Supporting information for

Defining Alternating Sequences in Polyurethanes: Sequence-Controlled Photo-Degradation in Step Polymerization

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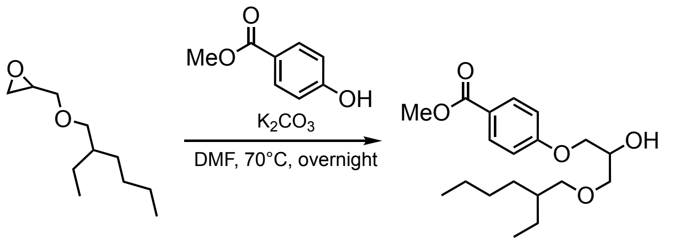
1. General Methods

^{1}H- (400 MHz) and ^{13}C- (100 MHz) NMR spectra were recorded on a Bruker AVANCE III Microbay spectrometer using deuterated solvents, calibrated using residual undertreated solvent or tetramethylsilane as the internal standard. Attenuated total reflection-Fourier transform infrared (ATR-FT-IR) spectra were recorded on a Bruker Vertex 80 with a mid-wavelength to far infrared spectrum from 4000 to 500 cm^{-1}. Analytical GPC was performed in THF (at 25 °C) or in DMAc (at 50 °C) using a on a Tosoh Bioscience HLC-8320GPC EcoSEC system equipped with 3 PSS SDV columns, 5 µm (100, 1000, 100 000 Å) (8 Å~ 300 mm ^{2}), and a differential refractive index (RI) detector. The number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (M_w / M_n) of the polymers were calculated based on a polystyrene calibration. Thermal gravimetric analysis (TGA) was carried out using a TGA 5500 (TA Instruments) at a heating rate of 10 K min^{-1} under a nitrogen atmosphere up to 800 °C, and differential scanning calorimetry was conducted using a DSC Q200 (TA Instruments) ranging from −50 °C to 200 °C (2nd heating) with a scan rate of 10 K min^{-1} after the 1st heating from r. t. to 110–180 °C. UV/Vis absorption spectra were recorded using an Ocean optics spectrometer. Commercially available reagents and solvents were used without further purification unless otherwise noted. To test the degradability of polymers under UV exposure, their solution in THF or DMAc (1 mg/ 1 mL) were irradiated by four 36W 365 nm-Hg lamps for 2h, and samples for SEC were taken at the start and at 5 min, 10 min, 15 min, 30 min, 60 min, 120 min of irradiation.

All compounds given below bear the same formula numbers as used in the main text. Compounds unlabeled in the main text are labeled with letters [**S1**–**S4**]. Literature known compound **M1** and **M2** were synthesized accordingly by the given literature information. [1]

2. Chemical Synthesis

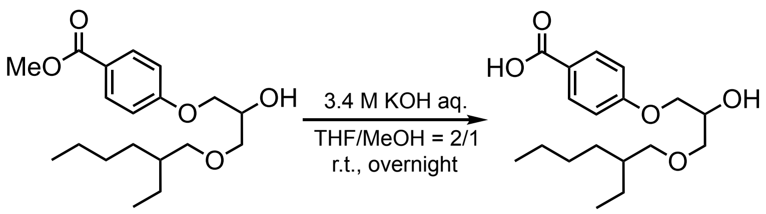
Synthesis of S1



S1

2-Ethylhexyl glycidyl ether (9.30 g, 1.0 mL, 50.0 mmol) was added to a solution of K_2CO_3 (10.0 g, 79.2 mmol) and methyl 4-hydroxybenzoate (8.10 g, 53.0 mmol) in dry DMF (50 mL), then the mixture was stirred at 80 °C overnight. The resulting mixture was poured into water and collected the precipitate. The product was dried *in vacuo* to give **S1** (16.0 g, 95%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] 7.91 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 4.21 – 4.05 (m, 1H), 4.05 – 3.93 (m, 2H), 3.81 (s, 3H), 3.55 – 3.45 (m, 2H), 3.37 – 3.19 (m, 2H), 1.51 – 1.37 (m, 1H), 1.33 – 1.14 (m, 8H), 0.86 – 0.72 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm]166.83, 162.44, 131.58, 122.80, 114.13, 74.47, 71.56, 69.25, 68.89, 51.85, 39.53, 30.50, 29.05, 23.81, 23.05, 14.07, 11.03. ATR-IR ṽ [cm−1]: 2956; 2928; 2860; 1717; 1605; 1511; 1435; 1279; 1253; 1169; 103; 1033; 846; 770; 696; 653; 511.

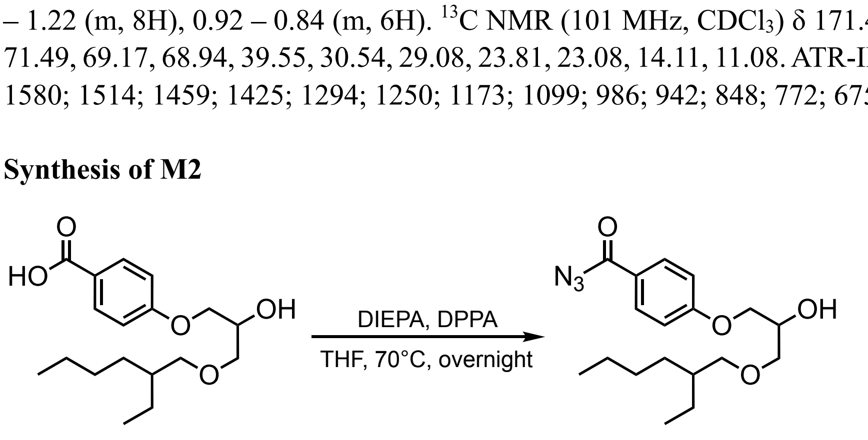
Synthesis of S2



S1 **S2**

3.5M KOH aq. (KOH 16.0 g, 285 mmol, H_2O, 82 ml) was added to a solution of **S1** (11.3 g, 40.0 mmol) in a mixed solvent (THF 160 ml/ MeOH 80 ml), then the mixture was stirred at room temperature overnight. The organic solvent was evaporated, water was added, 1M HCl aq., extracted by EtOAc dried by $MgSO_4$ and dried *in vacuo* to give **S2** (10.7 g, 82%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] 8.06 (d, *J* = 8.9 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 4.22 – 4.15 (m, 1H), 4.14 – 4.07 (m, 2H), 3.65 – 3.53 (m, 2H), 3.43 – 3.35 (m, 2H), 1.55 – 1.48 (m, 1H), 1.40 – 1.22 (m, 8H), 0.92 – 0.84 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.47, 163.05, 132.36, 122.10, 114.27, 74.56, 71.49, 69.17, 68.94, 39.55, 30.54, 29.08, 23.81, 23.08, 14.11, 11.08. ATR-IR ṽ [cm−1]:3335; 2928; 2860; 1684; 1605; 1580; 1514; 1459; 1425; 1294; 1250; 1173; 1099; 986; 942; 848; 772; 675; 635 ;548; 507.

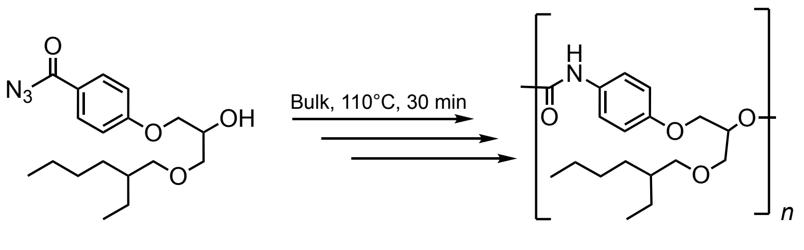
Synthesis of M2



S2 **M2**

Diphenylphosphorylazide (DPPA) (13.3 g, 10,5 ml, 48.3 mmol) was added to a solution of **S2** (10.4 g, 32.0 mmol) and N,N-diisopropylethylamine (DIEPA) (12.5 g, 16.8 mL, 96.7 mmol) in dry THF (128 mL), then, the mixture was stirred at room temperature overnight. Solvent was removed by rotary evaporator, CH_2Cl_2 was added to the mixture, washed with sat. $NaHCO_3$ aq., dried by $MgSO_4$, and purified by silica gel column chromatography (eluent; EtOAc/Hexane = 1/4) to give **M2** (3.86g, 35%) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.9 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 4.15 – 4.07 (m, 1H), 4.07 – 3.98 (m, 2H), 3.55 – 3.46 (m, 2H), 3.36 – 3.26 (m, 2H), 1.49 – 1.42 (m, 1H), 1.31 – 1.12 (m, 8H), 0.84 – 0.76 (m, 6H); ^{13}C NMR (101 MHz $CDCl_3$) δ [ppm] 171.65, 163.68, 131.75, 123.47, 114.45, 74.51, 71.43, 69.33, 68.88, 39.55, 30.53, 29.07, 23.84, 23.07, 14.09, 11.06. ATR-IR ṽ [cm−1]: 2958; 2927; 2871; 2860; 2132; 1688; 1600; 1577; 1508; 1458; 1422; 1313;1245; 1165; 1115; 1033; 1013; 980; 843; 753; 685; 661; 631.

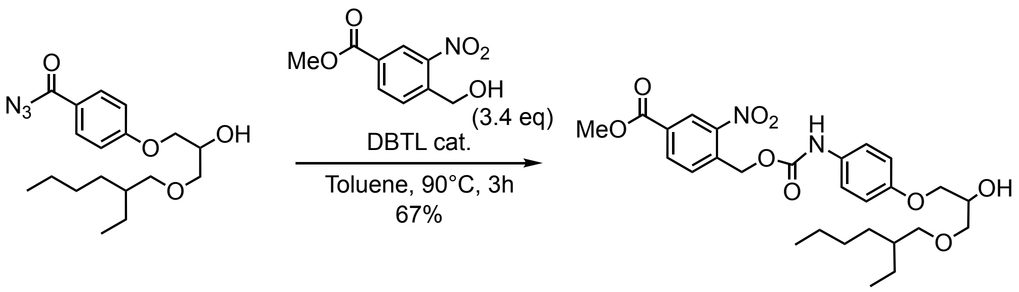
Synthesis of polyM2 [1b]



M2 **polyM2**

Dibutyltin dilaurate (DBTDL) (cat., 2 drops by syringe) was added to **M2** (70.0 mg, 0.20 mmol) then stirred for 30 min at 110 °C. The resulting mixture was diluted by DCM, poured into cold MeOH (~6 mL) and collected the precipitate. The residue was dried *in vacuo* to give **polyM2** (42.0 mg, 60%) as a white lump; ^{1}H NMR (400 MHz, 298 K, DMSO-d_6) ppm. ^{1}H NMR (400 MHz, DMSO): δ [ppm] 9.63 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.20 – 5.10 (m, 1H), 4.14 – 4.07 (m, 2H), 3.67 – 3.60 (m, 2H), 3.32 – 3.24 (m, 2H), 1.46 – 1.39 (m, 1H), 1.30 – 1.14 (m, 8H), 0.83 – 0.75 (m, 6H); ^{13}C NMR (101 MHz, DMSO) δ [ppm] 153.67, 153.03, 132.56, 119.64,114.59, 73.37, 70,74 68.95, 66.87, 30.07, 28.47, 23.35, 22.53,13.90, 10.93; ATR-IR ṽ [cm−1]: 3313; 2957; 2927; 2871; 2860; 1705 ;1601 ;1511 ;1460 ;1415 ;1295 ;1203 ;1045 ;827; 765; 519.

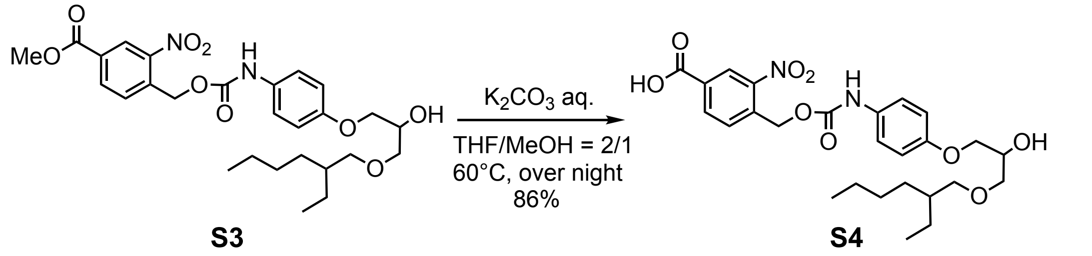
Synthesis of S3



M2 **S3**

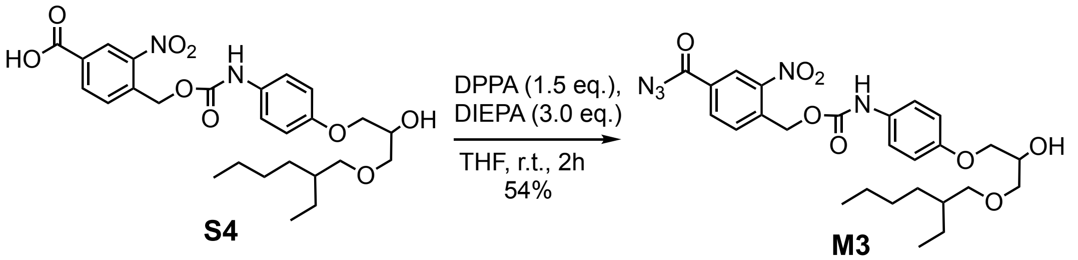
M2 (1.86 g, 5.3 mmol) and two drops of DBTL was added to a solution of 4-(hydroxymethyl)-3-nitrobenzoate (3.80 g, 18.0 mmol) in dry Toluene (55 mL), the mixture was stirred at 90 °C for 3h. The solvent was removed by rotary evaporator and purified and purified by silica gel column chromatography (eluent; EtOAc/Hexane = 1/4) to give **S3** (1.91 g, 67%) as a pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d) δ [ppm] = 9.80 (s, 1H), 8.57 (d, *J* = 1.8 Hz, 1H), 8.35 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 2H), 6.93 – 6.82 (m, 2H), 5.56 (s, 2H), 5.03 (d, *J* = 5.0 Hz, 1H), 3.92 (s, 3H), 3.91 – 3.86 (m, 2H), 3.86 – 3.80 (m, 1H), 3.46– 3.36 (m, 2H), 3.31 – 3.25 (m, 2H), 1.47 – 1.38 (m, 1H), 1.24 – 1.15 (m, 8H), 0.81 (s, 6H); ^{13}C NMR (101 MHz, DMSO-d) δ [ppm] = 164.3, 154.4, 152.9, 147.0, 137.8, 134.1, 131.8, 130.1, 129.4, 125.3, 119.8, 114.6, 73.4, 71.9, 69.9, 68.0, 62.2, 52.8, 30.1, 28.5, 23.4, 22.5, 13.9, 10.9; ATR-IR ṽ [cm−1] =3295, 3092, 2957, 2927, 2871, 2859, 1723, 1704, 1625, 1599, 1568, 1528, 1488, 1460, 1433, 1418, 1366, 1338, 1312, 1289, 1256, 1229, 1172, 1153, 1109, 1078, 1061, 973, 935, 905, 862, 825, 799, 786, 773, 743, 701, 667, 632, 517, 480, 435.

Synthesis of S4



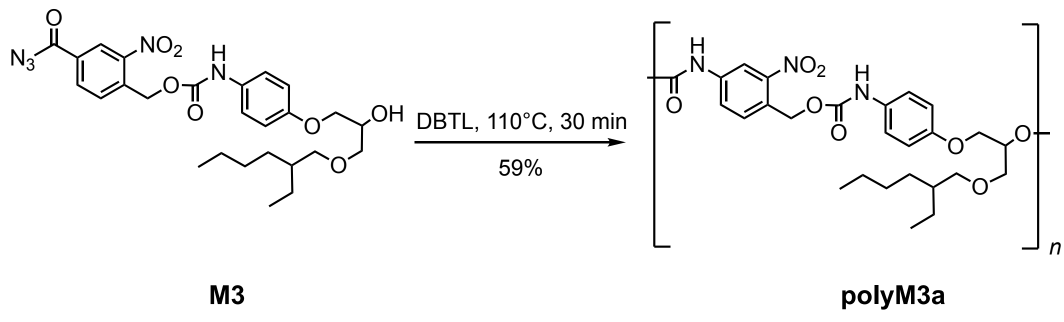
K_2CO_3 aq. (2.49 g, 18.0 mmol, H_2O, 5 ml) was added to a solution of **S3** (1.33 g, 2.50 mmol) in a mixed solvent (THF 12 ml/ MeOH 6 ml), then the mixture was stirred at 60 °C overnight. The organic solvent was evaporated, water was added, NH_4Cl aq., extracted by EtOAc, dried by $MgSO_4$ and dried *in vacuo* to give **S4** (1.11 g, 86%) as an orange solid. ^{1}H NMR (400 MHz, DMSO-d) δ [ppm] = 9.78 (s, 1H), 8.59 (d, 1H), 8.30 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 2H), 6.89 – 6.79 (m, 2H), 5.53 (s, 2H), 3.94 – 3.85 (m, 3H), 3.83 (d, *J* = 3.6 Hz, 1H), 3.41 (dd, *J* = 5.2, 2.1 Hz, 3H), 3.28 (d, *J* = 5.9 Hz, 3H), 1.42 (q, *J* = 5.9 Hz, 1H), 1.24 – 1.16 (m, 8H), 0.86 – 0.75 (m, 6H); ^{13}C NMR (101 MHz, DMSO-d) δ [ppm] = 182.3, 154.4, 153.0, 146.9, 135.7, 134.3, 131.9, 131.2, 128.9, 125.4, 119.8, 114.6, 73.4, 72.0, 69.9, 68.0, 62.3, 30.1, 28.5, 23.4, 22.6, 14.0, 10.9; ATR-IR ṽ [cm^{-1}] =3326, 2958, 2927, 2871, 2860, 1710, 1625, 1600, 1534, 1512, 1460, 1416, 1341, 1309, 1213, 1176, 1082, 1061, 924, 862, 826, 800, 746, 692, 600, 520.

Synthesis of M3



Diphenylphosphorylazide (DPPA) (990 mg, 0.78 ml, 3.60 mmol) was added to a solution of **S4** (1.24 g, 2.40 mmol) and N,N-diisopropylethylamine (DIEPA) (930 mg, 1.22 mL, 7.20 mmol) in dry THF (10 mL), then, the mixture was stirred at room temperature for 2 hours. Solvent was removed by rotary evaporator, CH_2Cl_2 was added to the mixture, washed with sat. $NaHCO_3$ aq., dried by $MgSO_4$, and purified by silica gel column chromatography (eluent; EtOAc/Hexane = 1/4) to give **M3** (707 mg, 54%) as a yellow powder. ^{1}H NMR (400 MHz, DMSO-d) δ [ppm] = 9.82 (s, 1H), 8.58 (d, *J* = 1.8 Hz, 1H), 8.36 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.37 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 9.1 Hz, 2H), 5.58 (s, 2H), 5.05 – 4.99 (m, 1H), 3.95 – 3.87 (m, 2H), 3.87– 3.81 (m, 1H), 3.45 – 3.38 (m, 2H), 3.31 – 3.27 (m, 2H), 1.51 – 1.40 (m, 1H), 1.27 – 1.15 (m, 8H), 0.90 – 0.72 (m, 6H); ^{13}C NMR (101 MHz, DMSO-d) δ [ppm] = 170.2, 154.4, 152.9, 147.1, 139.1, 133.8, 131.8, 130.6, 129.5, 125.1, 119.8, 114.6, 73.4, 71.9, 69.9, 68.0, 62.2, 30.1, 28.5, 23.4, 22.5, 13.9, 10.9; ATR-IR ṽ [cm−1] = 3356, 2957, 2925, 2857, 2204, 2147, 1727, 1682, 1622, 1606, 1567, 1548, 1512, 1459, 1418, 1371, 1340, 1308, 1276, 1244, 1226, 1179, 1113, 1083, 1063, 1036, 954, 917, 862, 851, 835, 799, 767, 735, 709, 666, 559, 525, 494, 468.

