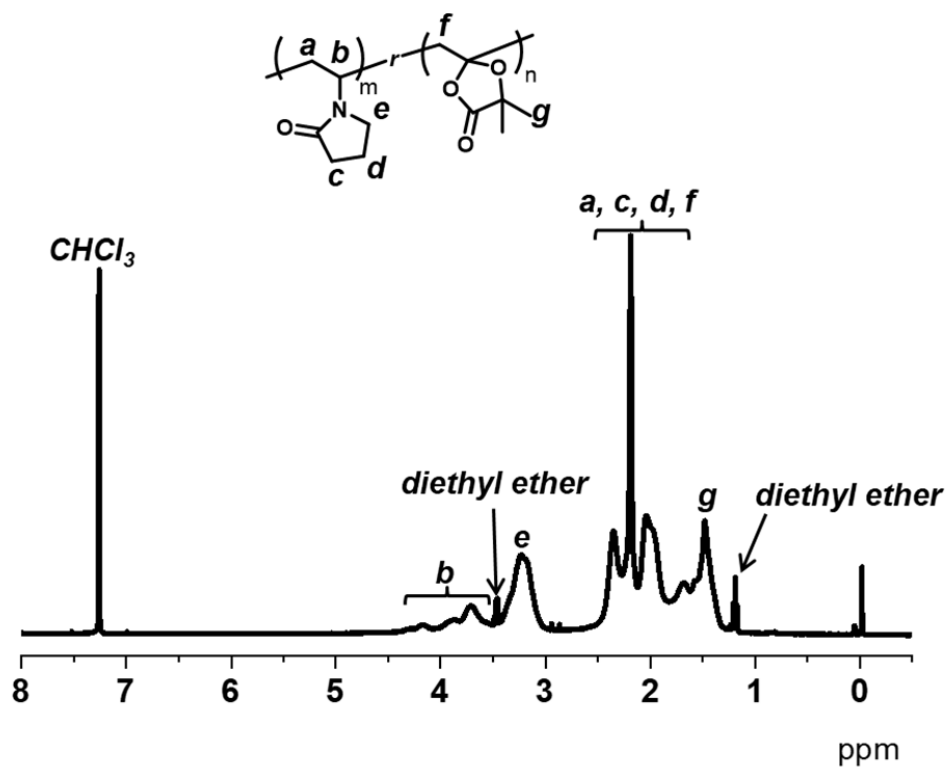


Fig. S21. ^1H NMR spectrum of PNVP-*r*-PDMDL (Table 1, entry 8) (400 MHz, 298 K, CDCl_3).

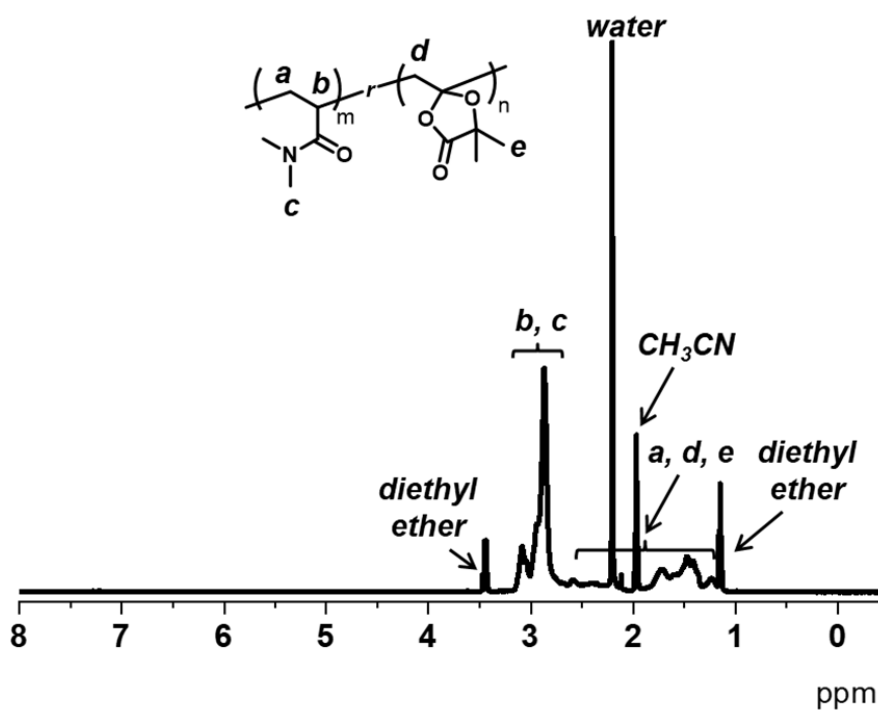


Fig. S22. ^1H NMR spectrum of PDMA-*r*-PDMDL (Table 1, entry 9) (400 MHz, 298 K, CD_3CN).

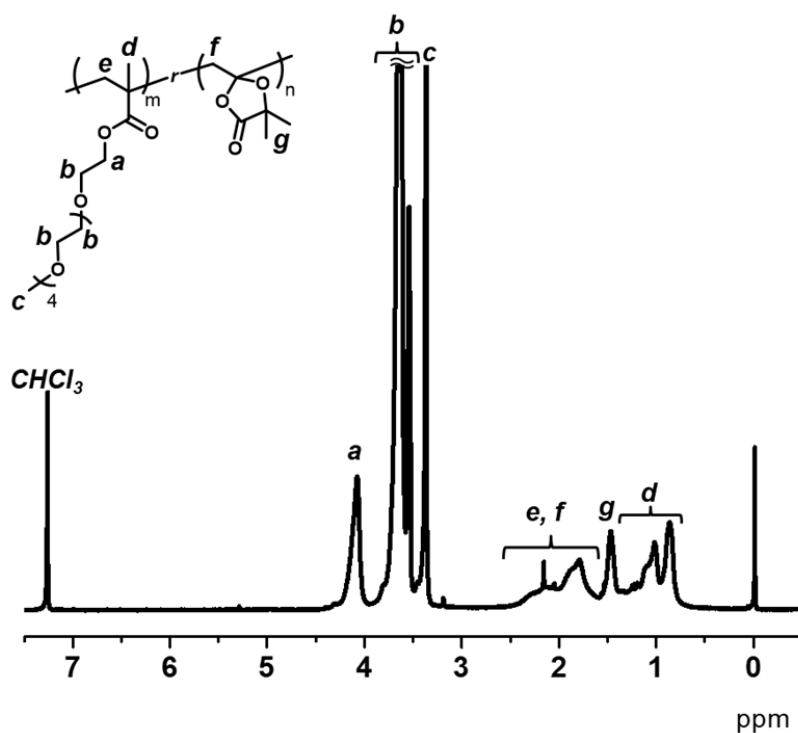


Fig. S23. ^1H NMR spectrum of PPEGMA-*r*-PDMDL (Table 1, entry 10) (400 MHz, 298 K, CDCl_3).

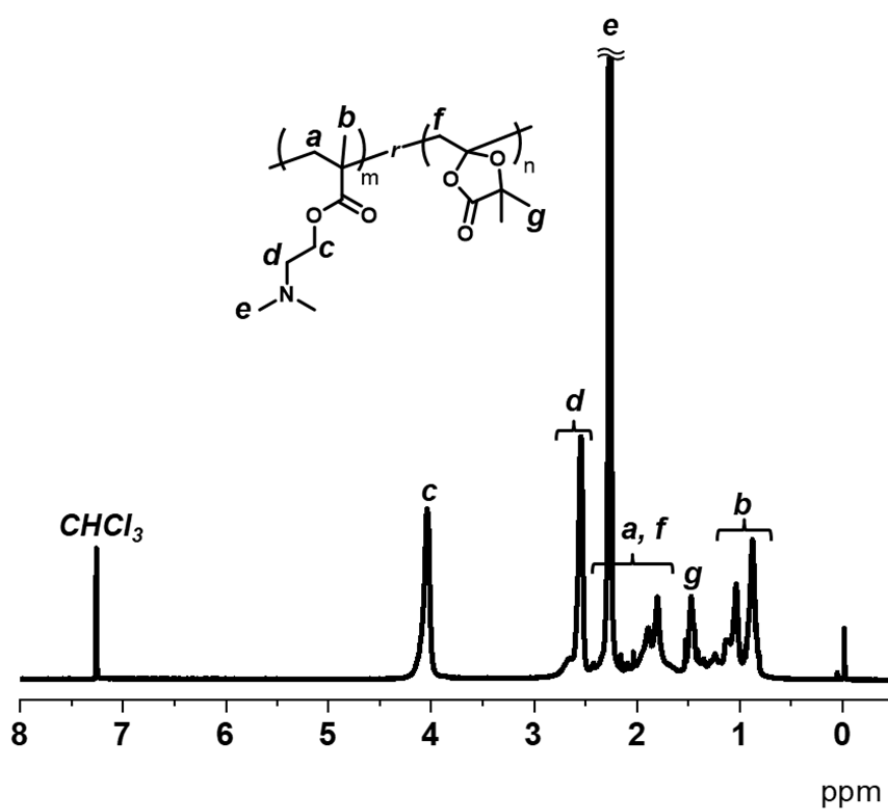


Fig. S24. ^1H NMR spectrum of PDMAEMA-*r*-PDMDL (Table 1, entry 11) (400 MHz, 298 K, CDCl_3).

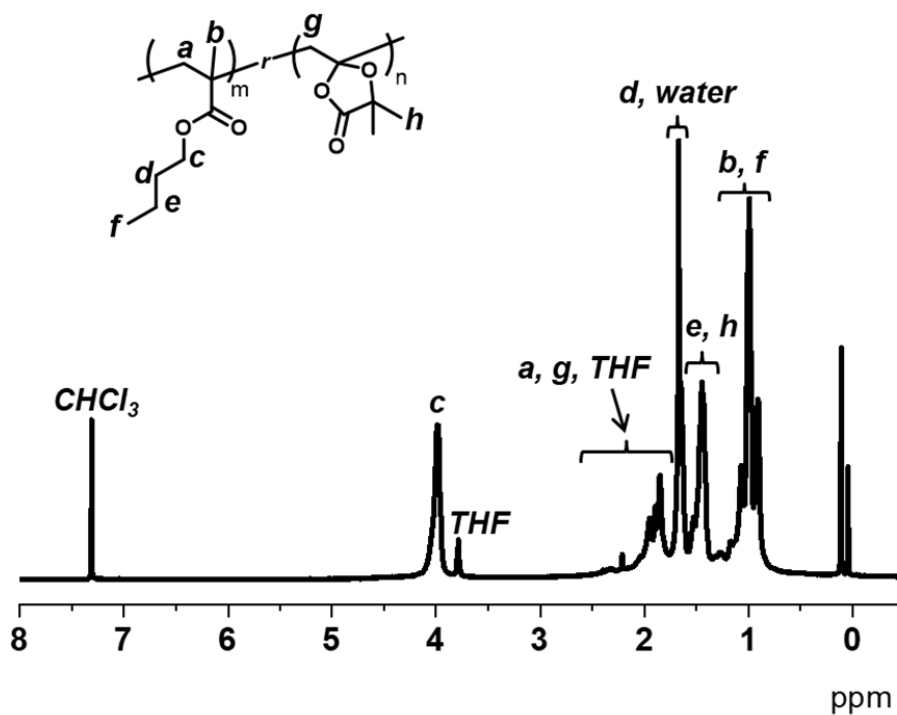


Fig. S25. ^1H NMR spectrum of PBMA-*r*-PDMDL (Table 1, entry 12) (400 MHz, 298 K, CDCl_3).

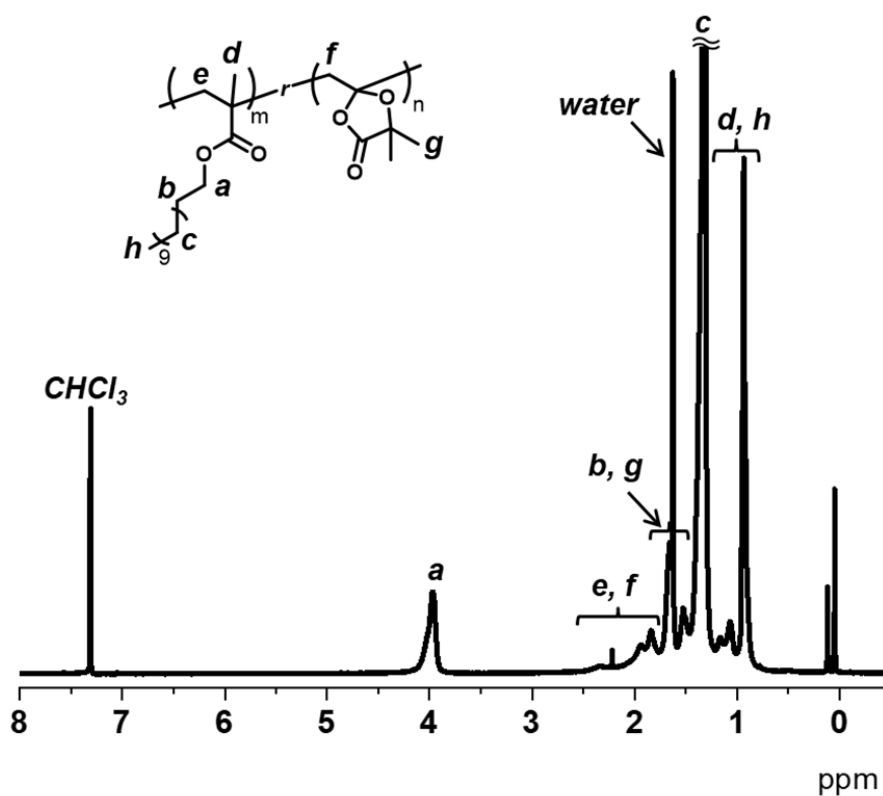


Fig. S26. ^1H NMR spectrum of PLMA-*r*-PDMDL (Table 1, entry 13) (400 MHz, 298 K, CDCl_3).

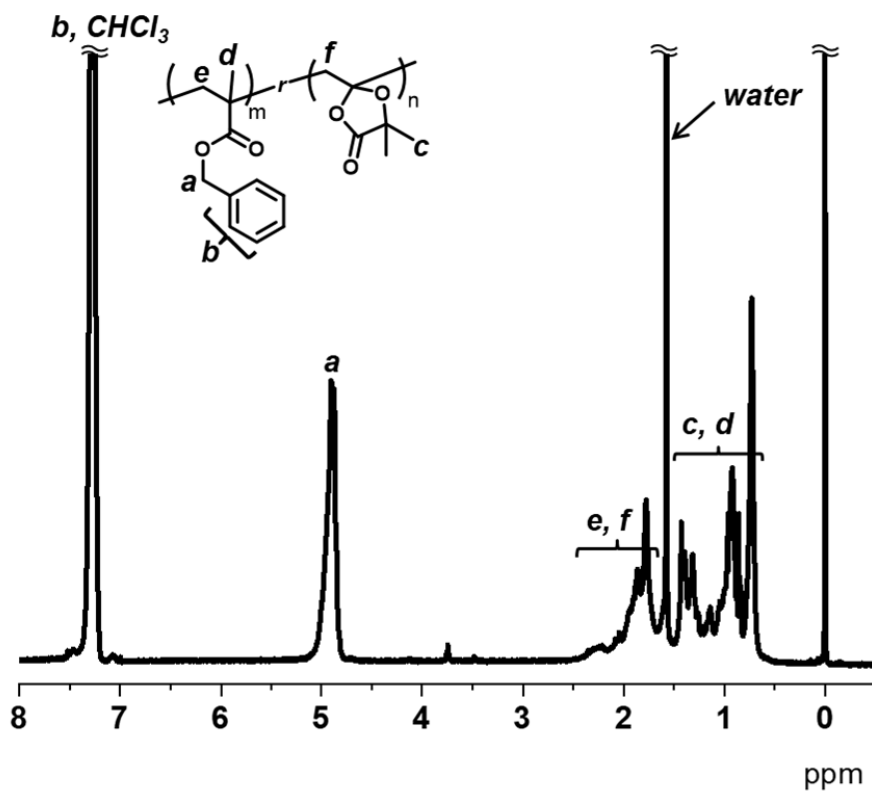


Fig. S27. ^1H NMR spectrum of PBzMA-*r*-PDMDL (Table 1, entry 14) (400 MHz, 298 K, CDCl_3).