Polymerization of M3

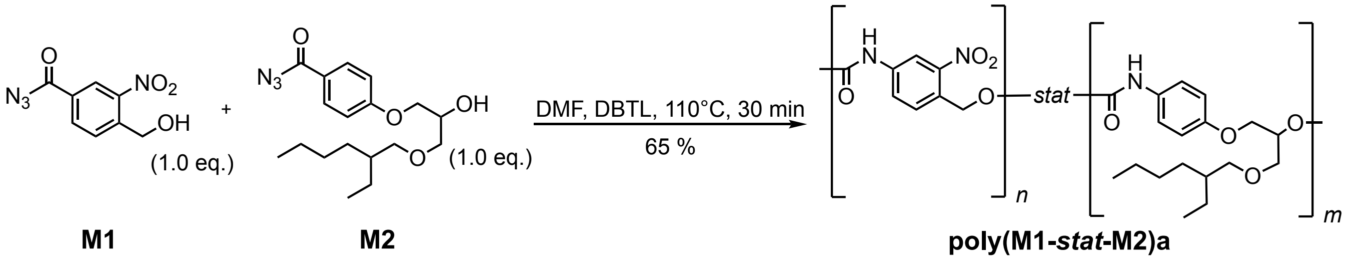


Synthesis of **polyM3** was carried out under various reaction condition as depicted in **Table 1** in the main text. Here, the representative protocol was described and the rest of entries in **Table 1** were conducted accordingly.

polyM3a

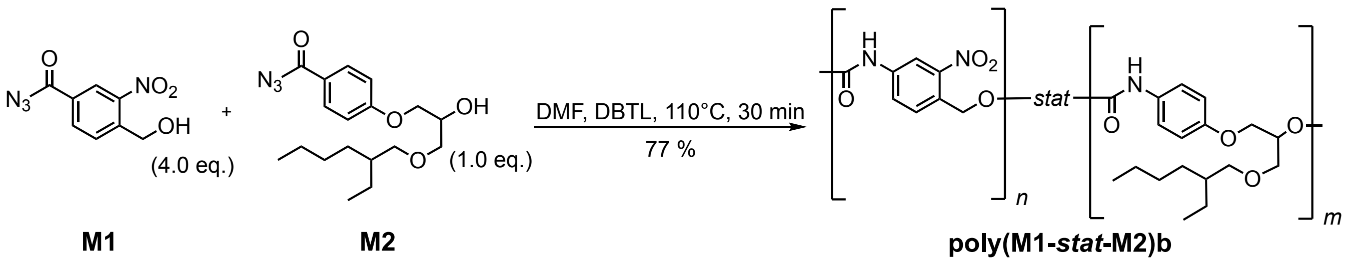
Dibutyltin dilaurate (DBTDL) (cat., 2 drops by syringe) was added to **M3** (40.9 mg, 0.08 mmol) the mixture was stirred for 30 min at 110 °C. The resulting mixture was diluted by THF, poured into cold MeOH (~6 mL) and collected the precipitate. The residue was dried *in vacuo* to give **polyM3a** (23.0 mg, 59%) as a white yellow lump. $M_{n,SEC}$= 11 kDa; $Đ$= 1.6; ^{1}H NMR (400 MHz, DMSO-d) δ [ppm] = 10.37 (s, 1H), 9.65 (s, 1H), 8.32 (s, 1H), 7.80–7.73 (m, 1H), 7.62 (d, J = 8.6 Hz, 1H), 7.35 (d, J = 8.1 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 5.35 (s, 2H), 5.25 – 5.17 (m, 1H), 4.18 – 4.09 (m, 2H), 3.72–3.63 (m, 2H), 3.33–3.23 (m, 2H), 1.46 –1.35 (m, 1H), 1.23–1.09 (m, 8H), 0.89– 0.69 (m, 6H); ^{13}C NMR (101 MHz, DMSO-d) δ [ppm] = 153.7, 153.0, 147.7, 139.9, 132.4, 130.5, 130.0, 125.6, 122.9, 119.7, 114.7, 113.5, 73.3, 71.6, 68.8, 67.0, 62.2, 30.1, 30.0, 28.5, 25.1, 23.4, 22.5, 13.9, 10.9; ATR-IR ṽ [cm^{-1}] = 3302, 2957, 2927, 2870, 1708, 1596, 1510, 1460, 1413, 1342, 1310, 1203, 1051, 960, 888, 824, 759, 686, 519.

Synthesis of Poly(M1-*stat*-M2)a



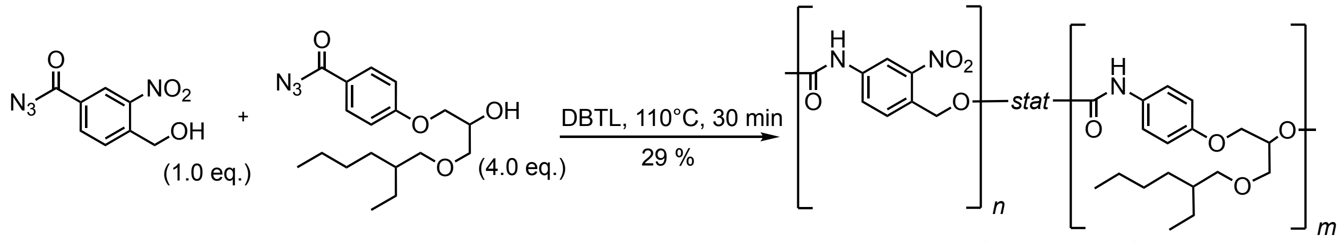
M1 (44.5 mg, 0.20 mmol) and Dibutyltin dilaurate (DBTDL) (cat., 2 drops by syringe) were added to a solution of **M2** (70.3 mg, 0.20 mmol) in DMF (0.40 mL) the mixture was stirred for 30 min at 110 °C. The resulting mixture was diluted by THF, poured into cold MeOH (~6 mL) and collected the precipitate. The residue was dried *in vacuo* to give **poly(M1-*stat*-M2)a** (67.4 mg, 65 %) as a yellow solid. $M_{n,SEC}$= 8.6 kDa; $Đ$= 1.3; ^{1}H NMR (400 MHz, DMSO-d) δ [ppm] = 10.39 (s, 0.98H), 9.62 (s, 1.02H), 8.37–8.27 (m, 0.98H), 7.76 (s, 0.98H), 7.70–7.58 (m, 0.98H), 7.42–7.28 (m, 2.04H), 6.92–6.77 (m, 2.04H), 5.48–5.31 (m, 1.98H), 5.30–5.07 (m, 1.02H), 4.18–4.03 (m, 2.04H), 3.73–3.60 (m, 2.04H), 3.31–3.19 (m, 2.04H), 1.47–1.36 (m, 1.02H), 1.23–1.09 (m, 8.16H), 0.81–0.71 (m, 6.12H); ATR-IR ṽ [cm^{-1}] = 3301, 2957, 2927, 2871, 1712, 1662, 1598, 1530, 1510, 1461, 1413, 1312, 1205, 1054, 890, 826, 759, 663, 520.

Synthesis of Poly(M1-*stat*-M2)b



M1 (89.1 mg, 0.40 mmol) and Dibutyltin dilaurate (DBTDL) (cat., 2 drops by syringe) were added to a solution of **M2** (34.9 mg, 0.10 mmol) in DMF (0.50 mL) the mixture was stirred for 30 min at 110 °C. The resulting mixture was transferred into cold MeOH (~8 mL) and collected the precipitate. The residue was dried *in vacuo* to give **poly(M1-*stat*-M2)b** (84.8 mg, 77 %) as a yellow solid. $M_{n,SEC}$= 8.0 kDa; $Đ$= 1.9; ^{1}H NMR (400 MHz, DMSO-d) δ [ppm] = 10.39 (s, 1.4H), 9.64 (s, 0.6H), 8.44–8.19 (m, 1.4H), 7.75–7.53 (m, 2.8H), 7.48–7.15 (m, 1.2H), 6.96 – 6.76 (m, 1.2H), 5.71–4.93 (m, 4H), 4.20–3.01 (m, 3.6H), 1.75–0.58 (m, 9H); ATR-IR ṽ [cm^{-1}] = 3262, 2958, 2927, 2870, 1731, 1660, 1596, 1529, 1409, 1343, 1316, 1208, 1056, 951, 889, 826, 758, 663, 522.

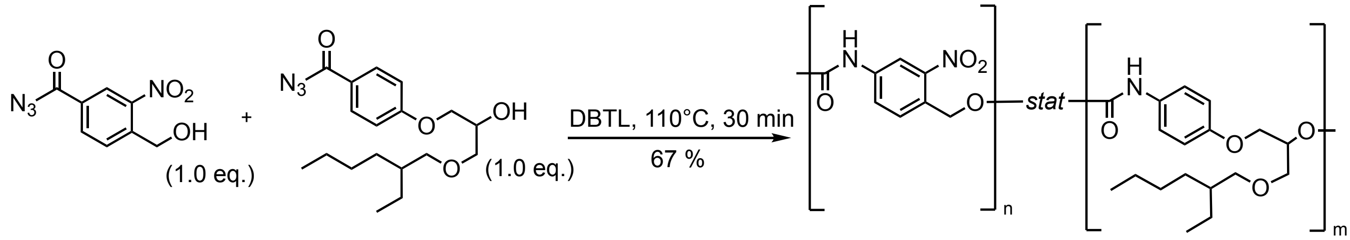
Synthesis of Poly(M1-*stat*-M2)c



M1 **M2** **poly(M1-*stat*-M2)c**

M1 (16.9 mg, 0.08 mmol) and Dibutyltin dilaurate (DBTDL) (cat., 2 drops by syringe) were added to **M2** (104 mg, 0.30 mmol), the mixture was stirred for 30 min at 110 °C. The resulting mixture was diluted by THF, poured into cold MeOH (~8 mL) and collected the precipitate. The residue was dried *in vacuo* to give **poly(M1-*stat*-M2)c** (30.8 mg, 29 %) as a yellow solid. $M_{n,SEC}$= 6.0 kDa; Đ= 1.7; ^{1}H NMR (400 MHz, DMSO-d) δ [ppm] = 10.36 (s, 0.44H), 9.60 (s, 1.56H), 8.31 (s, 0.44H), 7.75 (d, *J* = 8.6 Hz, 0.44H), 7.61 (d, *J* = 8.9 Hz, 0.44H), 7.39–7.28 (m, 3.12H), 6.88–6.80 (m, 3.12H), 5.59–5.30 (m, 0.88H), 5.23–5.10 (m, 1.56H), 4.18–4.01 (m, 3.12H), 3.70–3.52 (m, 3.12H), 3.30–3.19 (m, 3.12H), 1.49–1.28 (m, 1.56H), 1.27–1.03 (m, 12.48H), 0.78–0.69 (m, 9.36H); ATR-IR ṽ [cm^{-1}] = 3308, 2958, 2927, 2871, 1707, 1600, 1511, 1462, 1415, 1309, 1204, 1050, 826, 763, 520.

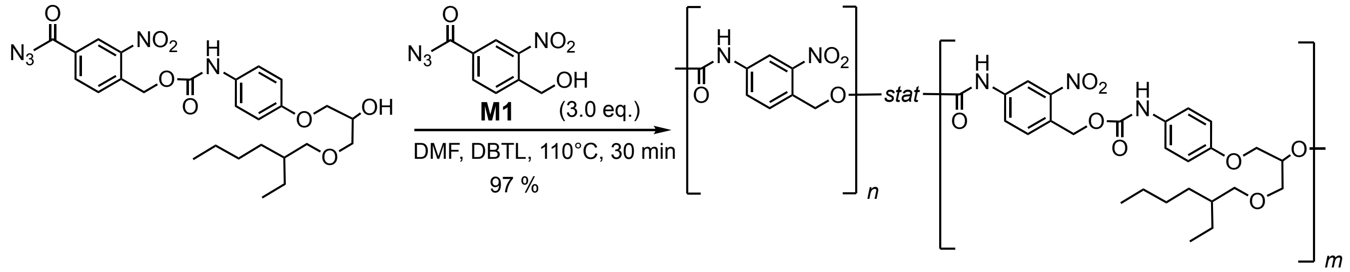
Synthesis of Poly(M1-*stat*-M2)d



M1 **M2** **poly(M1-*stat*-M2)d**

M1 (22.2 mg, 0.10 mmol) and Dibutyltin dilaurate (DBTDL) (cat., 2 drops by syringe) were added to **M2** (34.8 mg, 0.10 mmol) the mixture was stirred for 30 min at 110 °C. The resulting mixture was diluted by THF, poured into cold MeOH (~8 mL) and collected the precipitate. The residue was dried *in vacuo* to give **poly(M1-*stat*-M2)d** (31.9 mg, 62 %) as an orange-yellow solid. $M_{n,SEC}$= 13 kDa; Đ= 1.4; ^{1}H NMR (400 MHz, DMSO-d) δ [ppm] = 10.41 (s, 0.98H), 9.64 (s, 1.02H), 8.42–8.27 (m, 0.98H), 7.84–7.74 (m, 1.02H), 7.71–7.62 (m, 1.02H), 7.40–7.31 (m, 2.04H), 6.87 (d, *J* = 7.8 Hz, 2.04H), 5.52–5.38 (m, 1.96H), 5.25– 5.10 (m, 1.02H), 4.18–4.08 (m, 2.04H), 3.70–3.63 (m, 2.04H), 3.30 –3.24 (m, 2.04H), 1.46–1.38 (m, 1.02H), 1.36–1.08 (m, 8.16H), 0.87–0.70 (m, 6.12H); ATR-IR ṽ [cm^{-1}] = 3304, 2958, 2927, 2870, 2860, 1712, 1598, 1530, 1510, 1462, 1414, 1344, 1311, 1287, 1205, 1053, 953, 888, 826, 760, 684, 520.

Synthesis of Poly(M1-*stat*-M3)

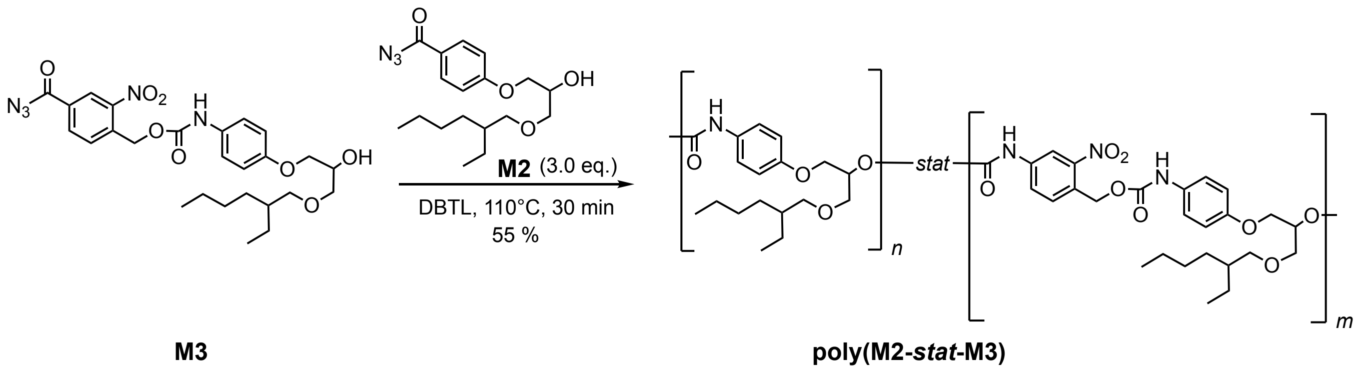


M3 **poly(M1-*stat*-M3)**

M1 (67.1 mg, 0.30 mmol) and Dibutyltin dilaurate (DBTDL) (cat., 2 drops by syringe) were added to a solution of **M3** (54.4 mg, 0.10 mmol) in DMF (0.50 mL) the mixture was stirred for 30 min at 110 °C. The resulting mixture was diluted by THF, poured into cold MeOH (~8 mL) and collected the precipitate. The residue was dried *in vacuo* to give **poly(M1-*stat*-M3)** (107 mg, 97 %) as a yellow solid. $M_{n,SEC}$= 8.2 kDa; Đ= 1.8; ^{1}H NMR (400 MHz, DMSO-

d) δ [ppm] = 10.42 (s, 1.44H), 9.67 (s, 0.56H), 8.41–8.19 (m, 1.44H), 7.84–7.51 (m, 2.88H), 7.48–7.08 (m, 1.12H), 6.92–6.78 (m, 1.12H), 5.49–5.08 (m, 3.44H), 4.20–4.01 (m, 1.12H), 3.71–3.01 (m, 2.24H), 1.62–0.58 (m, 8.4H); ATR-IR ṽ [cm−1] = 3252, 3176, 3102, 2957, 2927, 2870, 1731, 1658, 1596, 1528, 1409, 1343, 1316, 1208, 1055, 951, 889, 826, 758, 663, 52.

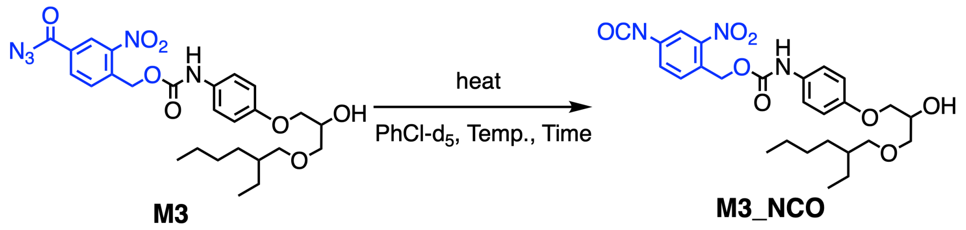
Synthesis of Poly(M2-*stat*-M3)



M3 (40.7 mg, 0.08 mmol) and Dibutyltin dilaurate (DBTDL) (cat., 2 drops by syringe) were added to **M2** (78,8 mg, 0.23 mmol), the mixture was stirred for 30 min at 110 °C. The resulting mixture was diluted by THF, poured into cold MeOH (~8 mL) and collected the precipitate. The residue was dried *in vacuo* to give **poly(M2-*stat*-M3)** (57 mg, 55 %) as a yellow solid. $M_{n,SEC}$= 9.3 kDa; Đ= 1.4; ^{1}H NMR (400 MHz, DMSO-d) δ [ppm] = 10.41 (s, 0.48H), 9.60 (s, 1.52H), 8.31 (s, 0.48H), 7.75 (d, J = 8.2 Hz, 0.48H), 7.62 (s, 0.48H), 7.47–7.26 (m, 3.04H), 6.92–6.77 (m, 3.04H), 5.47–5.38 (m, 0.96H), 5.24–5.08 (m, 1.52H), 4.22–4.03 (m, 3.04H), 3.71–3.59 (m, 3.04H), 3.29–3.17 (m, 3.04H), 1.48–1.09 (m, 13.68H), 0.88–0.70 (m, 9.12H); ATR-IR ṽ [cm^{-1}] = 3310, 2957, 2927, 2871, 1710, 1599, 1511, 1461, 1415, 1310, 1204, 1051, 826, 762, 520.

3. Kinetics analysis of the Curtius rearrangement

The kinetic analysis of the Curtius rearrangement of **M3** was carried out to follow previously reported standard method.[1-3] With the assumption of the back reaction that the isocyanate **M3_NCO** transforms into **M3** again does not take place, the kinetic equation of this Curtius rearrangement in PhCl-d_5 solvent can be written as following with the kinetic constant *k* (**Scheme S1**).



Scheme S1. Curtius rearrangement rate equation of **M3** to **M3_NCO**.

Defining the concentration of **M3** as [**M3**] and **M3_NCO** as [**M3_NCO**] respectively, following two equations are written.

$$\frac{d[\mathbf{M3}]}{dt} = -k[\mathbf{M3}] \qquad (1)$$

$$[\mathbf{M3}] + [\mathbf{M3\_NCO}] = [\mathbf{M3}]_0 \qquad (2)$$

When t = 0, [**M3**] = $[\mathbf{M3}]_0$ and [**M3_NCO**] = 0, the following equations were obtained as a result of using this initial condition.

$$[\mathbf{M3}] = [\mathbf{M3}]_0 e^{-kt} \qquad (3)$$

$$[\mathbf{M3\_NCO}] = [\mathbf{M3}]_0(1-e^{-kt}) \qquad (4)$$

Considering with these equations, the kinetic analysis of the Curtius rearrangement of **M3** to **M3_NCO** was carried out. **M3** (5.4 mg, 0.010 mmol) was dissolved in PhCl-d_5 (0.50 mL) and heated at 100 °C, then the reaction rate was traced by NMR (**Figure S1**). Characteristic benzyl signals observed at around 5.5–5.7 ppm were integrated to calculate their concentration.

On the basis of the assumption of the pseudo first order reaction, a time vs the log of the difference of the concentration of **M3** was plotted (**Figure S2**). Then, the first order approximate line has appeared, indicating the validity of this hypothesis. From this line, the slope (–k) was calculated by least squares approximation to be -1.0×10^{-3} [s^{-1}], and the half-life period τ of **M3** was estimated from the following equation to be 11 min.

$$\tau = \frac{ln2}{k}$$

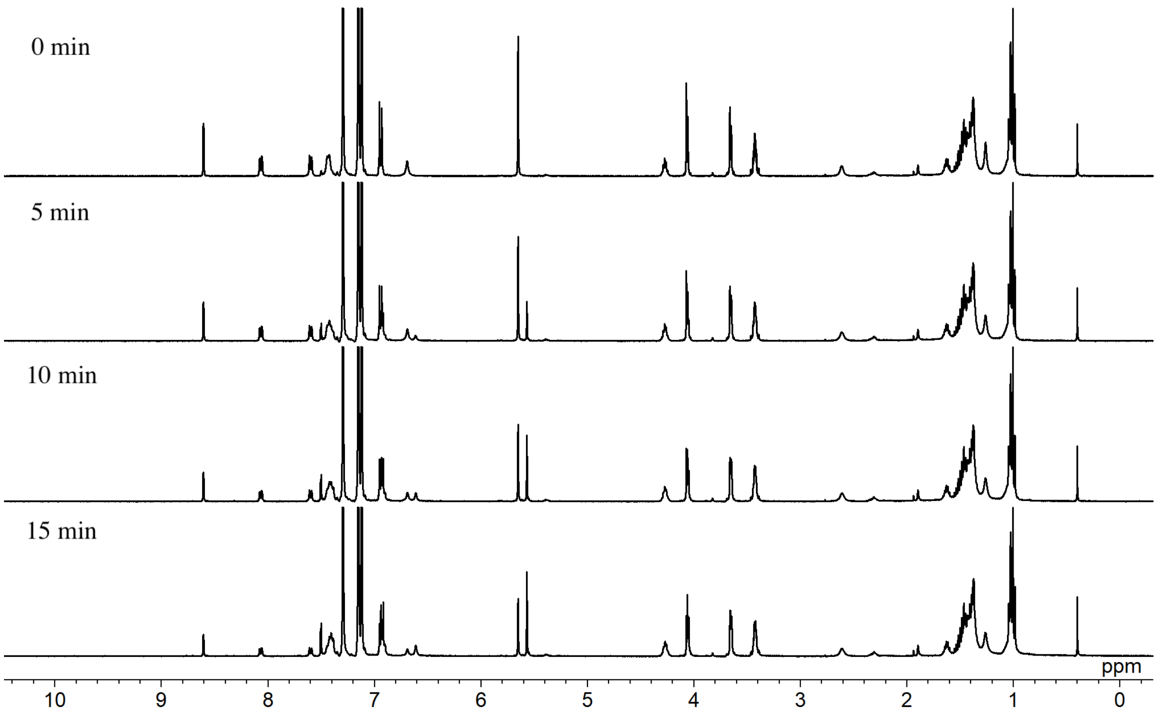


Figure S1. Spectral change of [1]H NMR spectra of **M3** heated at 100 °C for a given time (400 MHz, PhCl-d_5, 298 K)

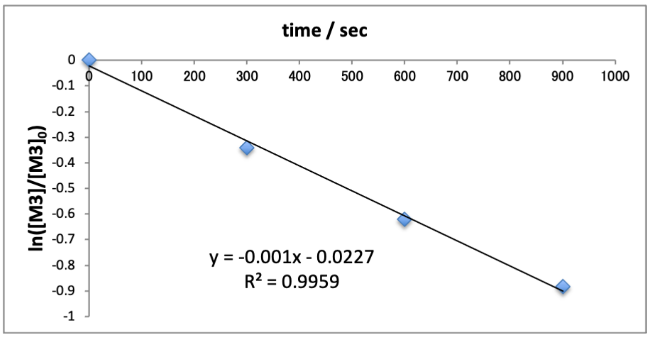
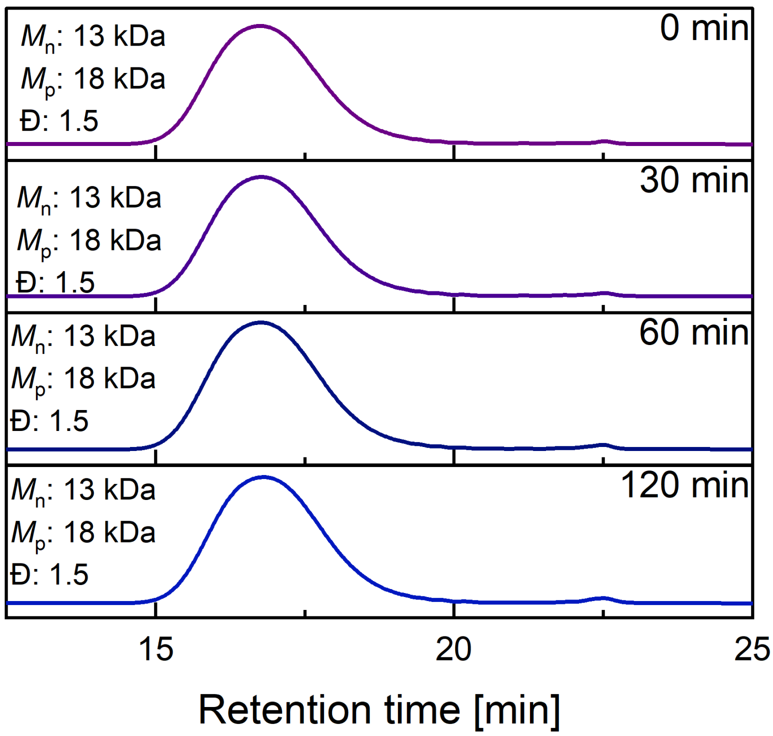


Figure S2. First-order kinetic plots of **M3** (PhCl-d_5, **Table S1**, 100 °C)

Table S1. Kinetic analysis for the Curtius rearrangement of **M3** (at 100 °C)

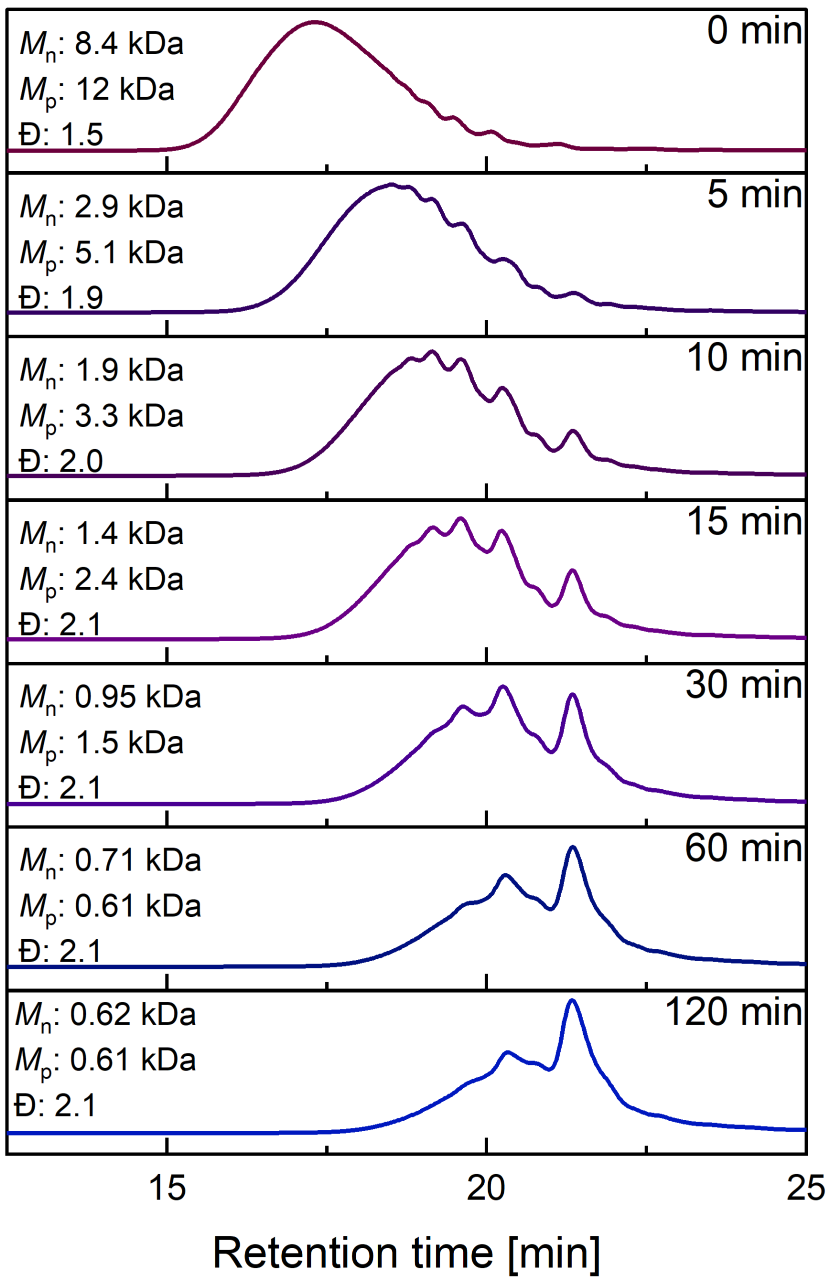
100 ° C		
time/ min	time/ sec	$\ln([M3]/[M3]_0)$
0	0	0.000
5	300	−0.344
10	600	−0.621
15	900	−0.884

4. Evaluation on photo-degradability of polymers

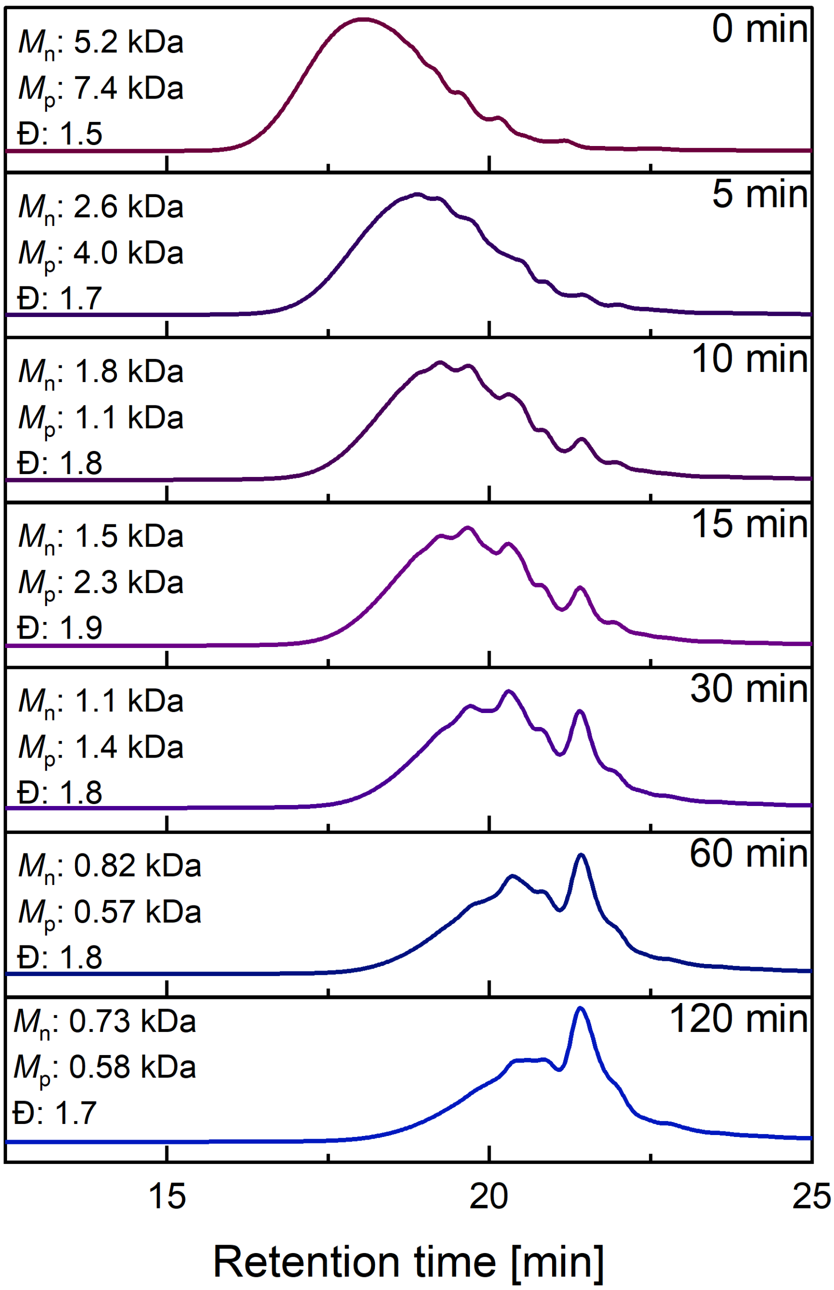


SEC profiles of **polyM2** according to the UV irradiation time (THF).

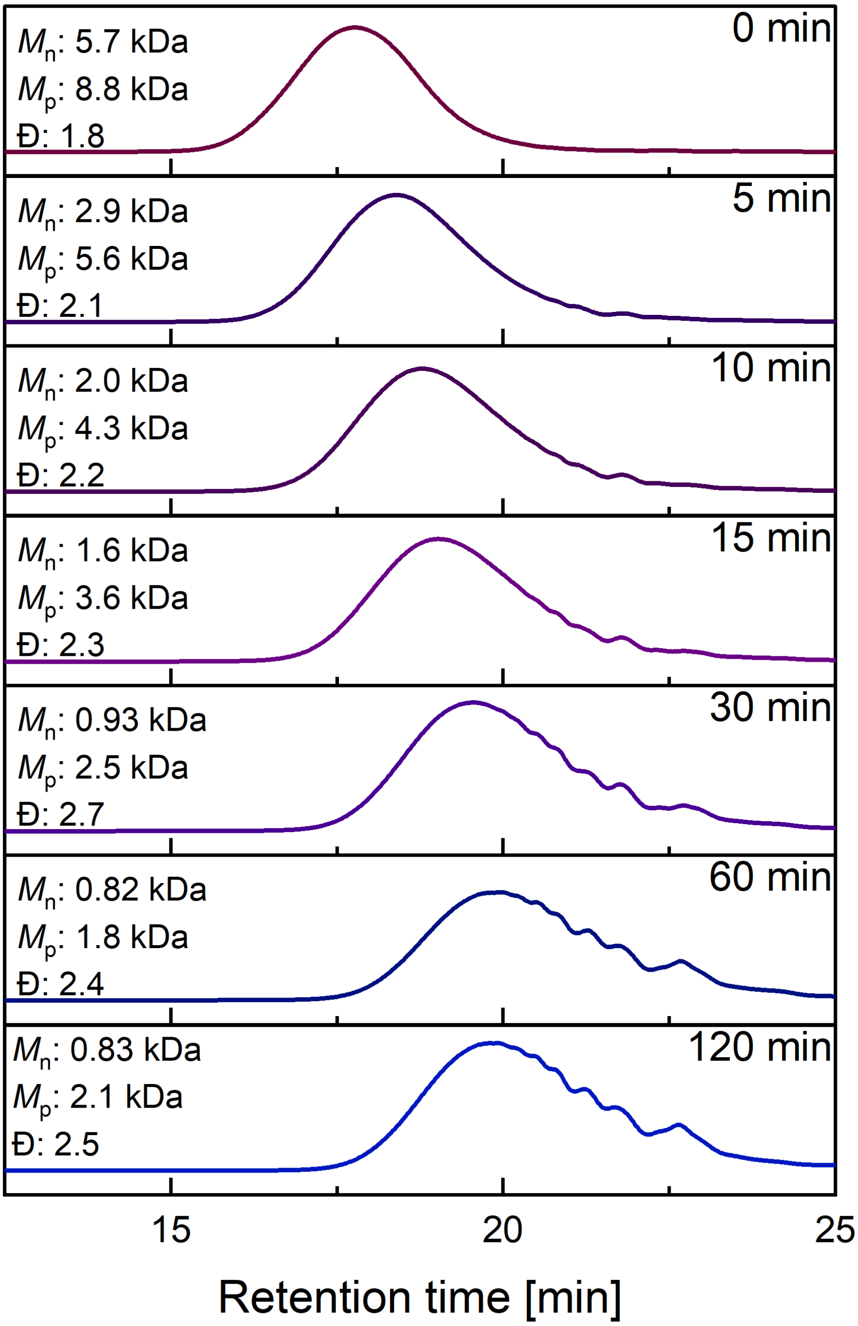
As no spectral change observed during the UV irradiation, **polyM2** did not have a photo-degradability under this condition, meaning the photo-degradation on **M1**/**M2** copolymers was induced by **M1** unit as same as the previous report.[1a]