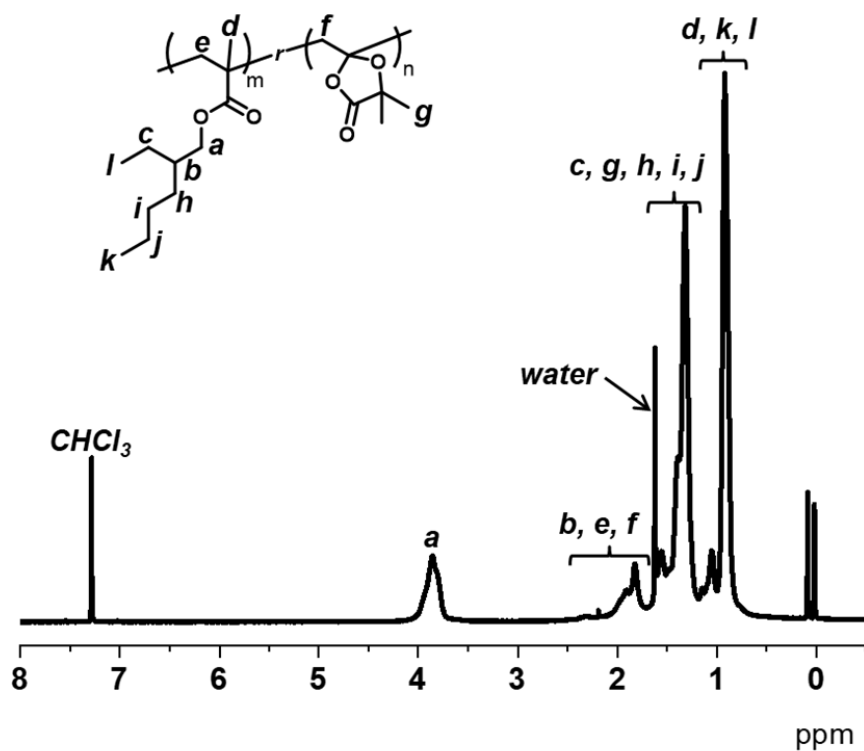


Fig. S28. ^1H NMR spectrum of PEHMA-*r*-PDMDL (Table 1, entry 15) (400 MHz, 298 K, CDCl_3).

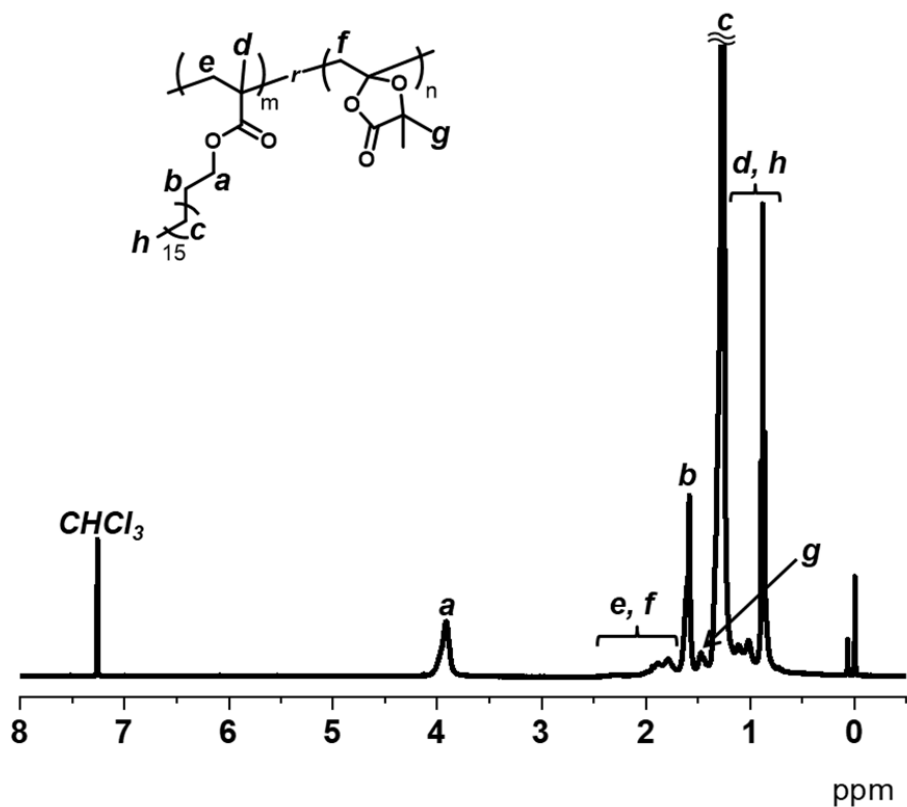


Fig. S29. ^1H NMR spectrum of PSMA-*r*-PDMDL (Table 1, entry 16) (400 MHz, 298 K, CDCl_3)

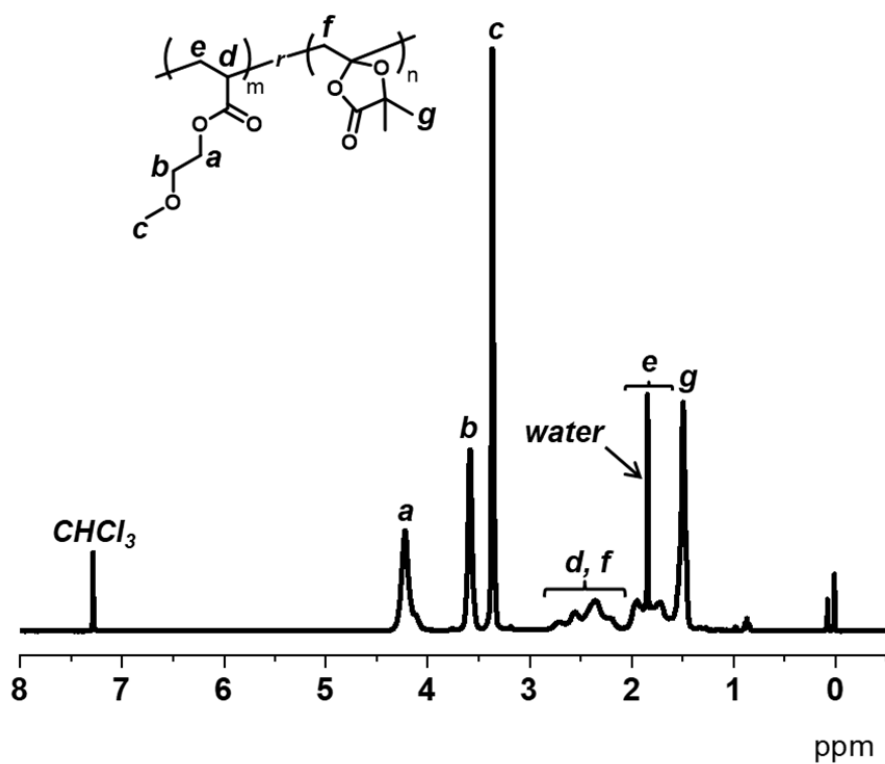


Fig. S30. ^1H NMR spectrum of PMEAr-PDMDL (Table 1, entry 17) (400 MHz, 298 K, CDCl_3).

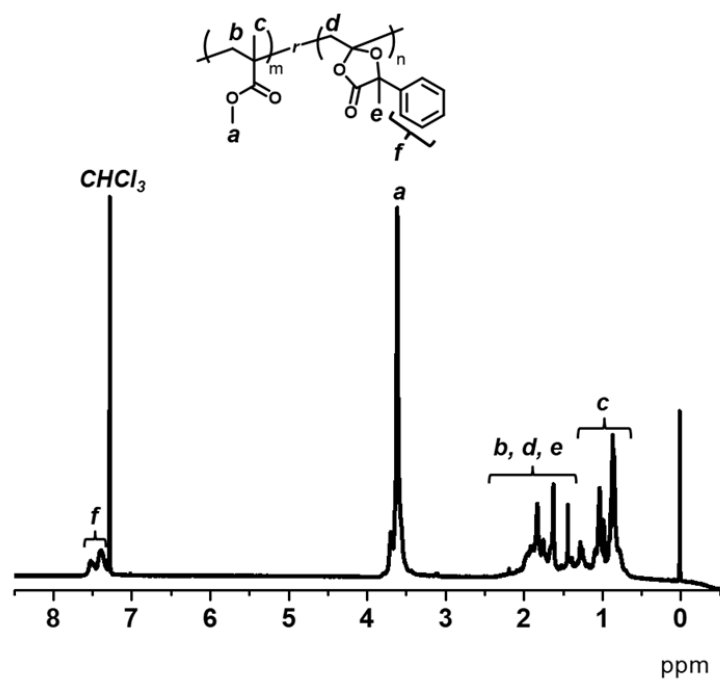


Fig. S31. ^1H NMR spectrum of PMMA-*r*-PPhDL (Table 2, entry 2) (400 MHz, 298 K, CDCl_3).

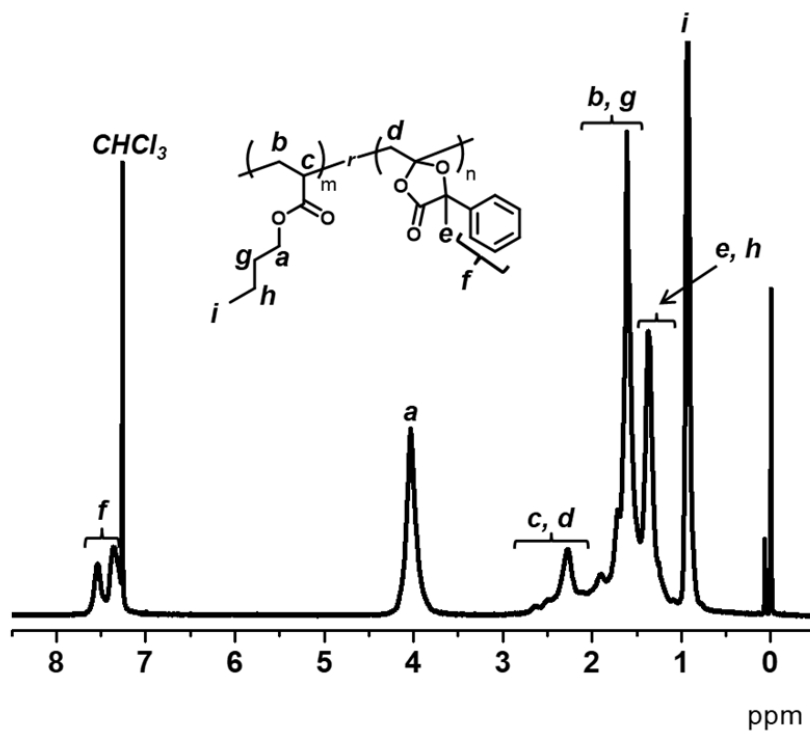


Fig. S32. ^1H NMR spectrum of PBA-*r*-PPhDL (Table 2, entry 4) (400 MHz, 298 K, CDCl_3).

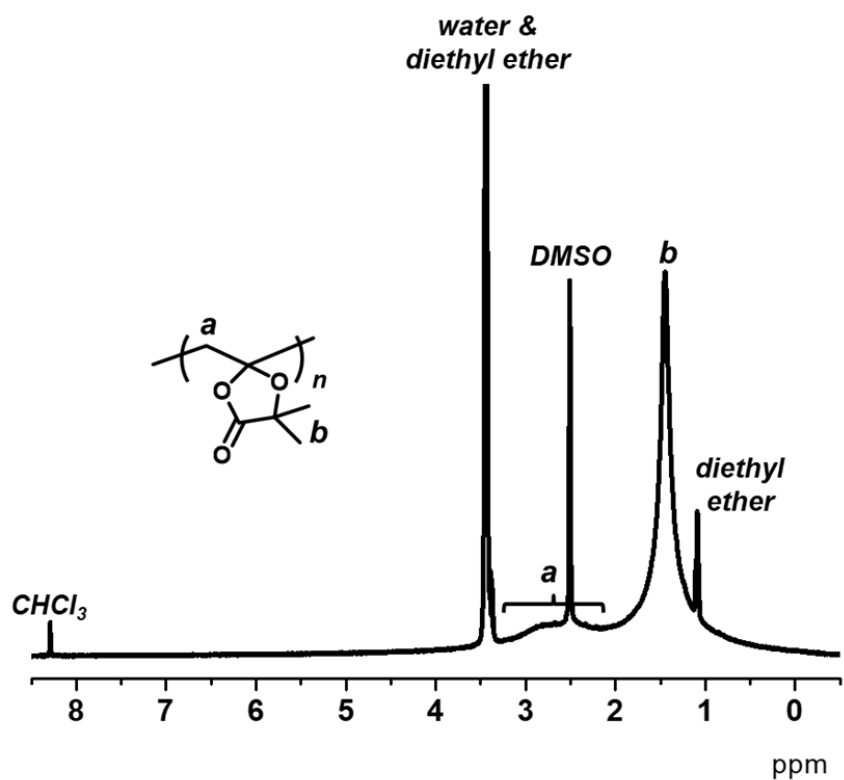


Fig. S33. ^1H NMR spectrum of non-degraded PDMDL in $\text{DMSO-}d_6/\text{D}_2\text{O}$ (77.2/20.4 wt%) mixture (400 MHz, 298 K, CDCl_3).

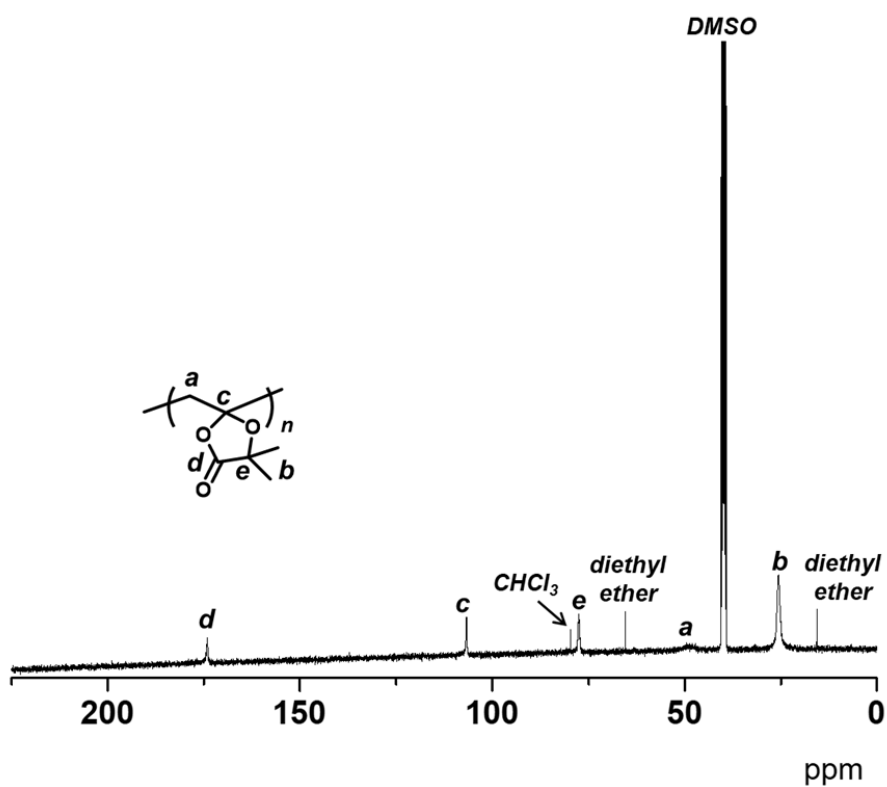


Fig. S34. ^{13}C NMR spectrum of non-degraded PDMDL (2.4 wt%) in $\text{DMSO-}d_6/\text{D}_2\text{O}$ (77.2/20.4 wt%) mixture (100 MHz, 298 K, CDCl_3).

NaOH-assisted degradation of PDMDL (2.4 wt%)
 in DMSO- d_6 /D $_2$ O (77.2 wt% / 20.4 wt%) at room temperature
 in valved (sealed) NMR tube.