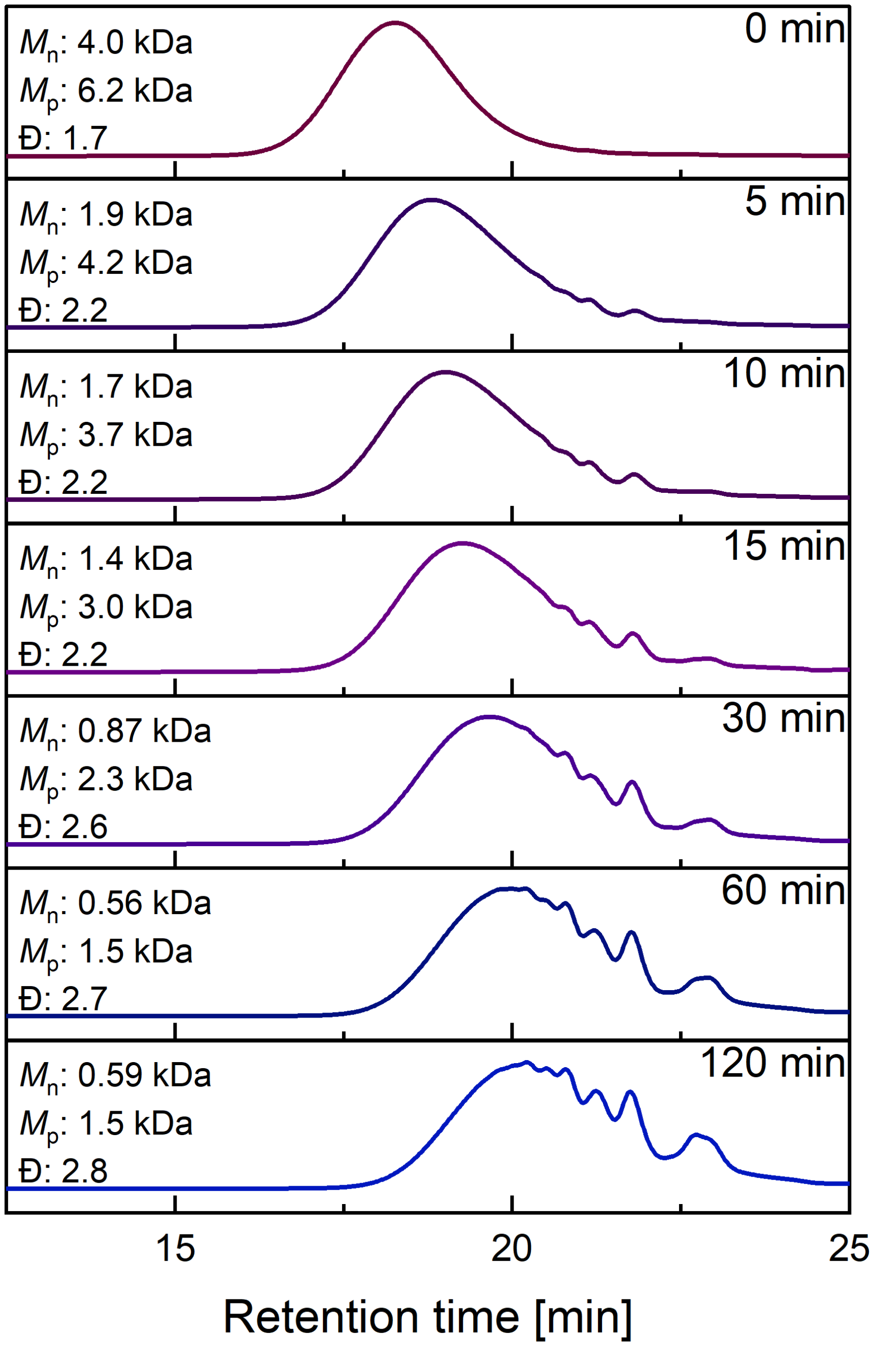
SEC monitored UV-degradation of **polyM3a** (THF).



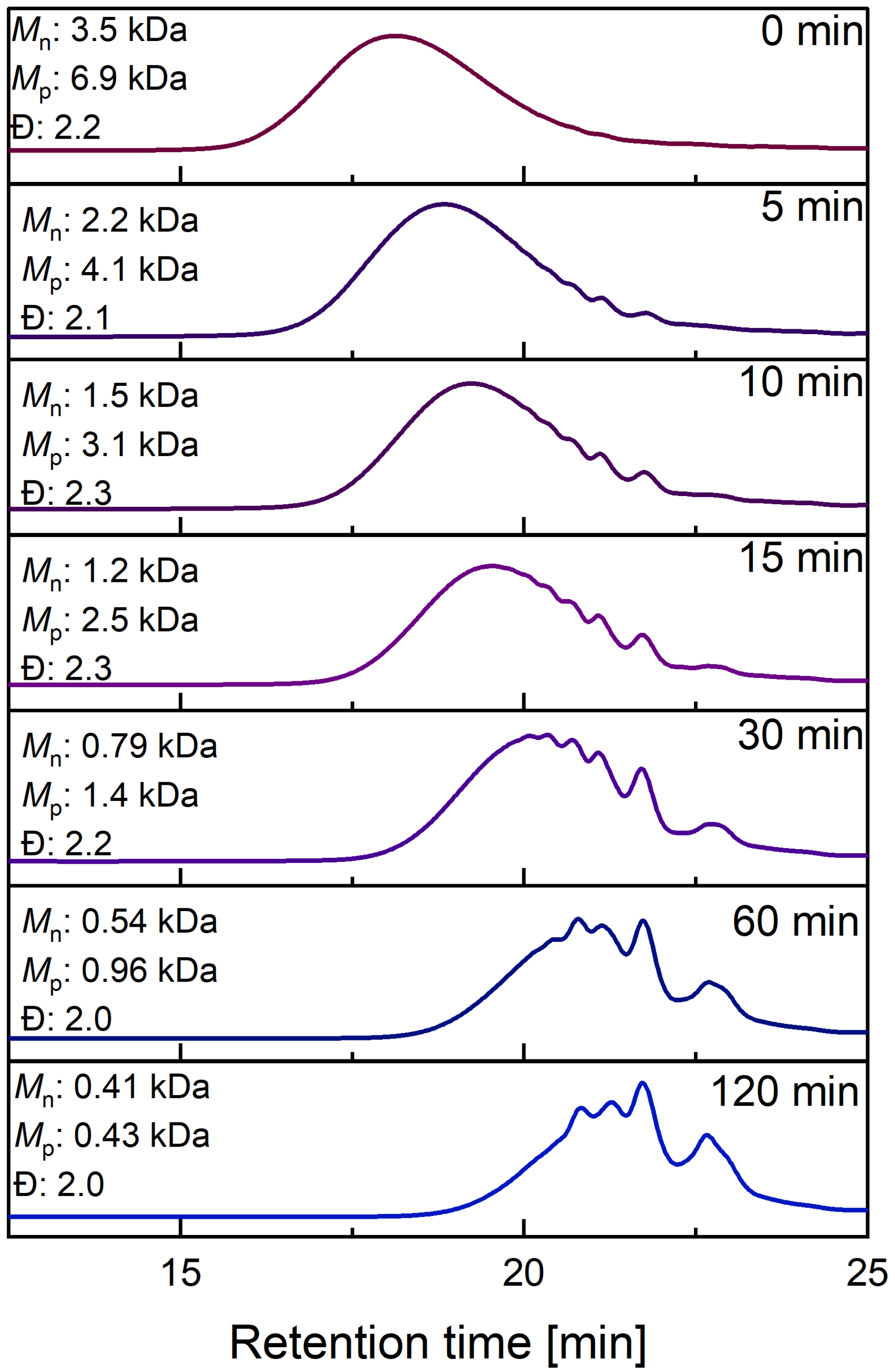
SEC monitored UV-degradation of **polyM3c** (THF).



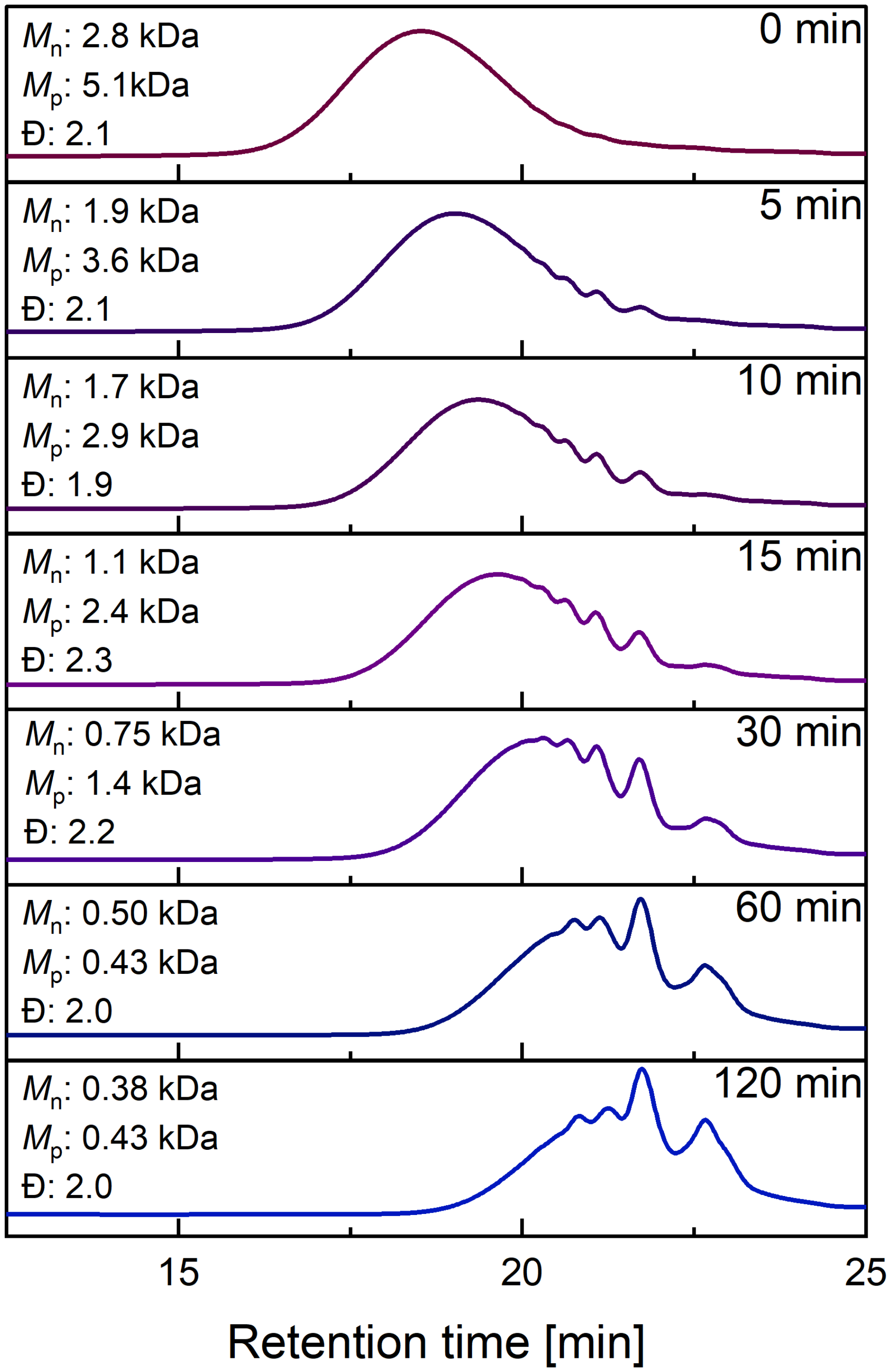
SEC monitored UV-degradation of **poly(M1-*stat*-M2)d** (THF).



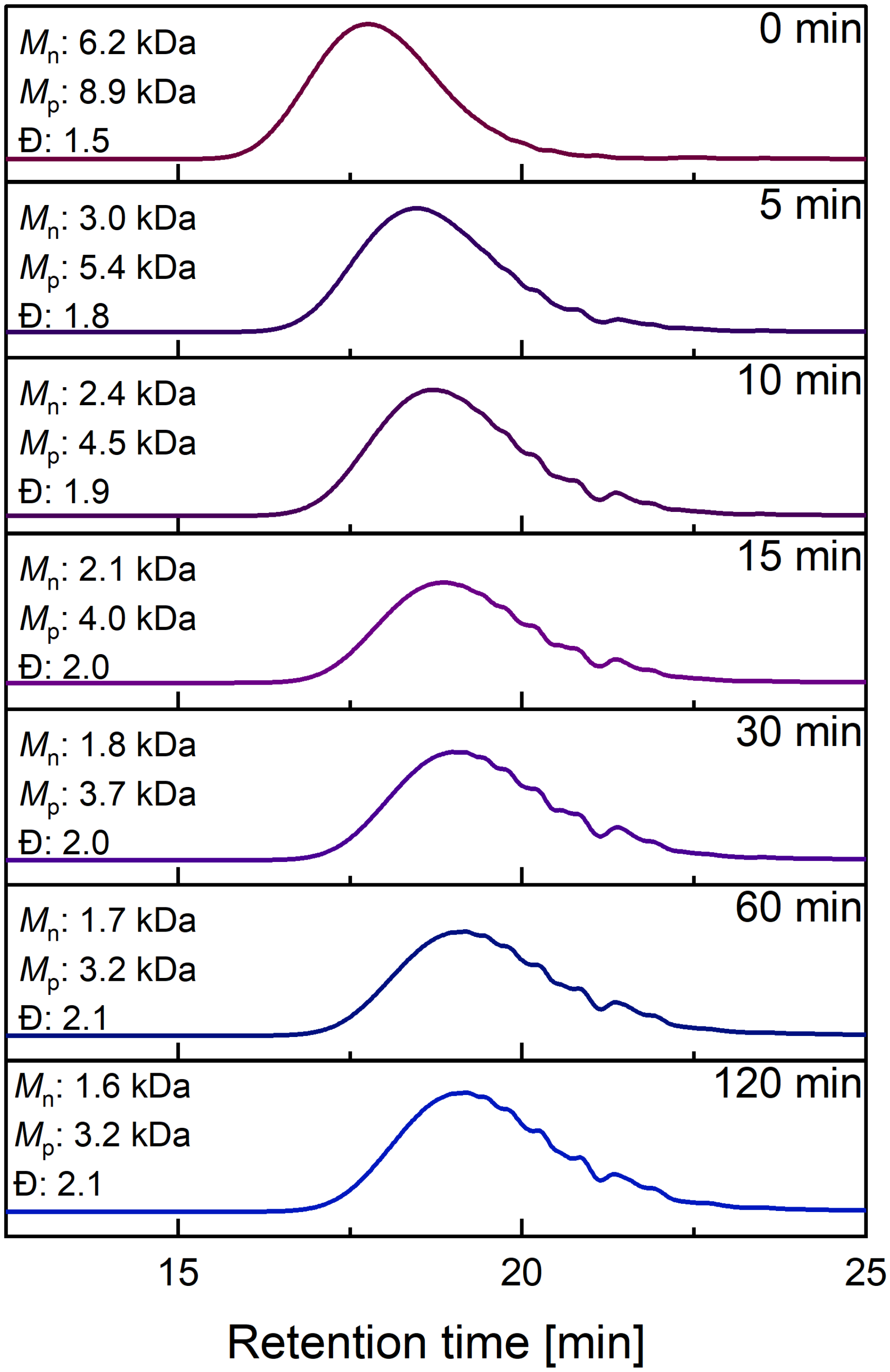
SEC monitored UV-degradation of **poly(M1-*stat*-M2)a** (THF).



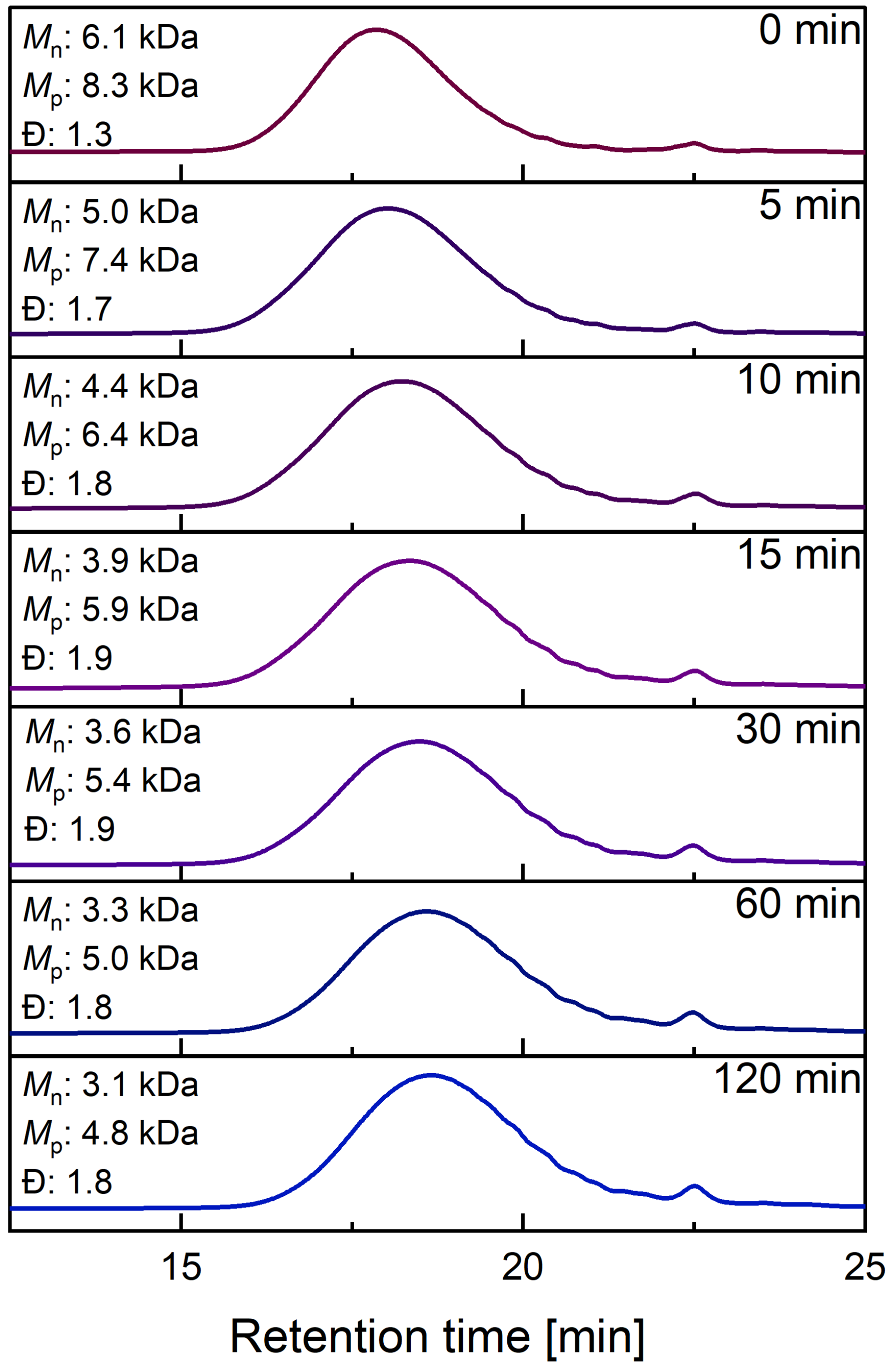
SEC monitored UV-degradation of **poly(M1-*stat*-M3)** (THF).