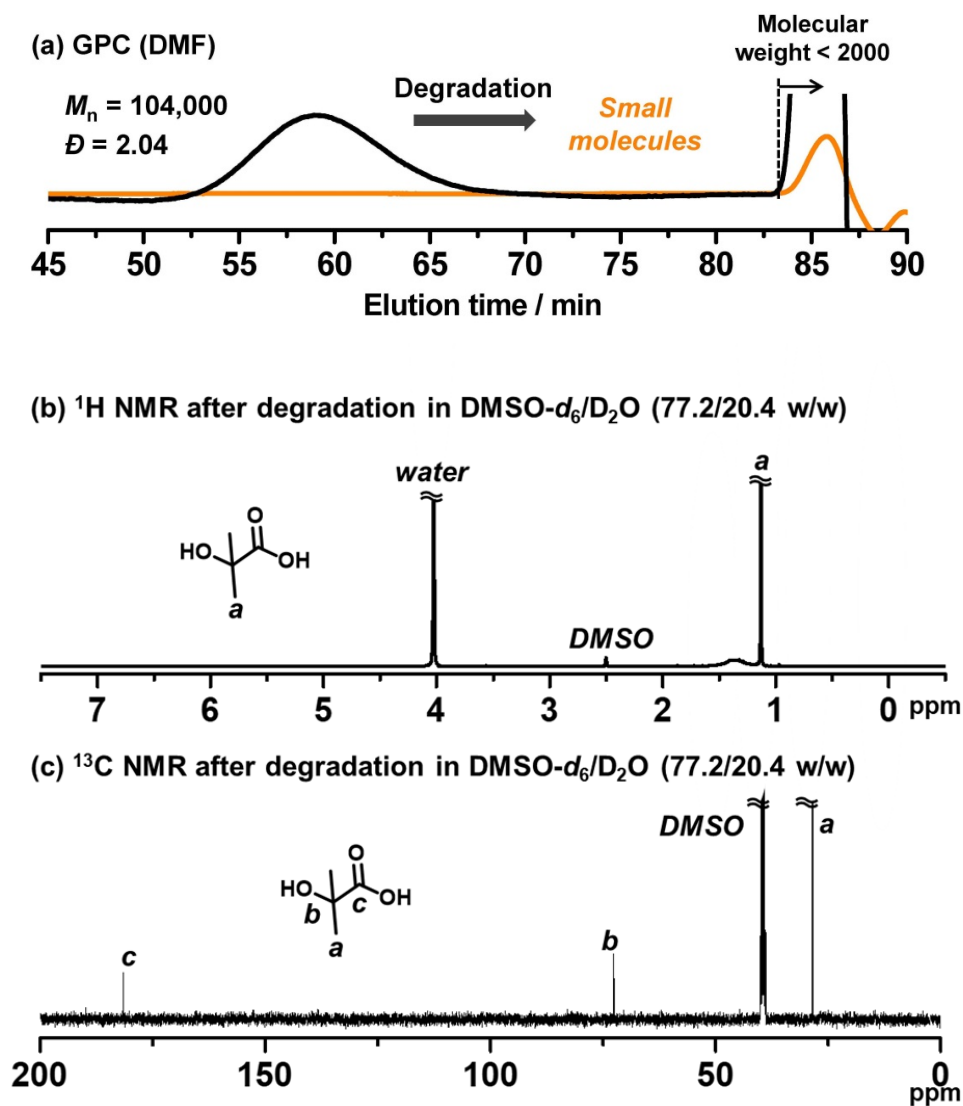


Fig. S35. Degradation of PDMDL ($M_n = 104,000$, $\bar{D} = 2.04$, 2.4 wt%, 1 equiv of the DMDL monomer unit) using 1 equiv of NaOH in a mixture of D $_2$ O (20.4 wt%) and DMSO- d_6 (77.2 wt%) at room temperature within 5 h. The reaction was conducted in a valved (sealed) NMR tube. The PDMDL used in Fig. S35 is the same as that given in Table 1 (entry 2), Fig. 3a, and Figs. S36, S37, and S38. The M_n and \bar{D} values of PDMDL determined with DMF-GPC (Table 1 (entry 2), Fig. 3a, and Figs. S35 and S38) were 104,000 and 2.04, respectively, and those determined with THF-GPC (Figs. S36 and S37) were 106,000 and 1.88, respectively. (a) GPC chromatogram before (black line) and after (orange line) degradation. (b) ^1H NMR and (c) ^{13}C NMR spectra of the reaction mixture after degradation (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR) (in DMSO- d_6 /D $_2$ O).

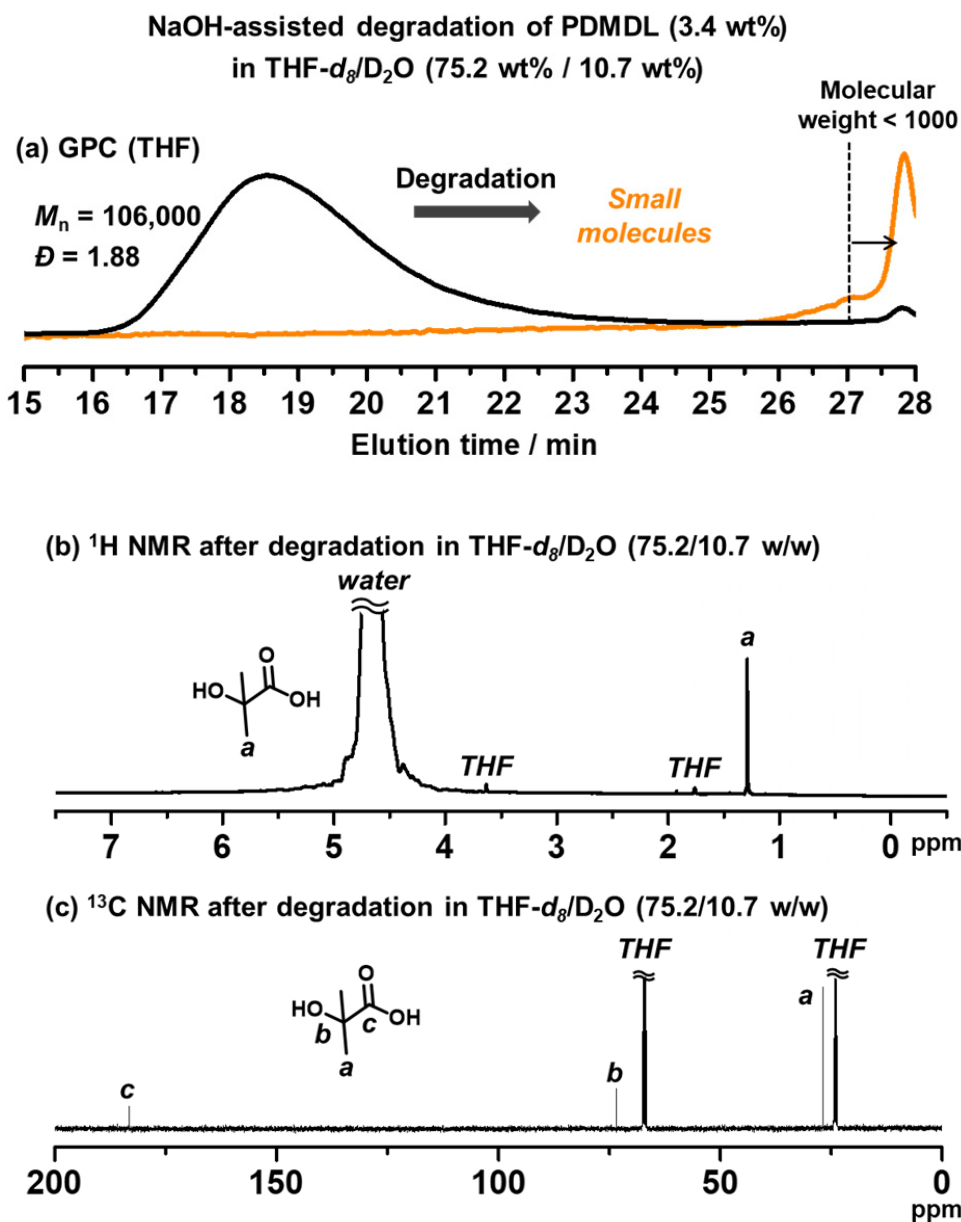


Fig. S36. Degradation of PDMDL ($M_n = 106,000$, $\bar{D} = 1.88$, 3.4 wt%) using 10 equiv of NaOH (10.7 wt%) in D $_2$ O (10.7 wt%) and THF- d_8 (75.2 wt%) at 50 °C for 30 min. The PDMDL used in Fig. S36 is the same as that given in Table 1 (entry 2), Fig. 3a, and Figs. S35, S37, and S38. The M_n and \bar{D} values of PDMDL determined with DMF-GPC (Table 1 (entry 2), Fig. 3a, and Figs. S35 and S38) were 104,000 and 2.04, respectively, and those determined with THF-GPC (Figs. S36 and S37) were 106,000 and 1.88, respectively. (a) GPC chromatogram before (black line) and after (orange line) degradation. (b) ^1H NMR and (c) ^{13}C NMR spectra of the reaction mixture after degradation (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR) (in THF- d_8 /D $_2$ O).

HCl-assisted degradation of PDMDL(2.4 wt%) in
DMSO- d_6 /aqueous HCl solution (78.7 wt% / 18.9 wt%)

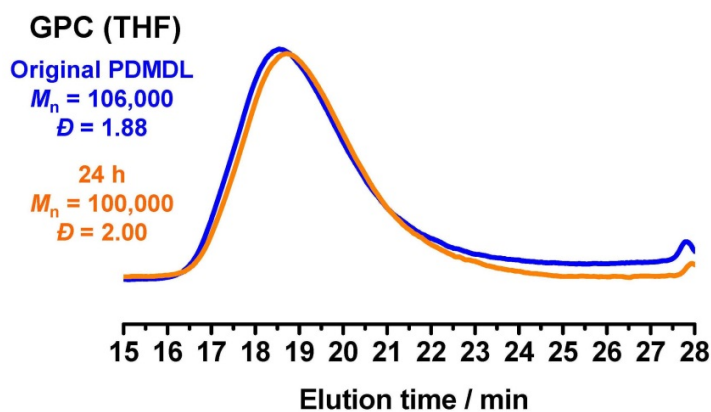
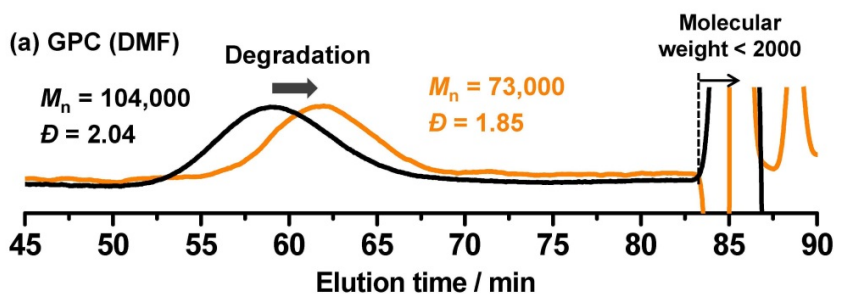
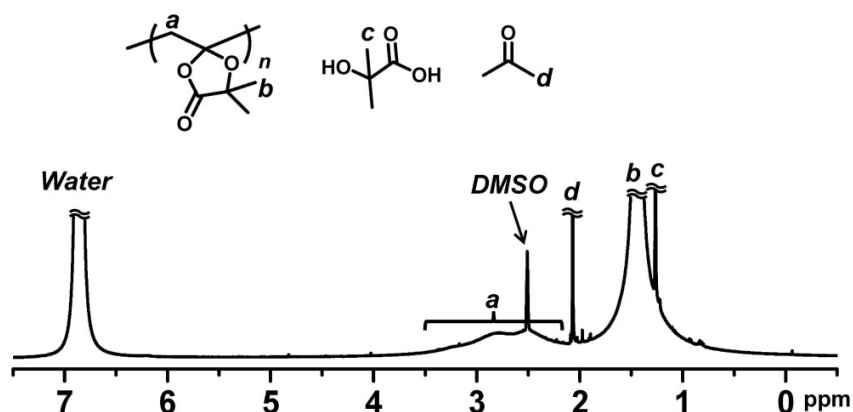


Fig. S37. Acid-assisted degradation of PDMDL ($M_n = 106,000$, $\bar{D} = 1.88$) (2.4 wt%) in a mixture of 1M HCl aqueous solution (18.9 wt%) and DMSO- d_6 (78.7 wt%) at 80 °C. The PDMDL used in Fig. S37 is the same as that given in Table 1 (entry 2), Fig. 3a, and Figs. S35, S36, and S38. The M_n and \bar{D} values of PDMDL determined with DMF-GPC (Table 1 (entry 2), Fig. 3a, and Figs. S35 and S38) were 104,000 and 2.04, respectively, and those determined with THF-GPC (Fig. S36 and S37) were 106,000 and 1.88, respectively.

Trifluoroacetic acid-assisted degradation of PDMDL (10.2 wt%)
in DMSO- d_6 /H $_2$ O (79.4 wt% / 1.4 wt%)



(b) ^1H NMR after degradation in DMSO- d_6 /H $_2$ O (79.4/1.4 w/w)



(c) ^{13}C NMR after degradation in DMSO- d_6 /H $_2$ O (79.4/1.4 w/w)

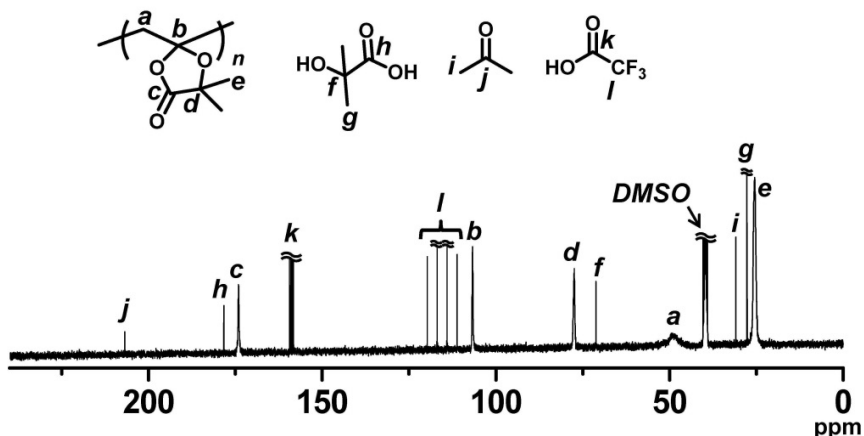


Fig. S38. Degradation of PDMDL ($M_n = 104,000$, $\bar{D} = 2.04$, 10.2 wt%, 1 equiv of the DMDL monomer unit) using 1 equiv of trifluoroacetic acid (9.0 wt%) and H $_2$ O (1.4 wt%) in DMSO- d_6 (79.4 wt%) at 80 °C for 3 days. The reaction was conducted in a valved (sealed) NMR tube. The PDMDL used in Fig. S38 is the same as that given in Table 1 (entry 2), Fig. 3a, and Figs. S35, S36, and S37. The M_n and \bar{D} values of PDMDL determined with DMF-GPC (Table 1 (entry 2), Fig. 3a, and Figs. S35 and S38) were 104,000 and 2.04, respectively, and those determined with THF-GPC (Fig. S36 and S37) were 106,000 and 1.88, respectively. (a) GPC chromatogram before (black line) and after (orange line) degradation. (b) ^1H NMR and (c) ^{13}C NMR spectra of the reaction mixture after degradation (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR) (in DMSO- d_6 /H $_2$ O).

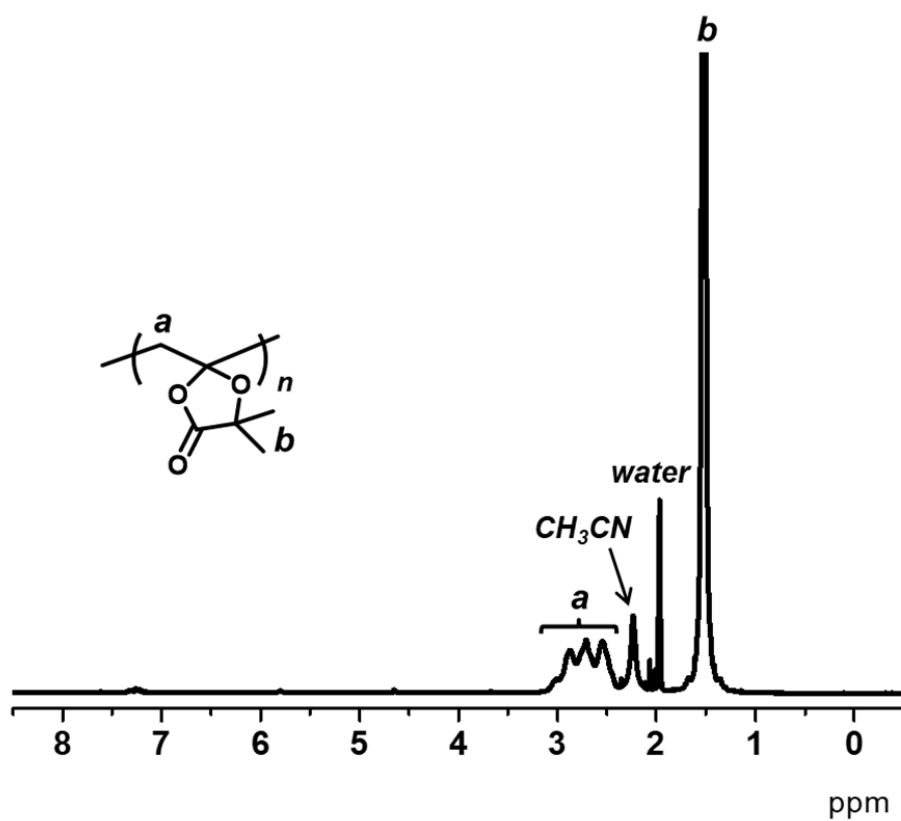


Fig. S39. ¹H NMR spectrum of non-degraded PDMDL (4.2 wt%) in CD₃CN (95.8 wt%) mixture (400 MHz, 298 K, CDCl₃).

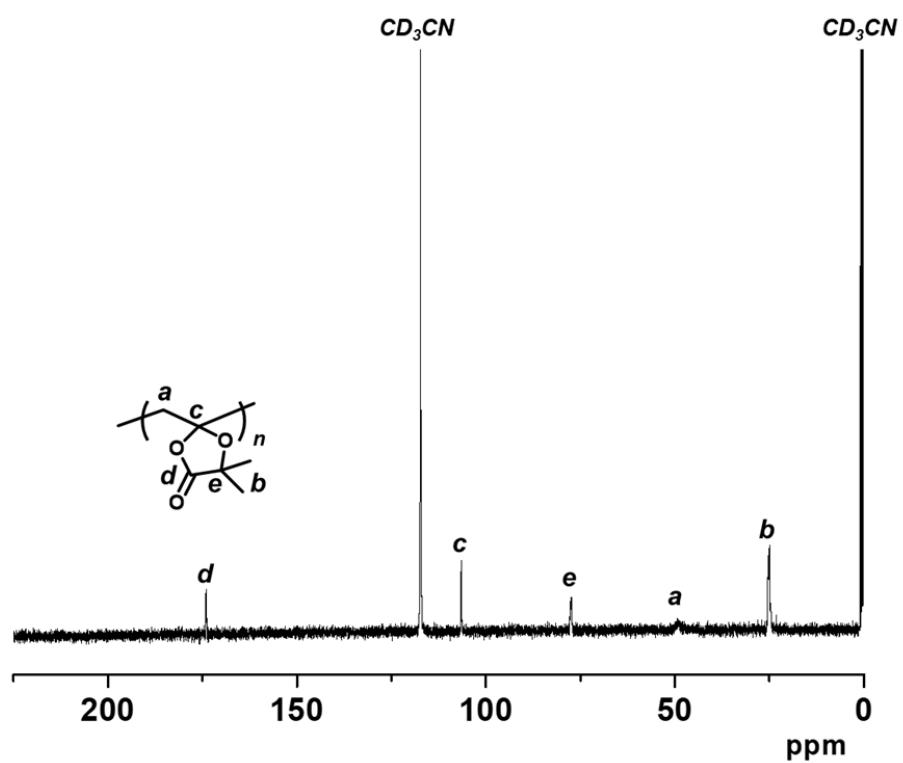


Fig. S40. ¹³C NMR spectrum of non-degraded PDMDL (4.2 wt%) in CD₃CN (95.8 wt%) mixture (100 MHz, 298 K, CDCl₃).