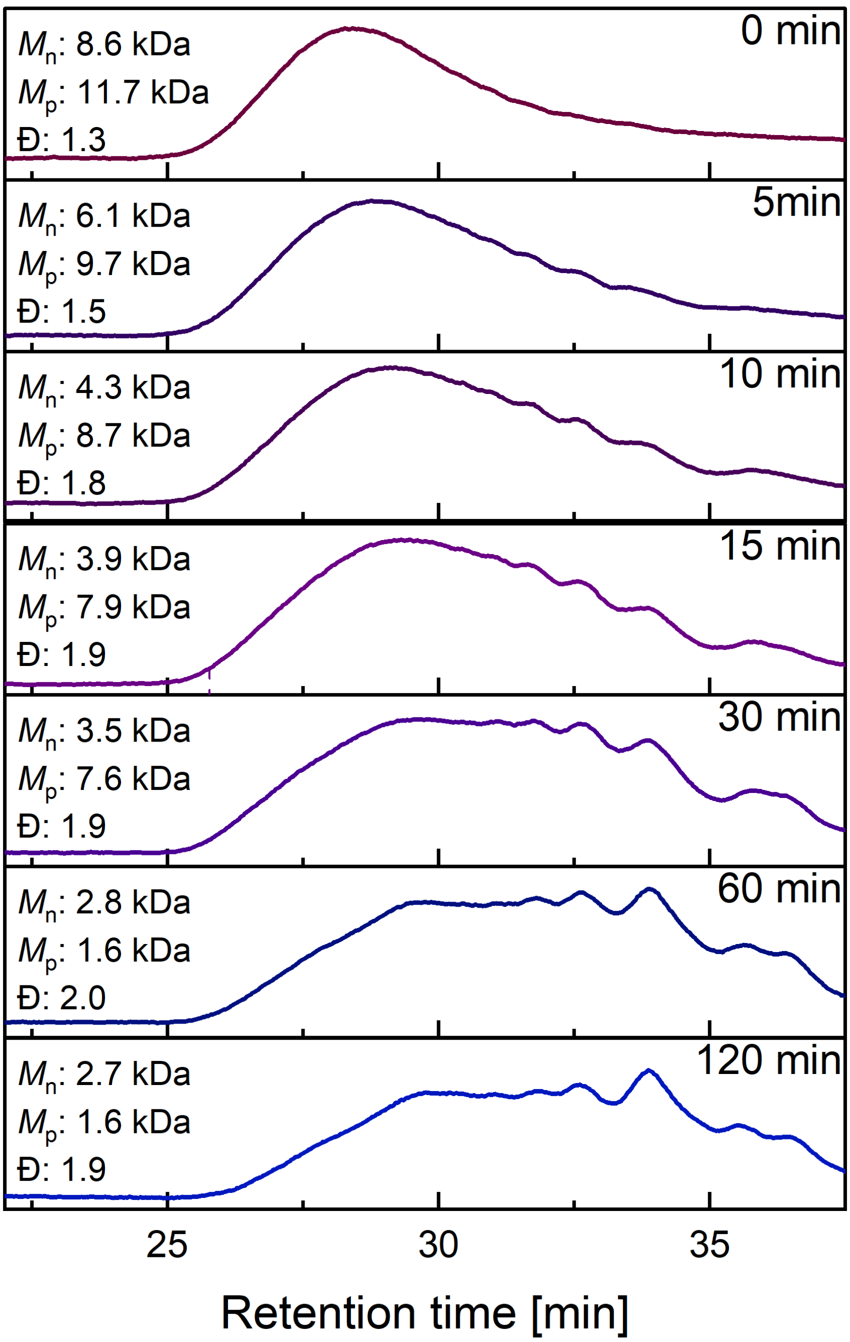
SEC monitored UV-degradation of **poly(M1-*stat*-M2)b** (THF).



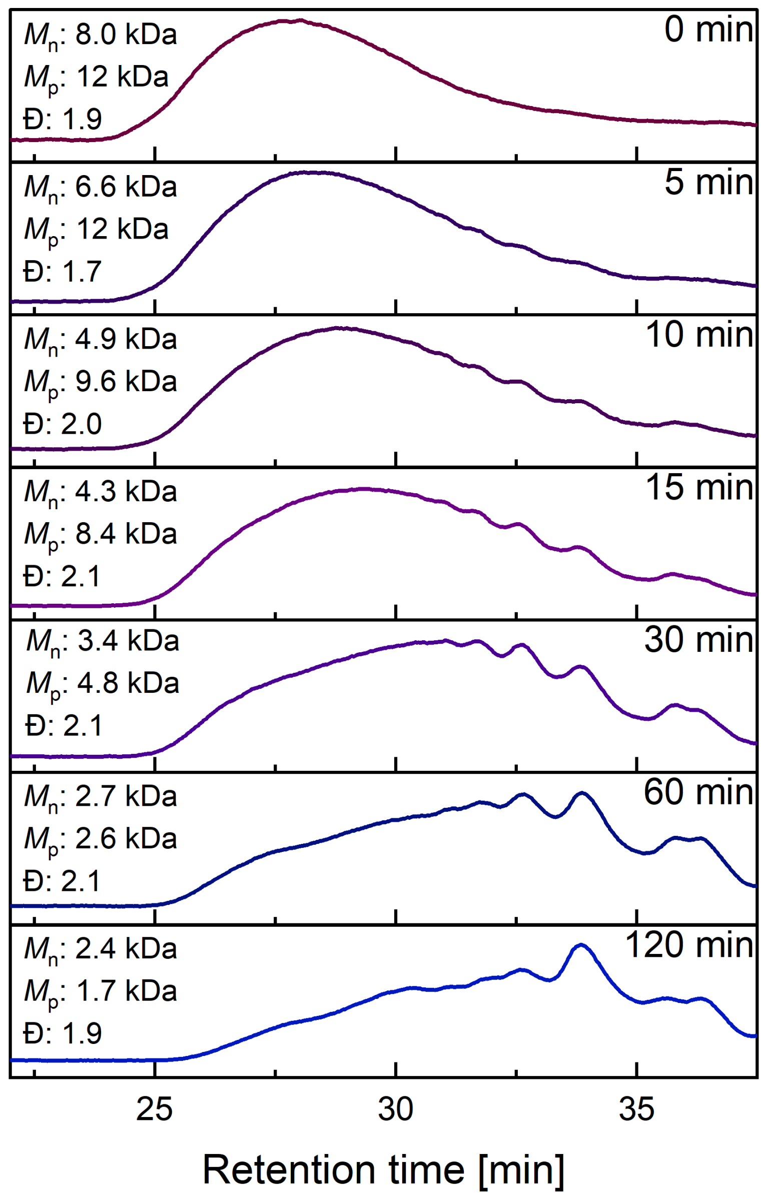
SEC monitored UV-degradation of **poly(M2-*stat*-M3)** (THF).



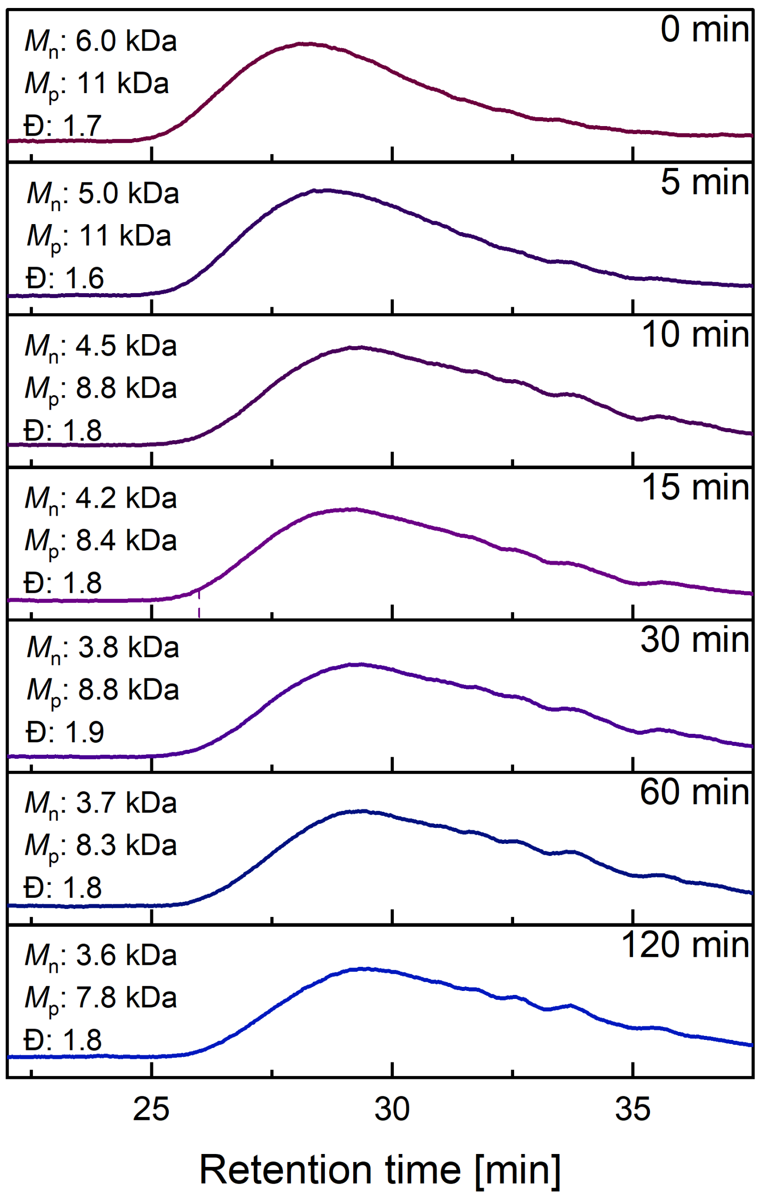
SEC monitored UV-degradation of **poly(M1-*stat*-M2)c** (THF).



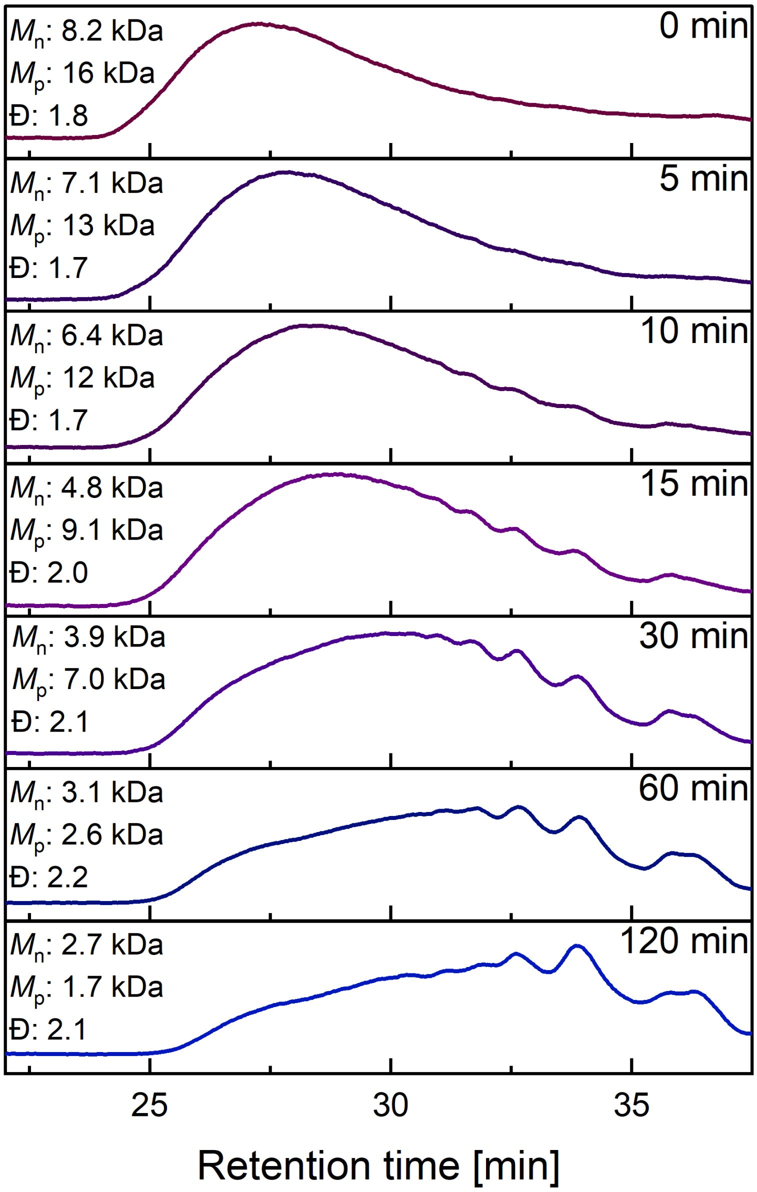
SEC monitored UV-degradation of **poly(M1-*stat*-M2)a** (DMAc).



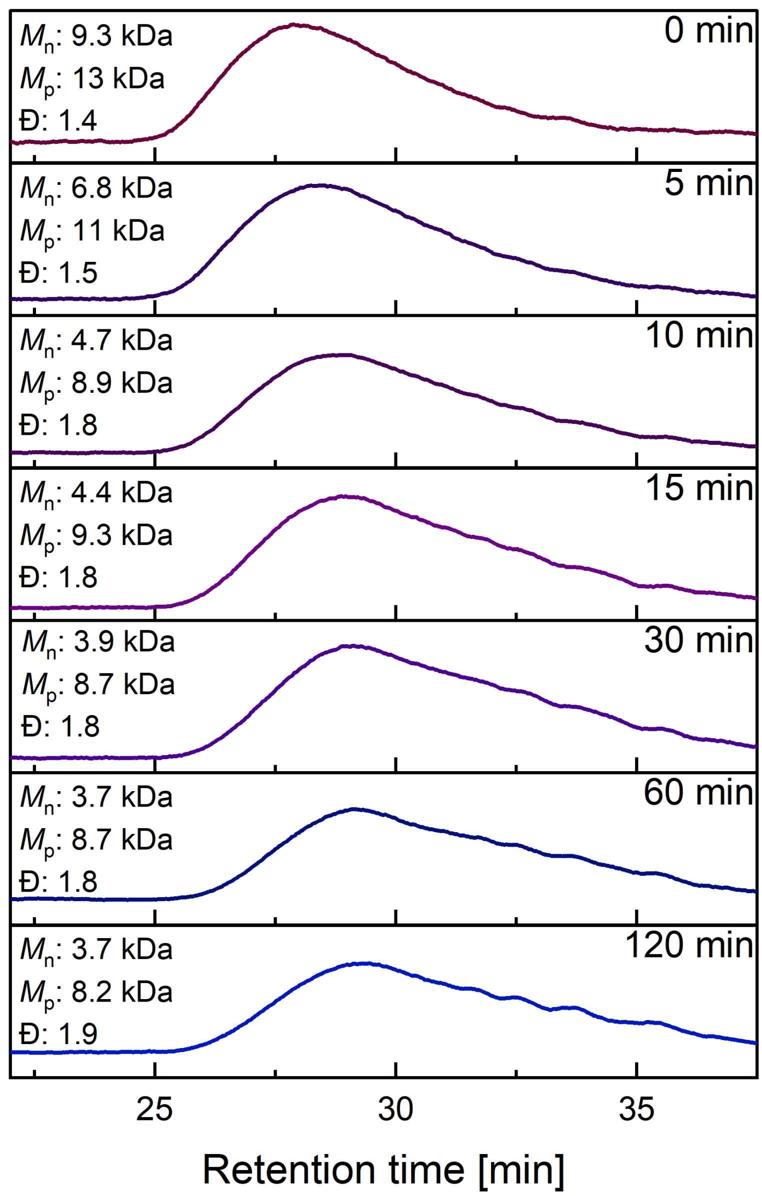
SEC monitored UV-degradation of **poly(M1-*stat*-M2)b** (DMAc).



SEC monitored UV-degradation of **poly(M1-*stat*-M2)c** (DMAc).

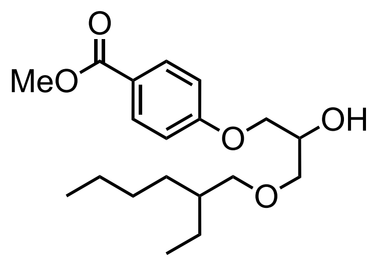


SEC monitored UV-degradation of **poly(M1-*stat*-M3)** (DMAc).

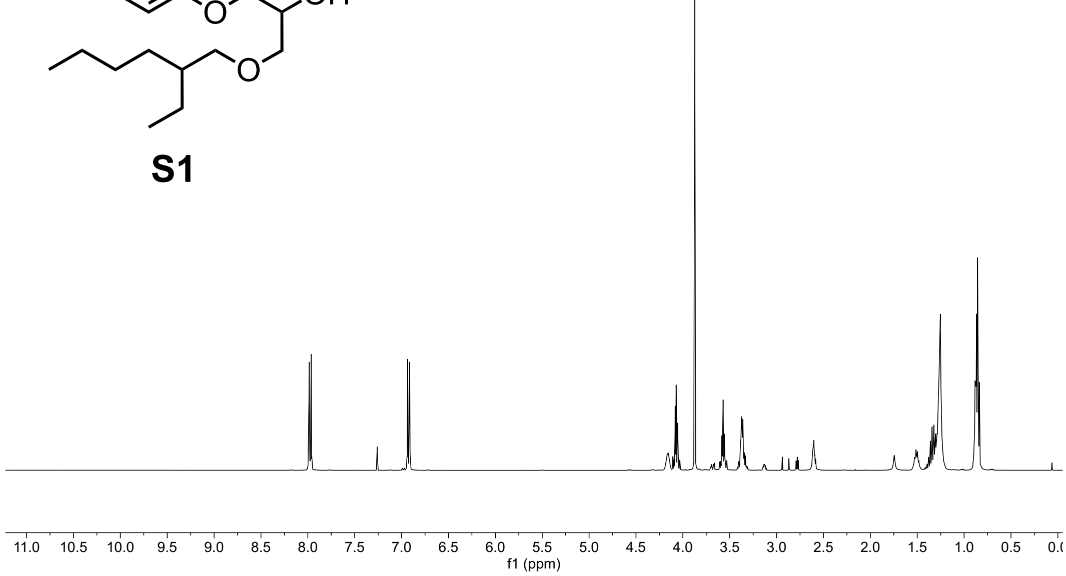


SEC monitored UV-degradation of **poly(M2-*stat*-M3)** (DMAc).

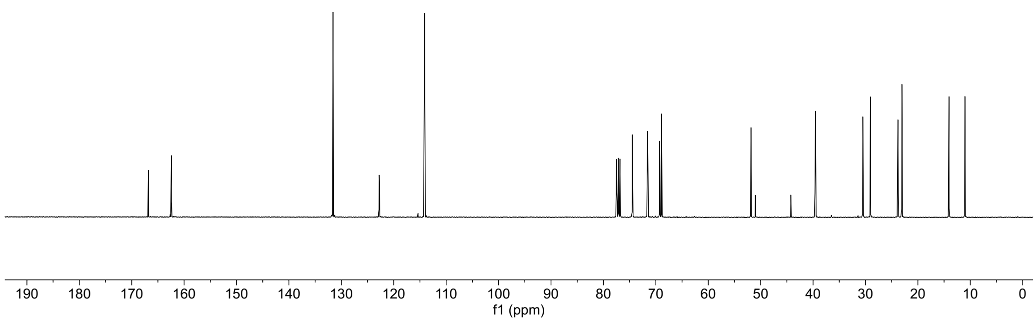
5. Spectra of synthesized compounds



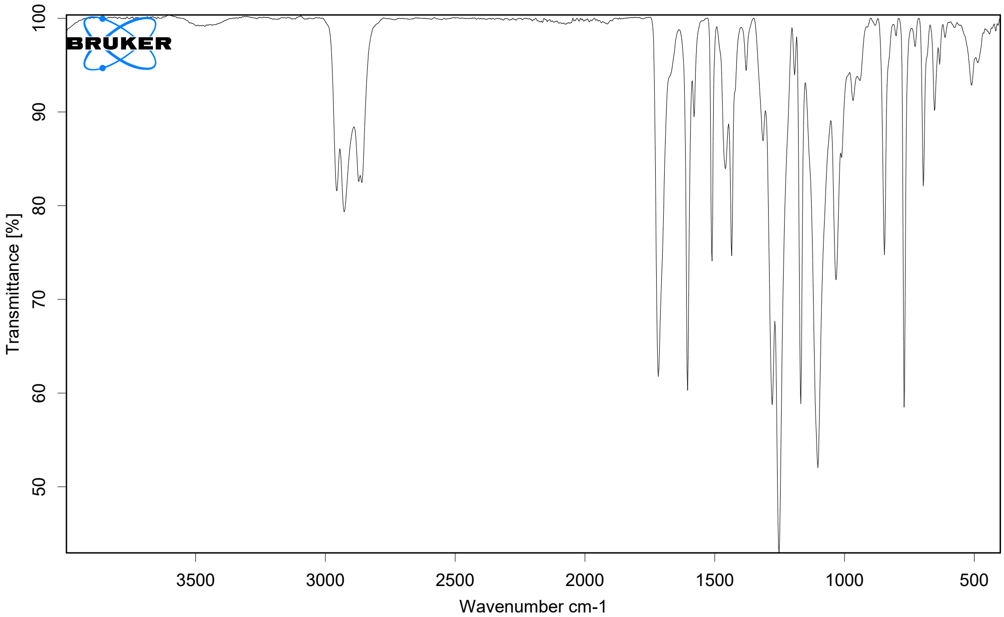
S1



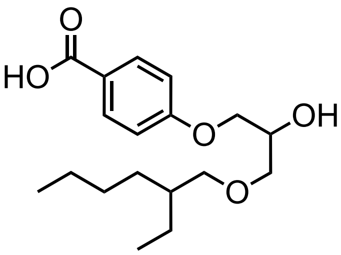
[1]H-NMR (400 MHz, Chloroform-d, 298K) spectrum of **S1**.