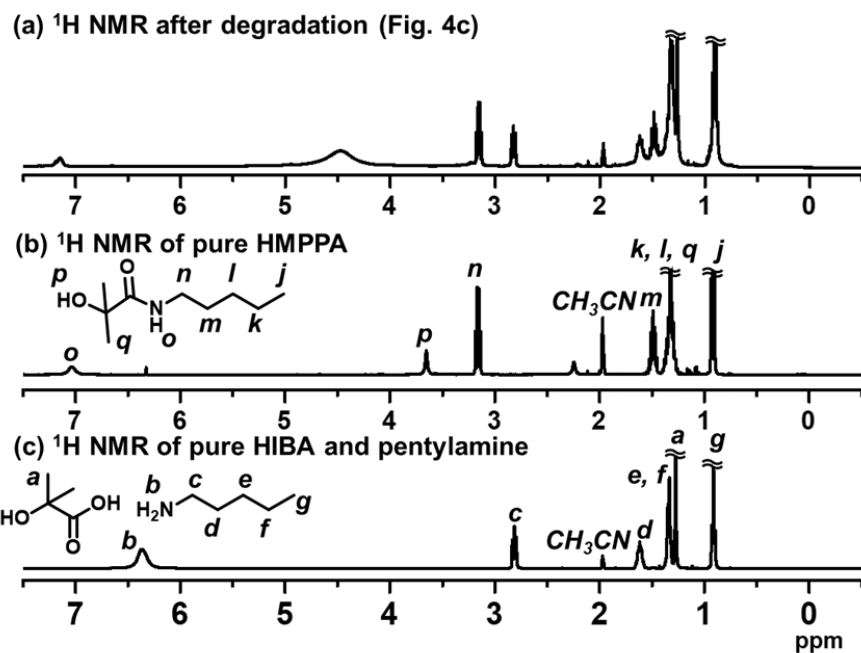


Fig. S41. ^1H NMR of (a) the reaction mixture after degradation (b) pure HMPPA (c) pure HIBA and pentylamine (400 MHz, 298K, CD_3CN).

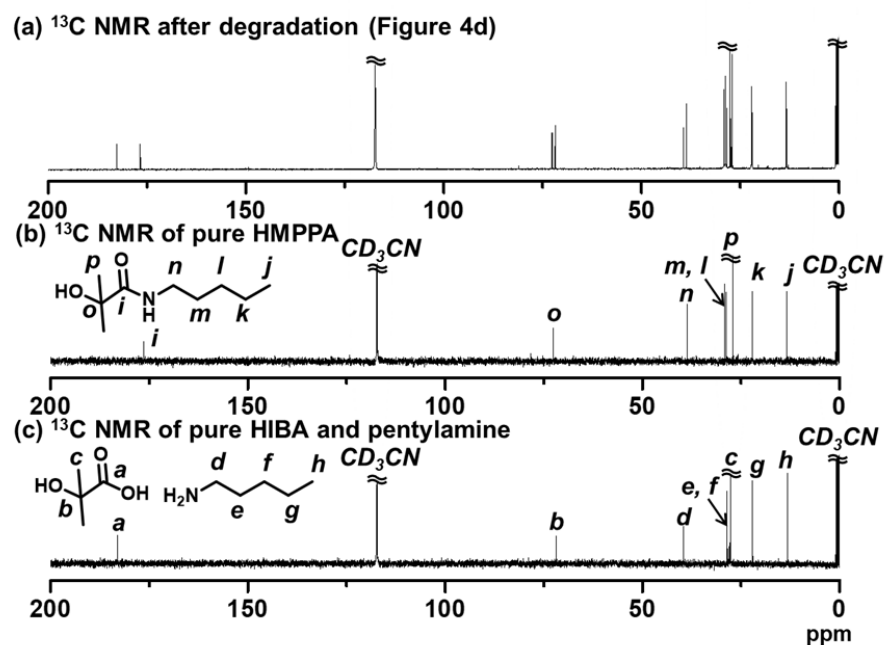


Fig. S42. ^{13}C NMR of (a) the reaction mixture after degradation, (b) pure HMPPA, (c) pure HIBA and pentylamine (100 MHz, 298K, CD_3CN).

Degradation of PPEGMA homopolymer

GPC (DMF)

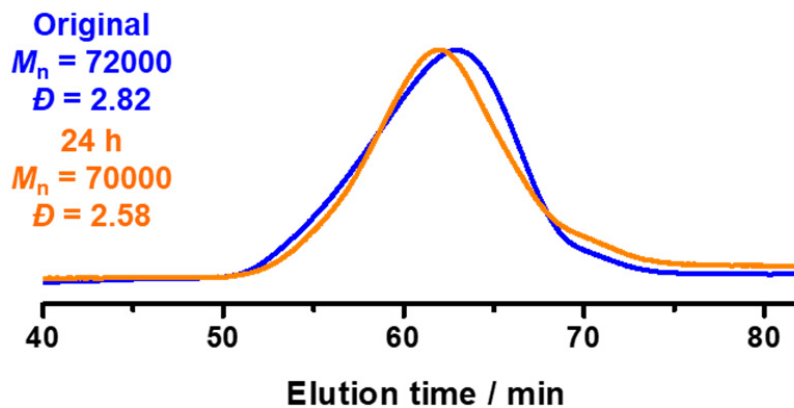


Fig. S43. Degradation of PPEGMA ($M_n = 72000$, $D = 2.82$) (1 wt%) using 0.9M KOH aqueous solution (99 wt%) at room temperature for 24 h.

Degradation of PLMA homopolymer

GPC (THF)

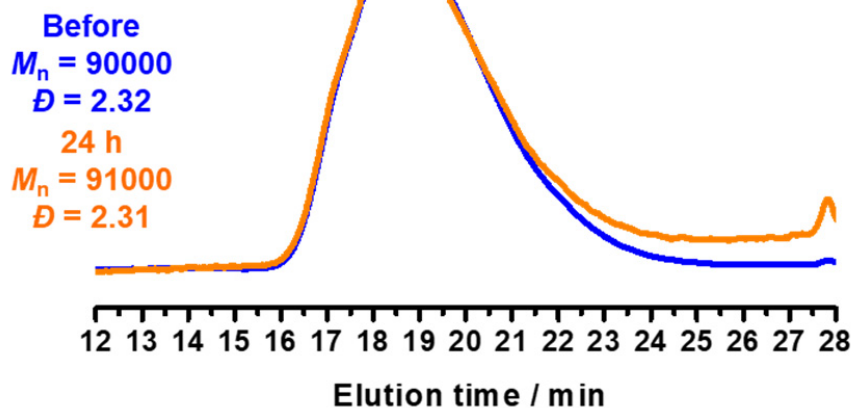


Fig. S44. Degradation of PLMA ($M_n = 90000$, $D = 2.32$) (2.0 wt%) using 0.9M KOH in a mixture of methanol (8.1 wt%) and THF (89.9 wt%) at room temperature for 24 h.

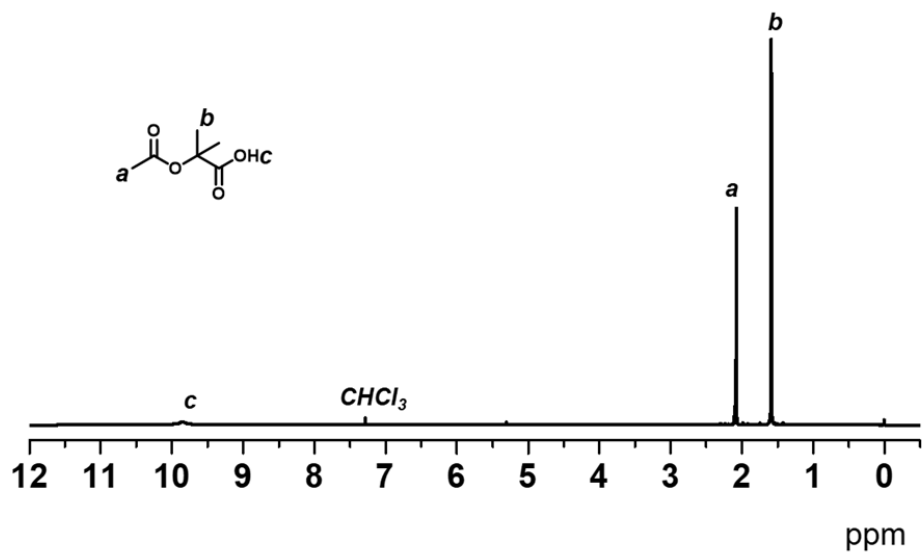


Fig. S45. ^1H NMR spectrum of compound **2** ($\text{R}_1 = \text{CH}_3$) synthesized from recovered HIBA (400 MHz, 298 K, CDCl_3).