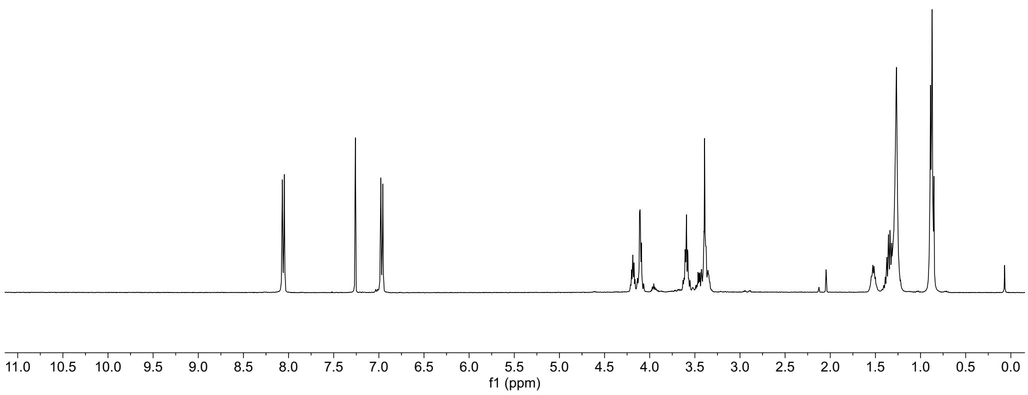
[13]C-NMR (101 MHz, Chloroform-d, 298k) spectrum of **S1**.



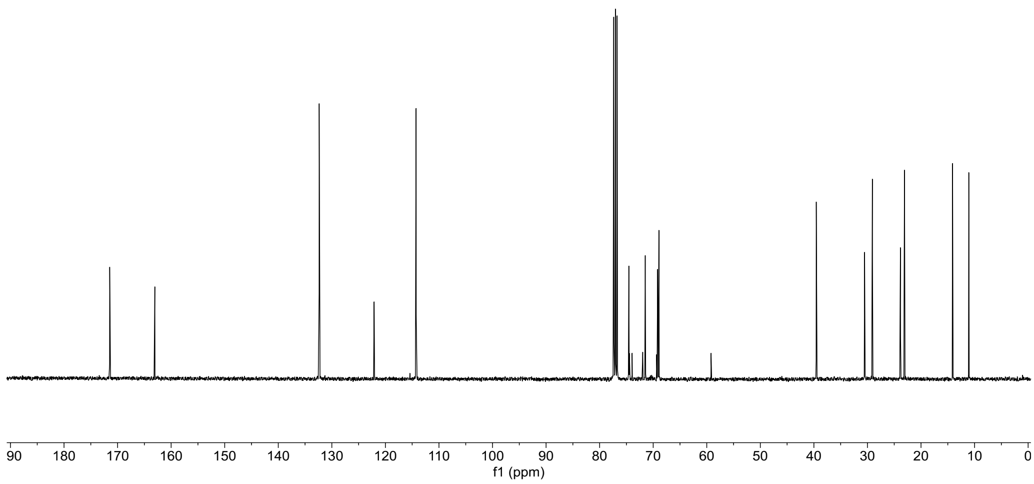
IR (ATR) spectrum of **S1**.



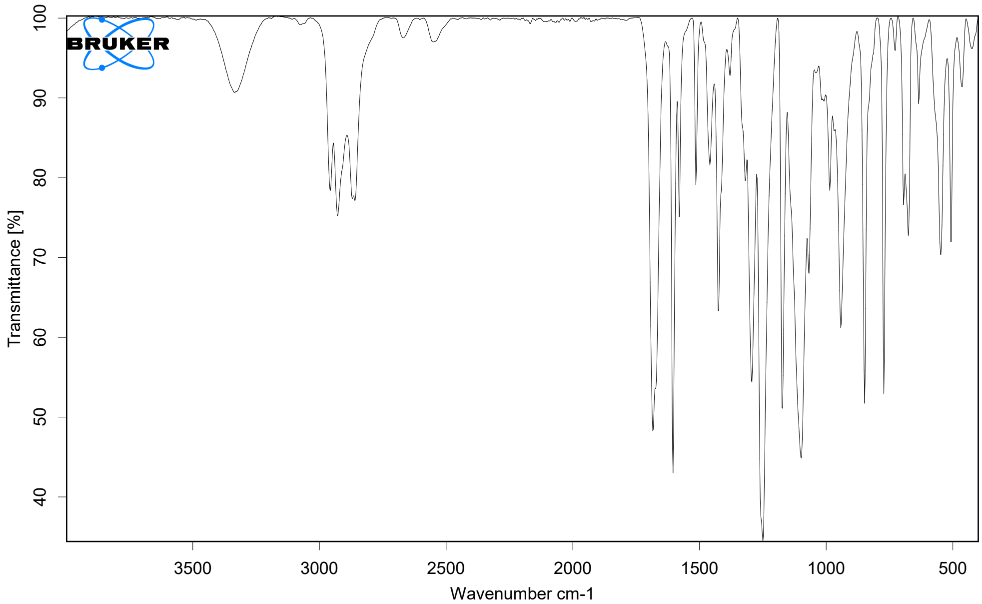
S2



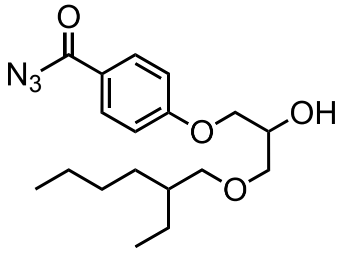
[1]H-NMR (400 MHz, Chloroform-d, 298k) spectrum of **S2.**



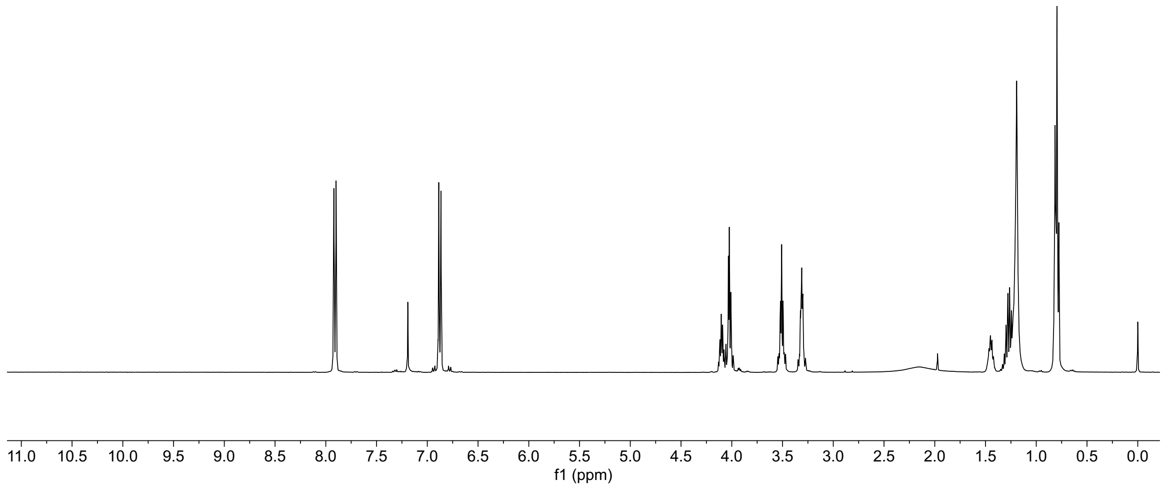
[13]C-NMR (101 MHz, Chloroform-d, 298k) spectrum of **S2.**



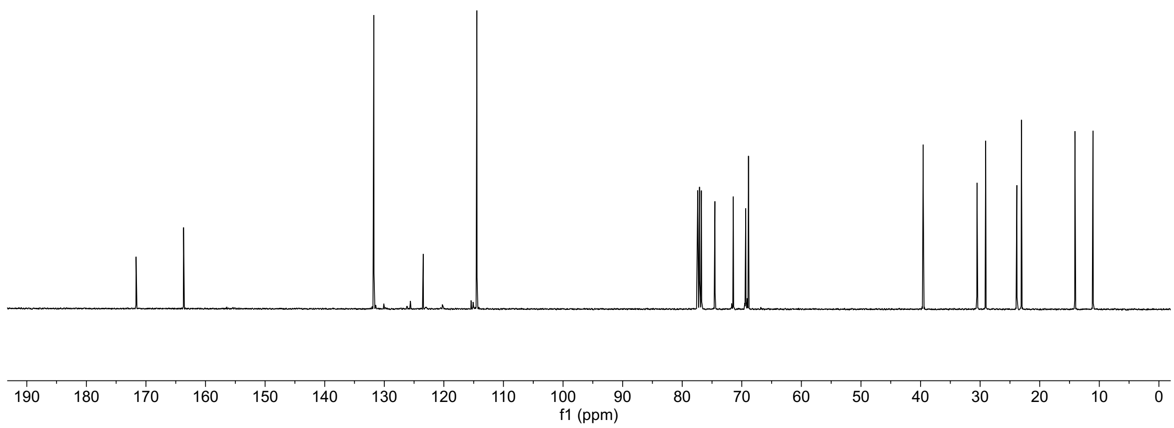
IR (ATR) spectrum of **S2.**



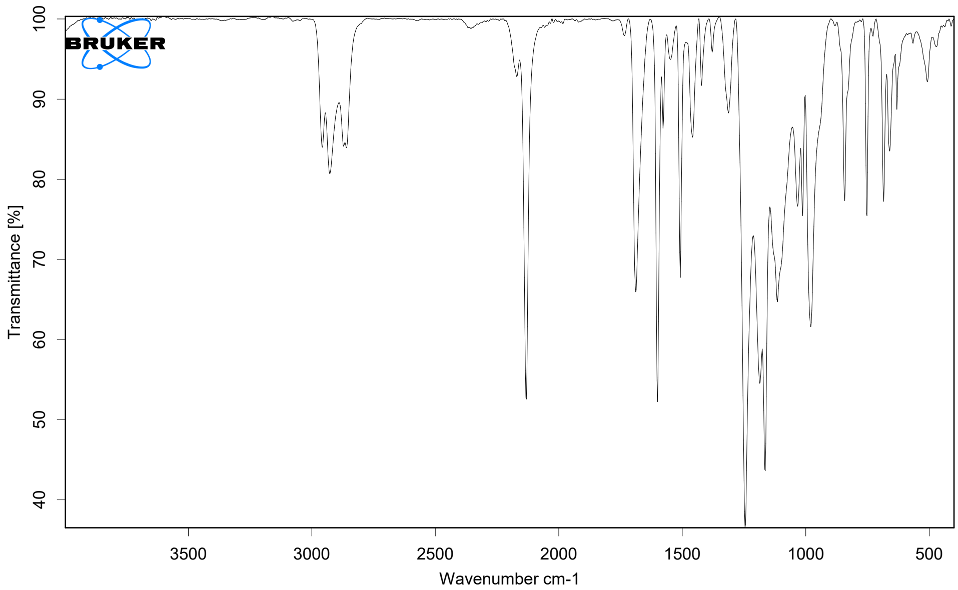
M2



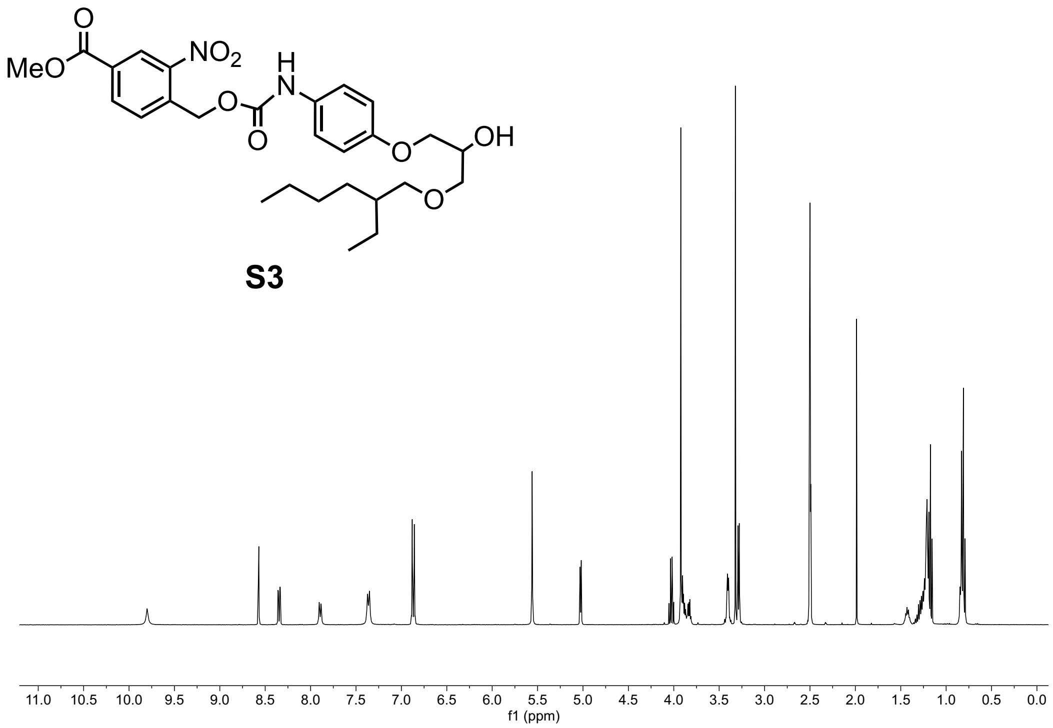
^{1}H-NMR (400 MHz, Chloroform-d, 298K) spectrum of **M2.**



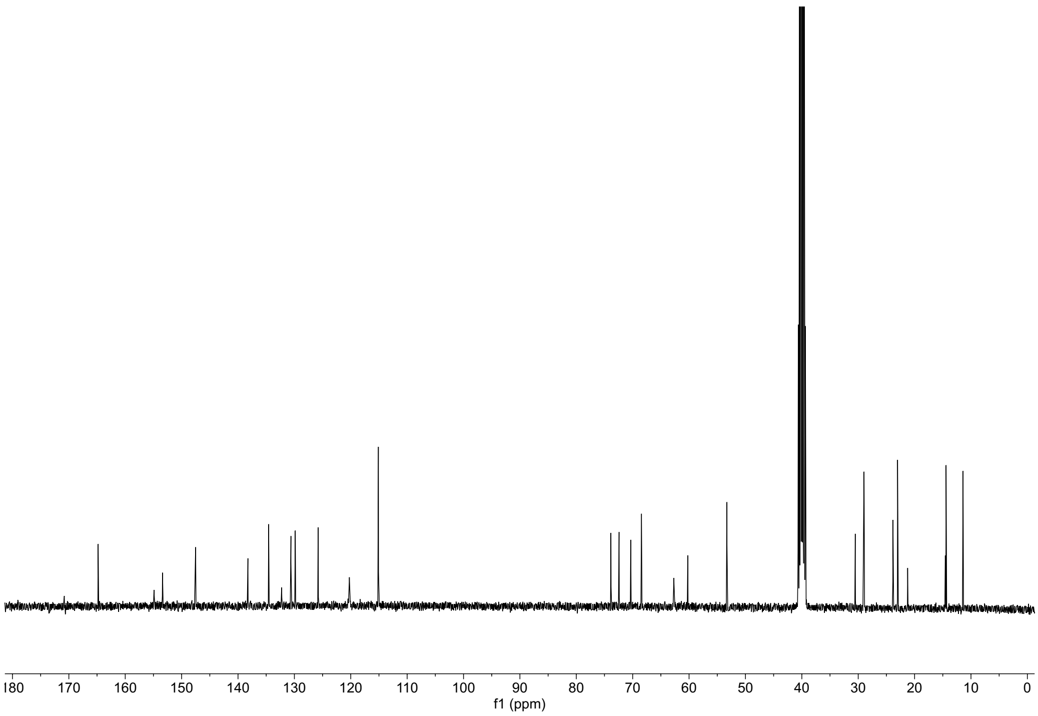
^{13}C-NMR (101 MHz, Chloroform-d, 298K) spectrum of **M2**.



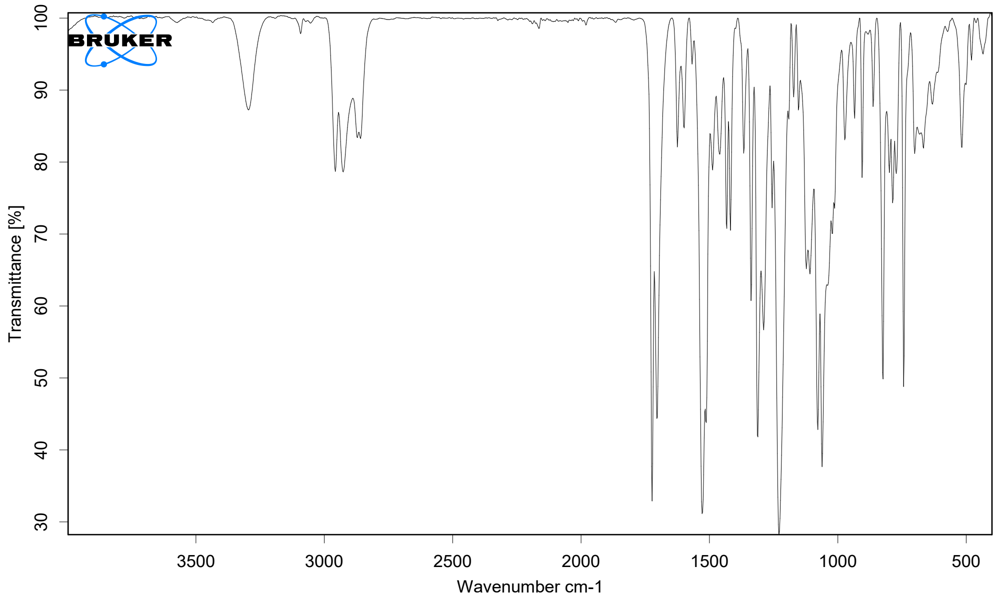
IR (ATR) spectrum of **M2.**



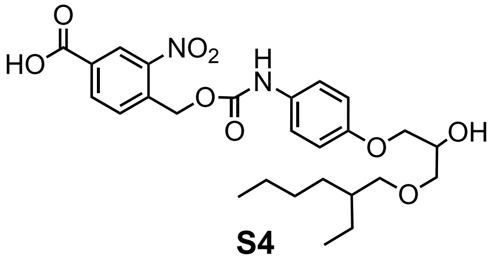
[1]H-NMR (400 MHz, DMSO-d, 298K) spectrum of **S3**.

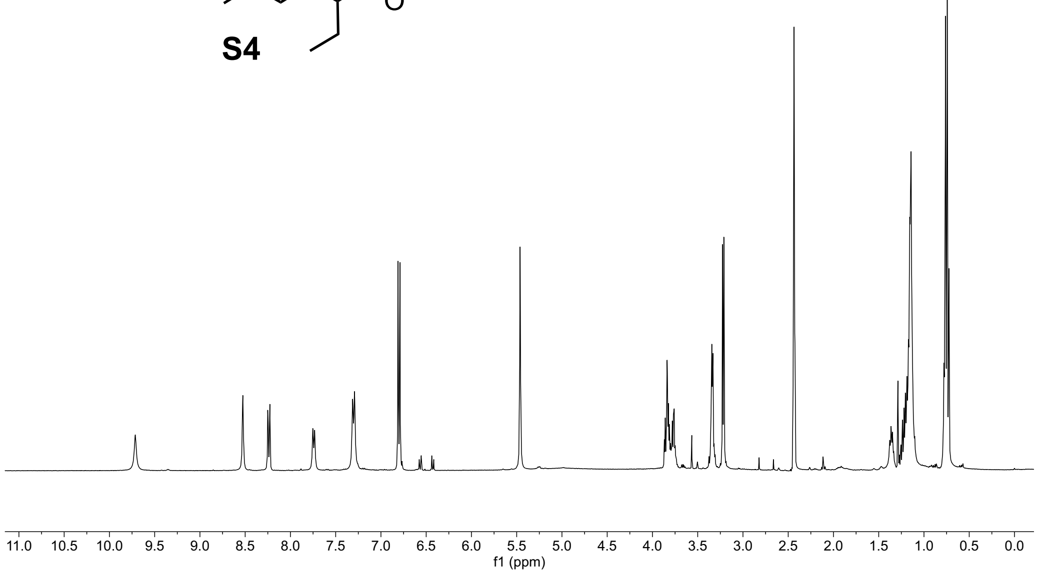


^{13}C-NMR (101 MHz, DMSO-d, 298K) spectrum of **S3**.

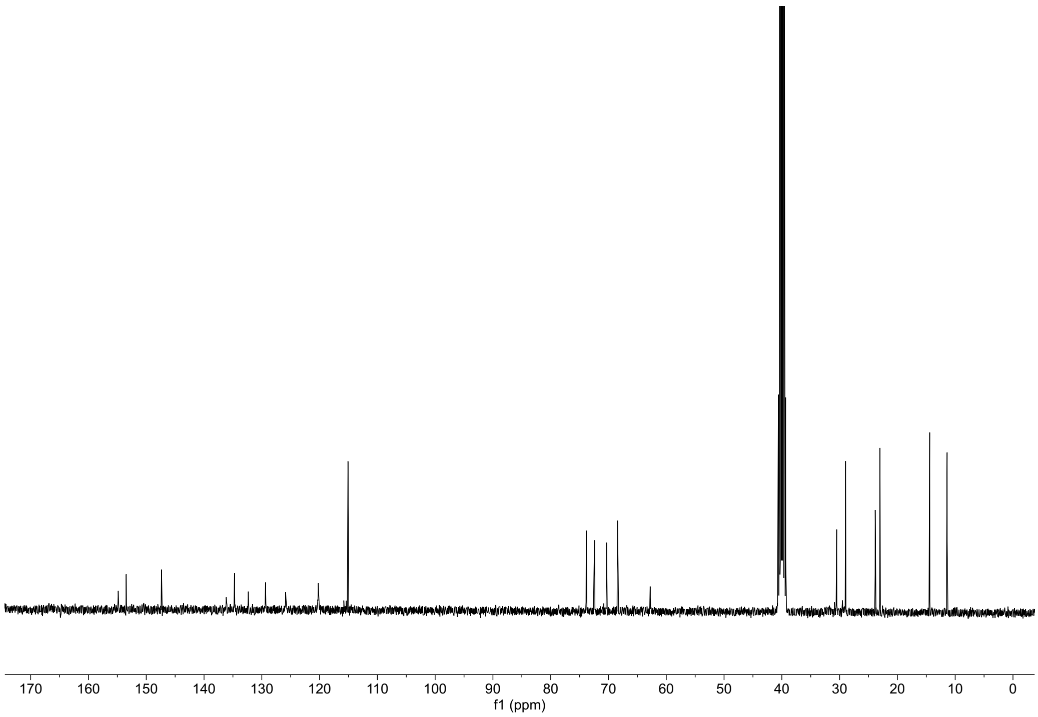


IR (ATR) spectrum of **S3**

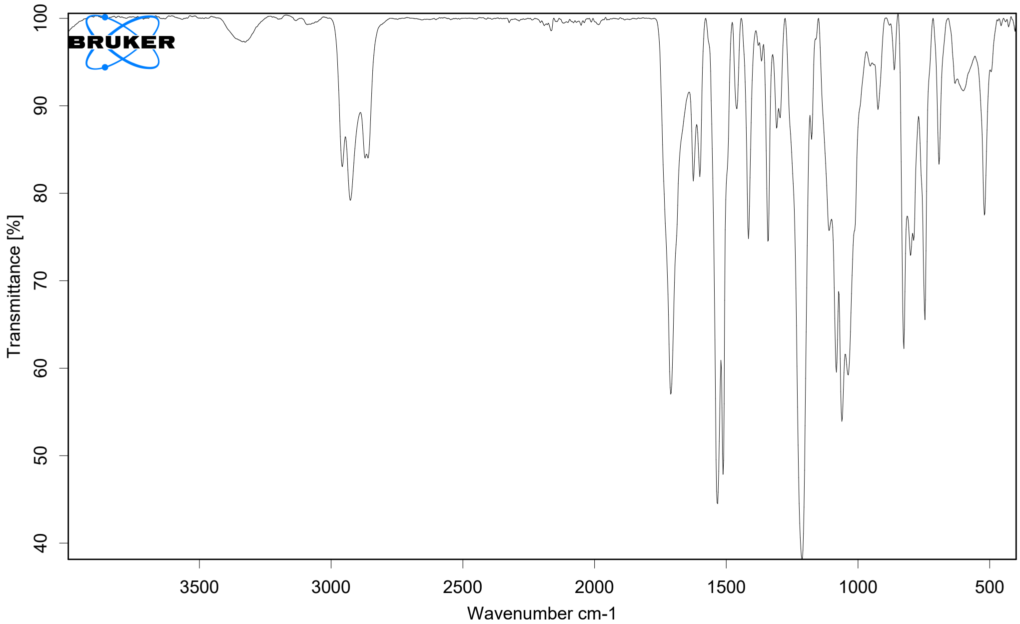




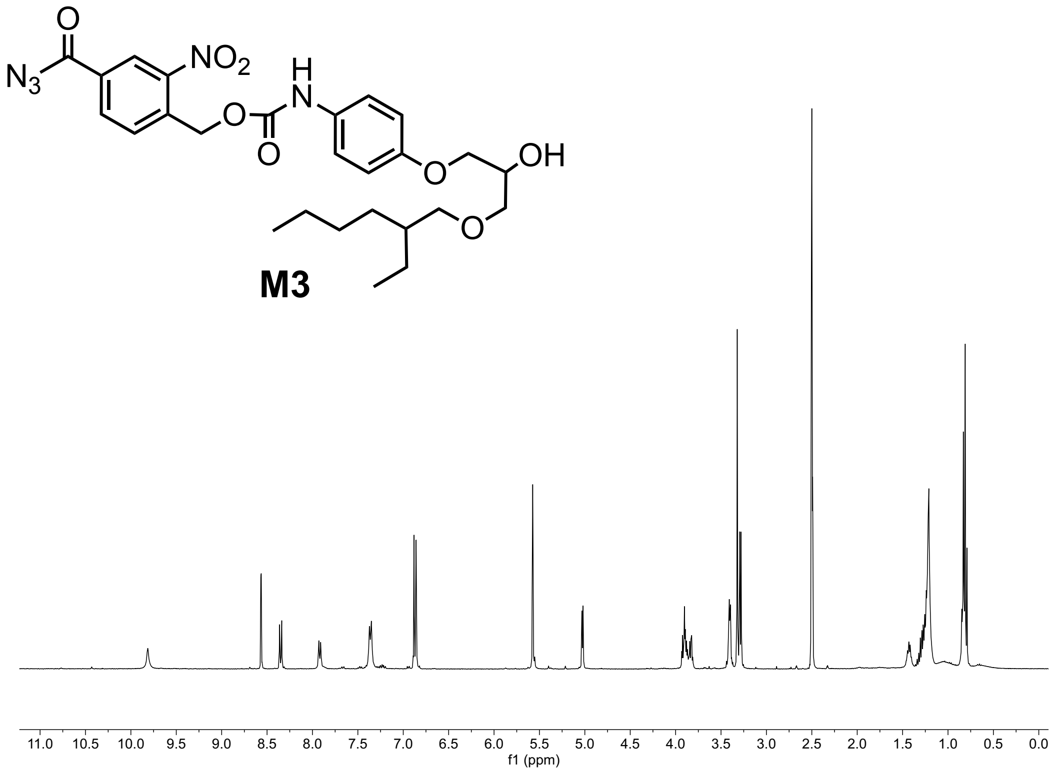
^{1}H -NMR (400 MHz, DMSO-d, 298K) spectrum of **S4**.



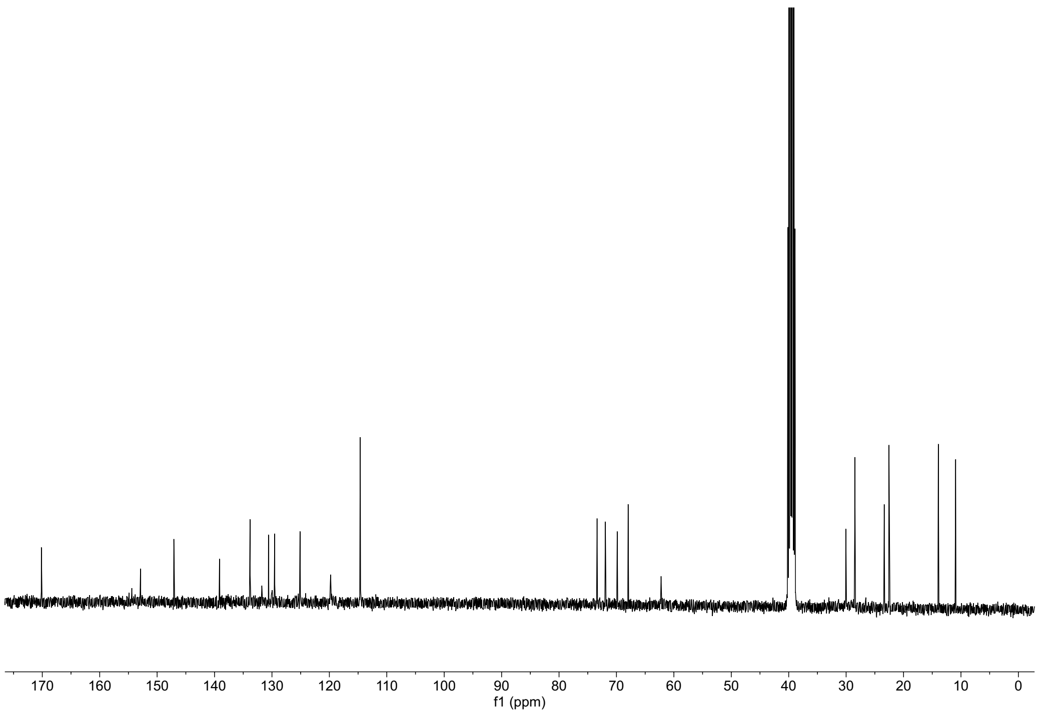
^{13}C -NMR (101 MHz, DMSO-d, 298K) spectrum of **S4**.



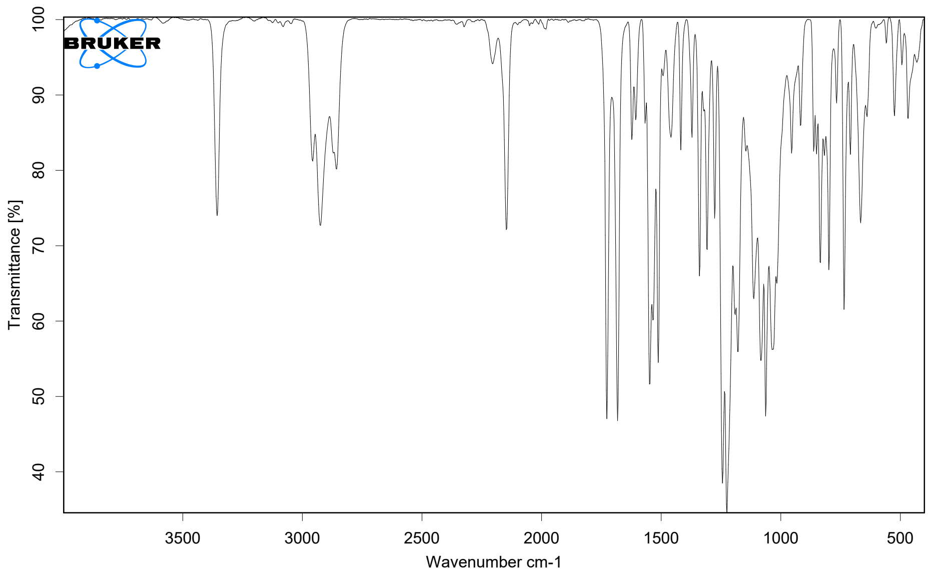
IR (ATR) spectrum of **S4.**



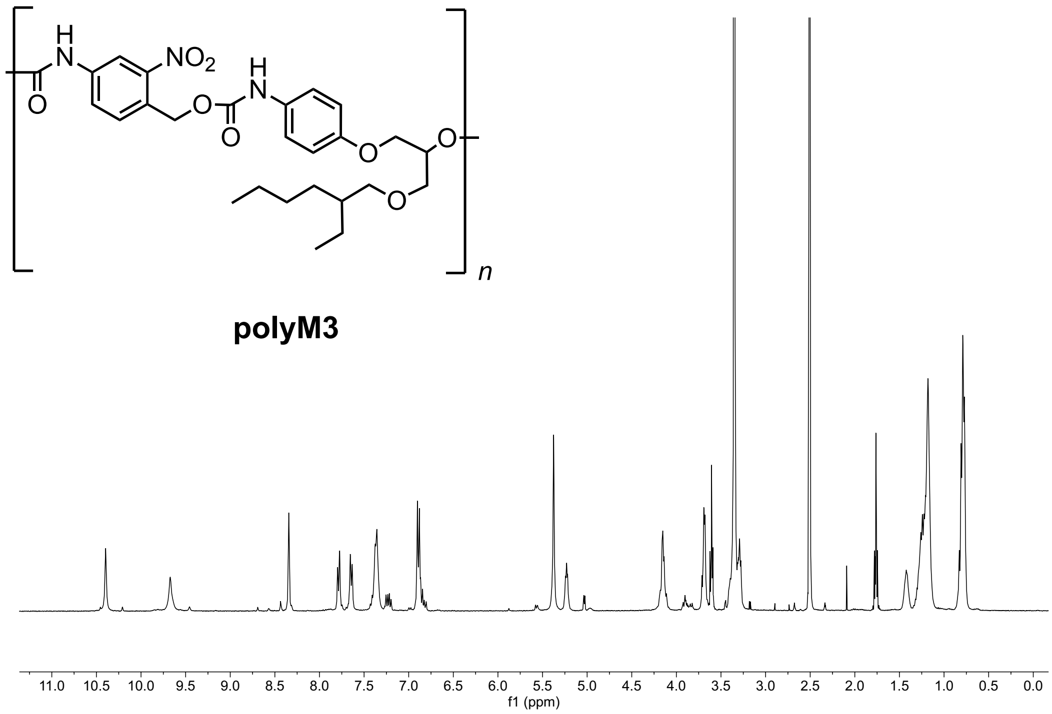
[1]H -NMR (400 MHz, DMSO-d, 298K) spectrum of **M3**.



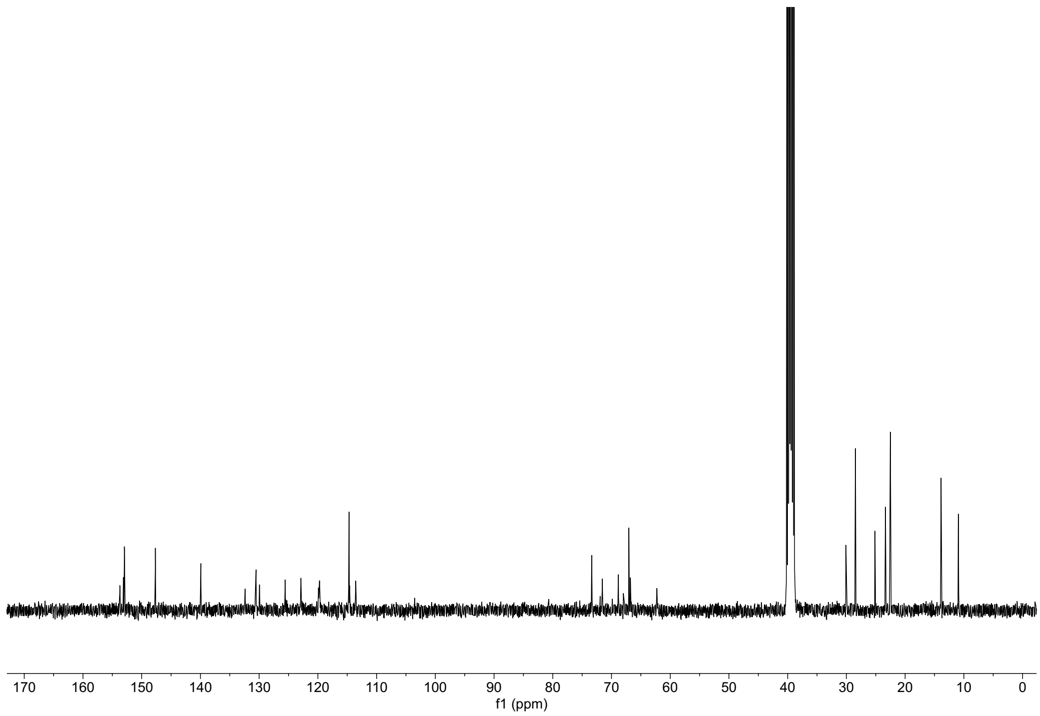
^{13}C -NMR (101 MHz, DMSO-d, 298K) spectrum of **M3**.