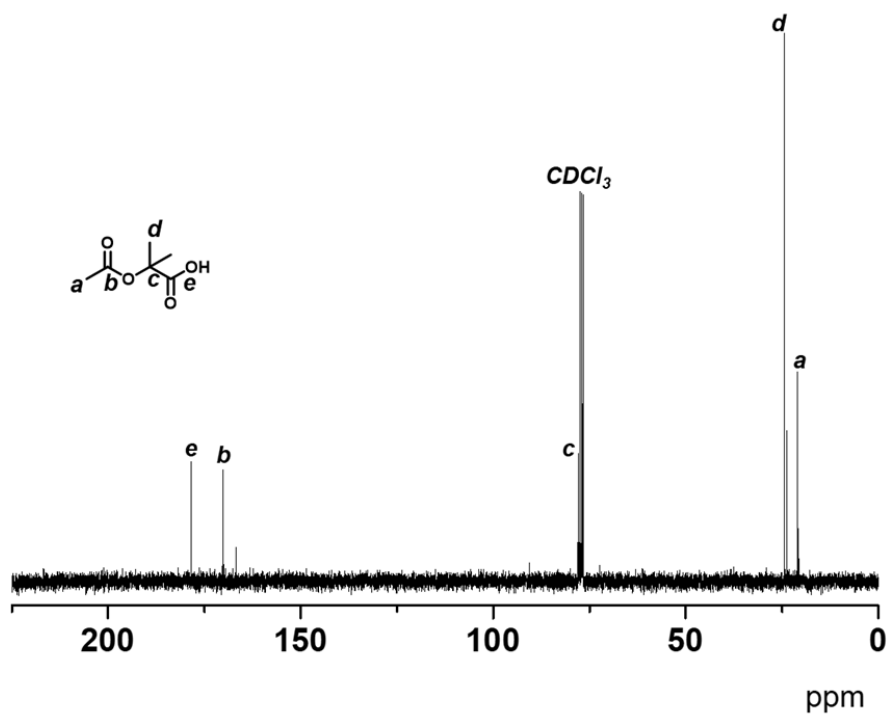


Fig. S46. ^{13}C NMR spectrum of compound **2** ($\text{R}_1 = \text{CH}_3$) synthesized from recovered HIBA (100 MHz, 298 K, CDCl_3).

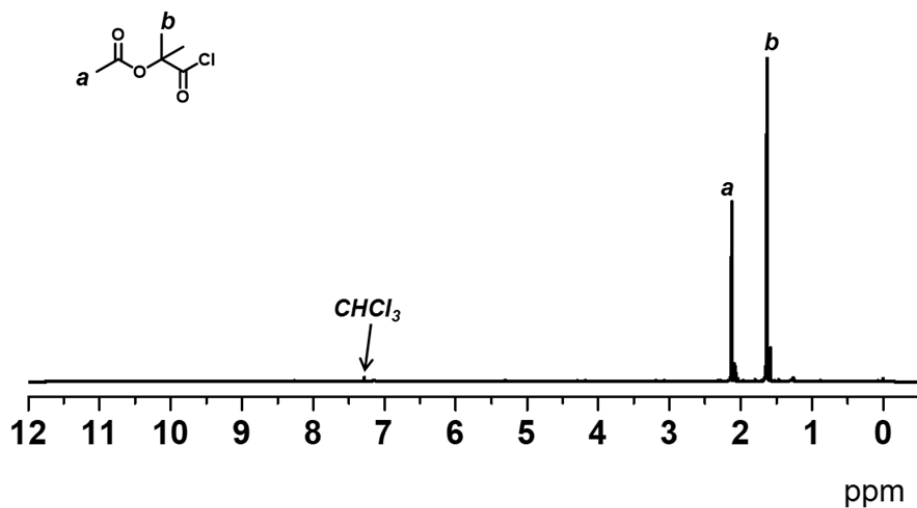


Fig. S47. ^1H NMR spectrum of compound **3** ($\text{R}_1 = \text{CH}_3$) synthesized from recovered HIBA (400 MHz, 298 K, CDCl_3).

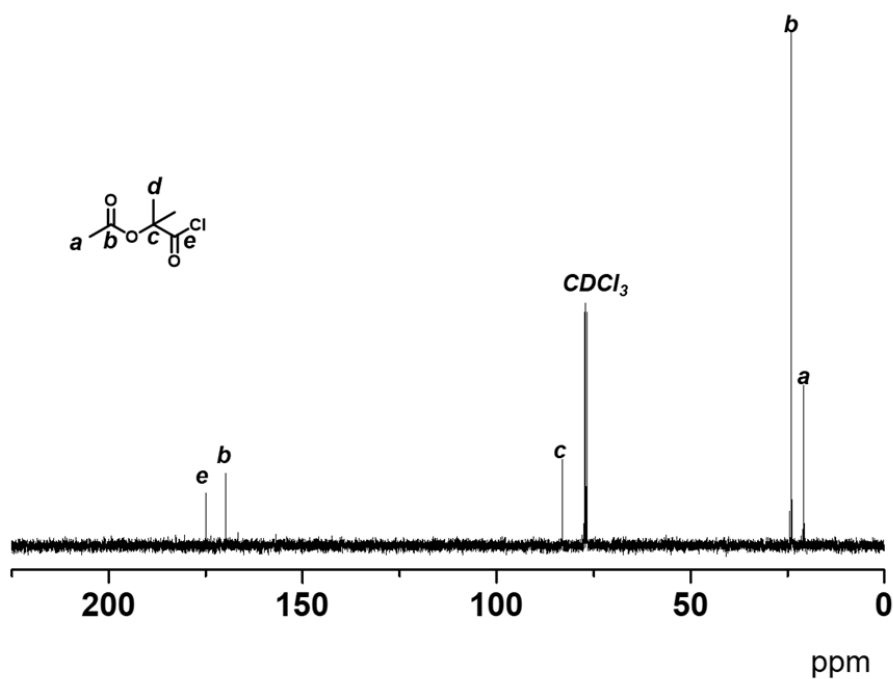


Fig. S48. ^{13}C NMR spectrum of compound **3** ($\text{R}_1 = \text{CH}_3$) synthesized from recovered HIBA (100 MHz, 298 K, CDCl_3).

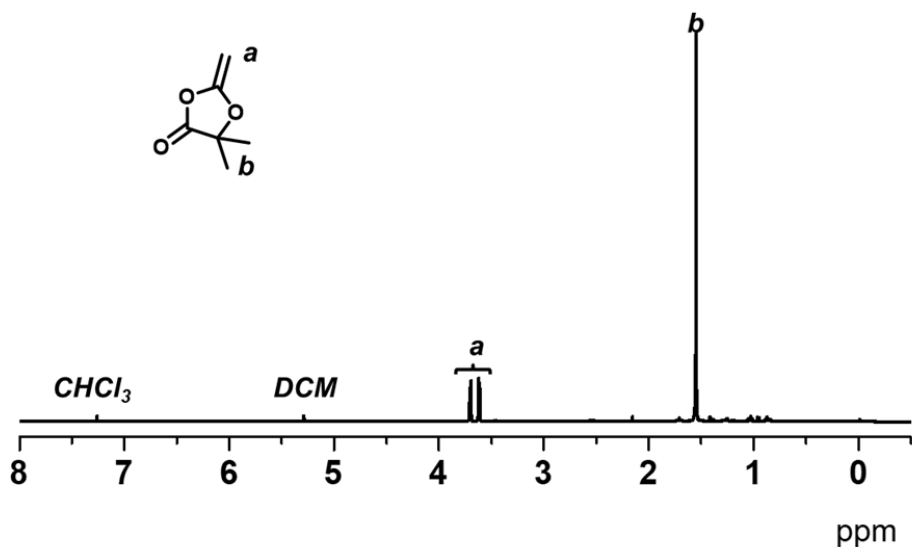


Fig. S49. ¹H NMR spectrum of DMDL synthesized from recovered HIBA (400 MHz, 298 K, CDCl₃).

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