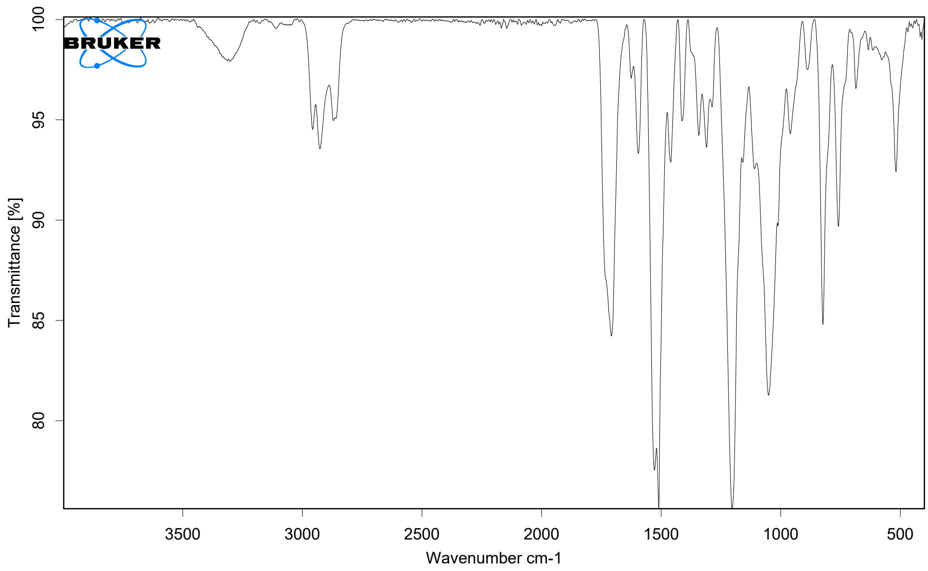
IR (ATR) spectrum of **M3**.



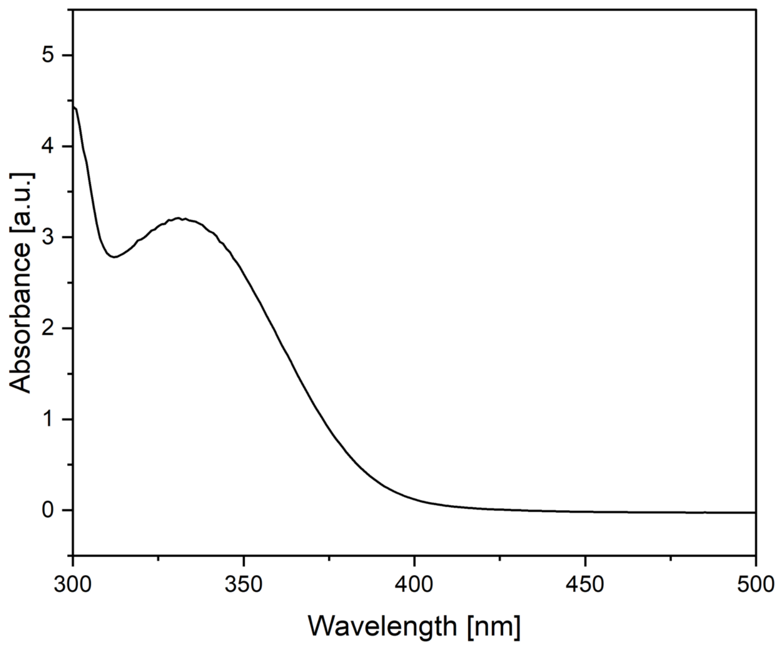
^{1}H -NMR (400 MHz, DMSO-d, 298K) spectrum of **polyM3a**.



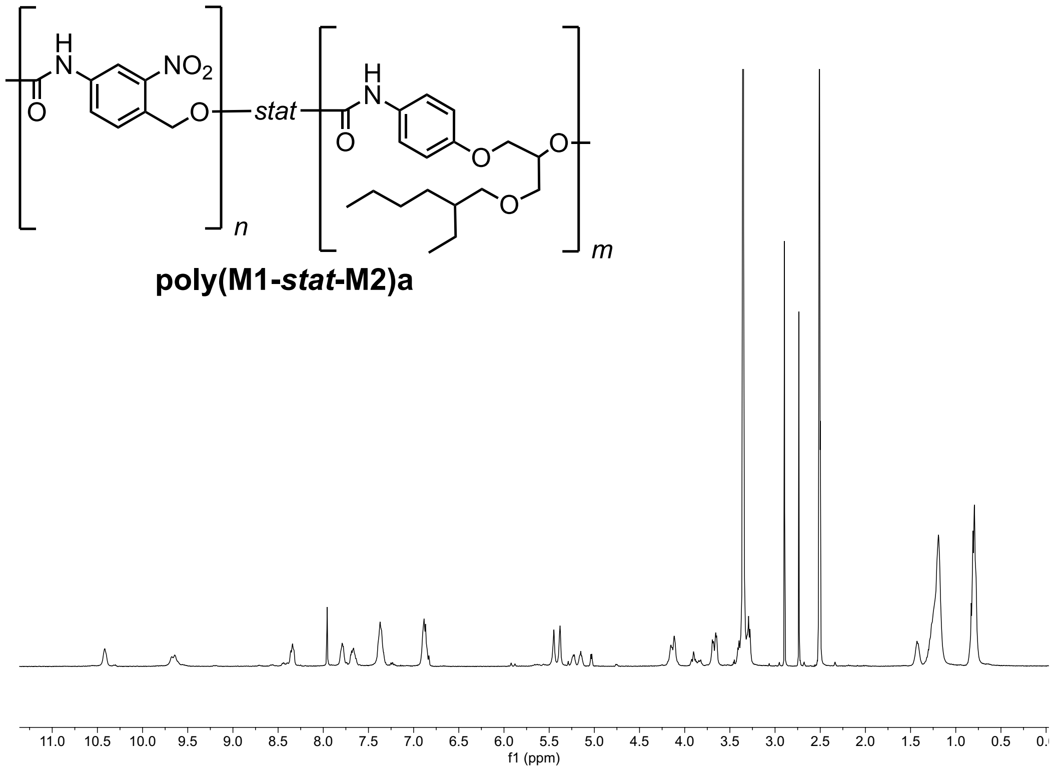
^{13}C -NMR (101 MHz, DMSO-d, 298K) spectrum of **polyM3a**.



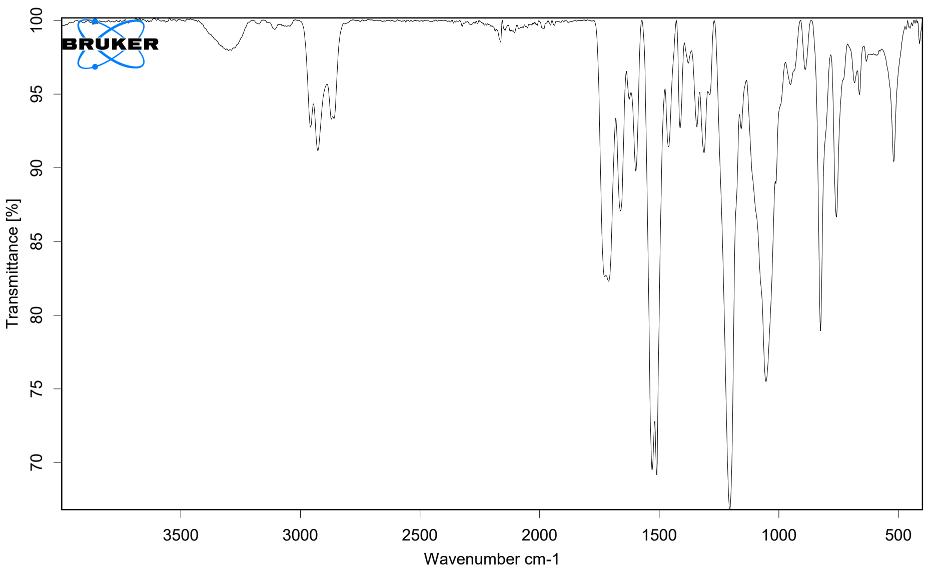
IR (ATR) spectrum of **polyM3a.**



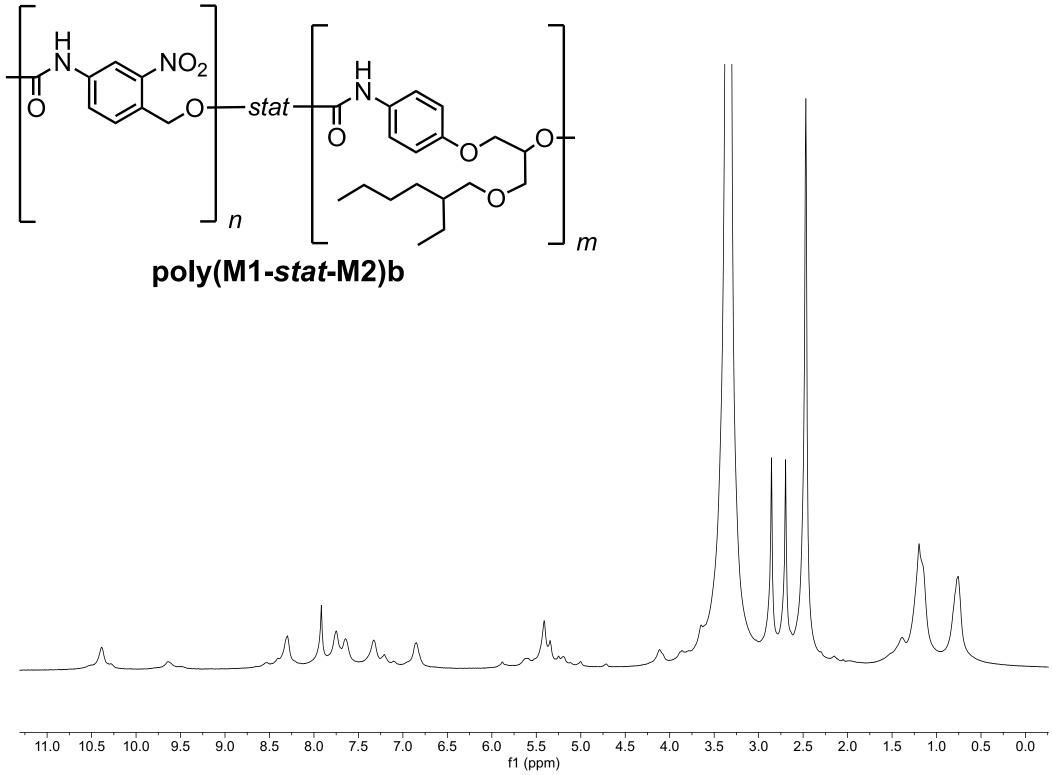
UV-Vis spectrum of **polyM3a** (THF, 1.0 mM).



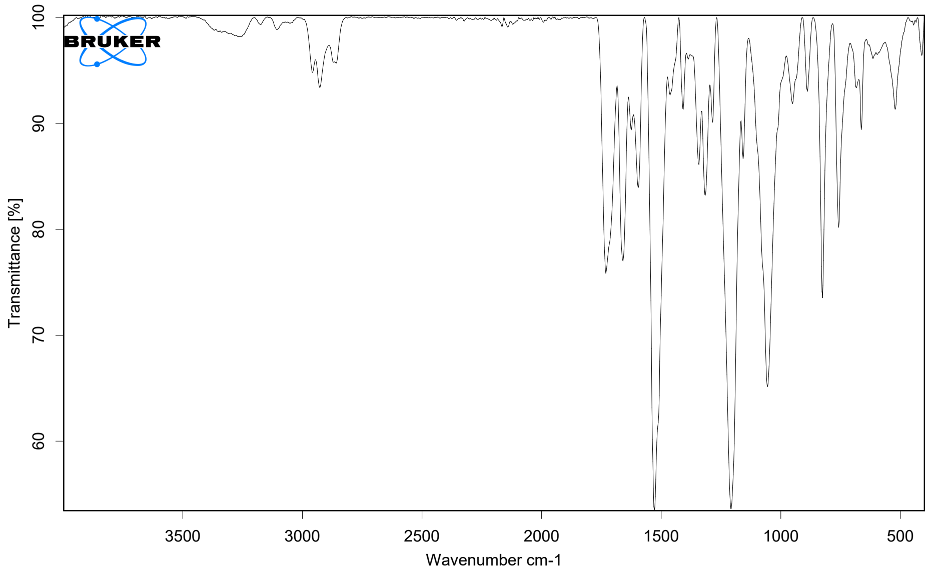
[1]H -NMR (400 MHz, DMSO-d, 298K) spectrum of **poly(M1-*stat*-M2)a**.



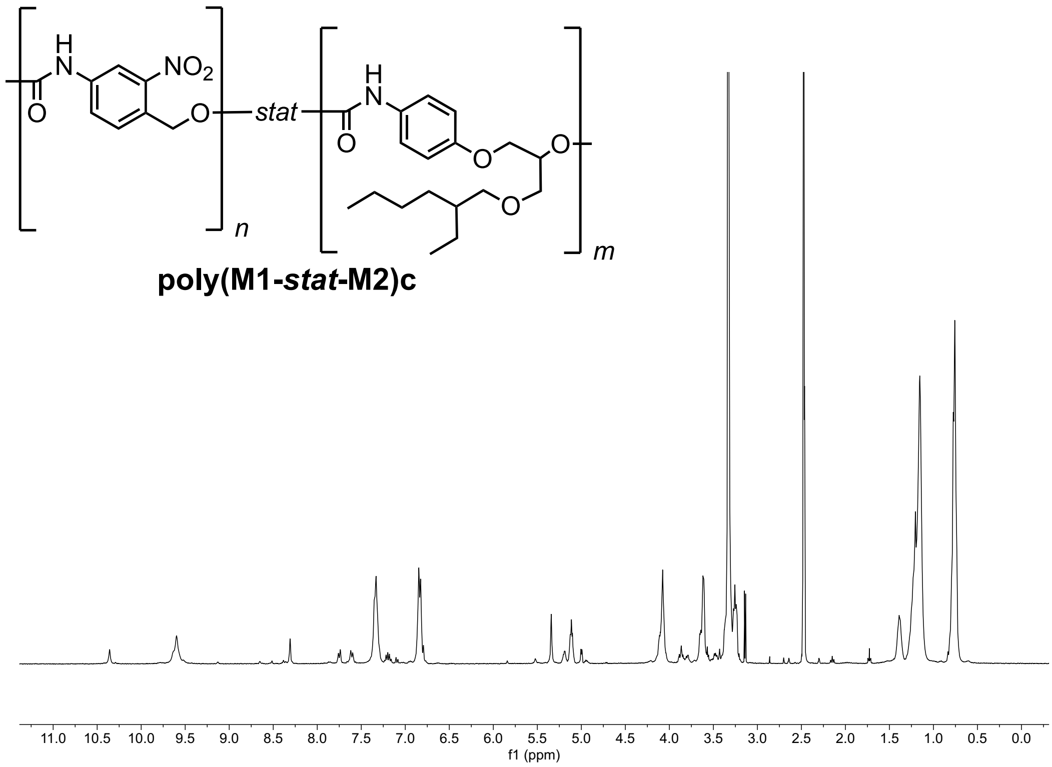
IR (ATR) spectrum of **poly(M1-*stat*-M2)a**.



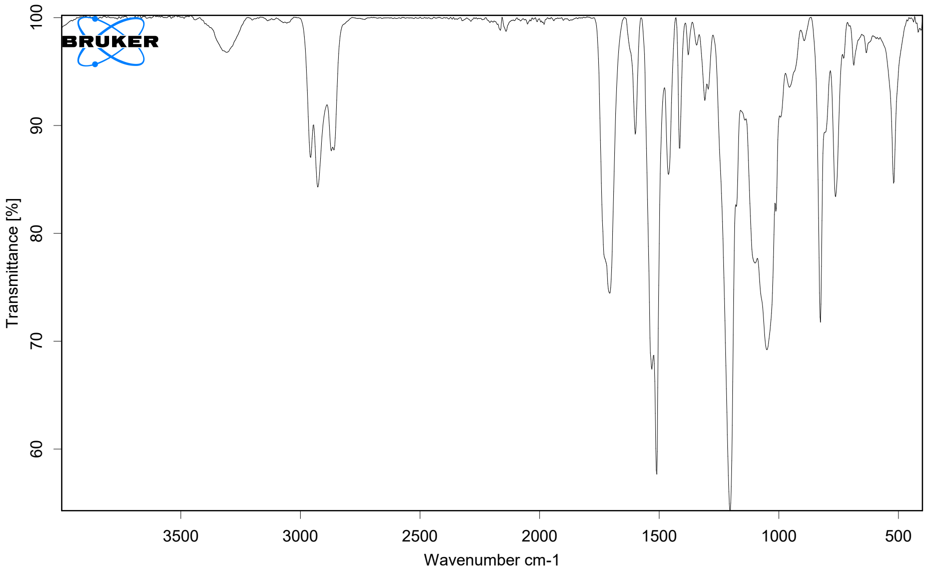
[1]H -NMR (400 MHz, DMSO-d, 298K) spectrum of **poly(M1-*stat*-M2)b**.



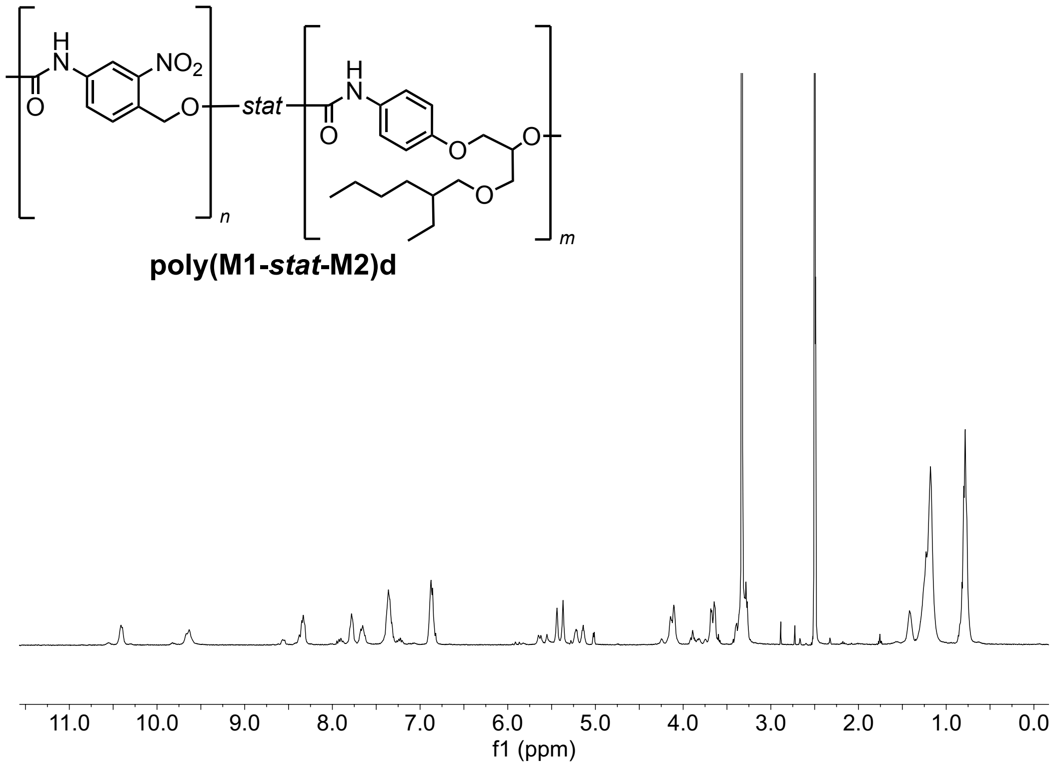
IR (ATR) spectrum of **poly(M1-*stat*-M2)b**.



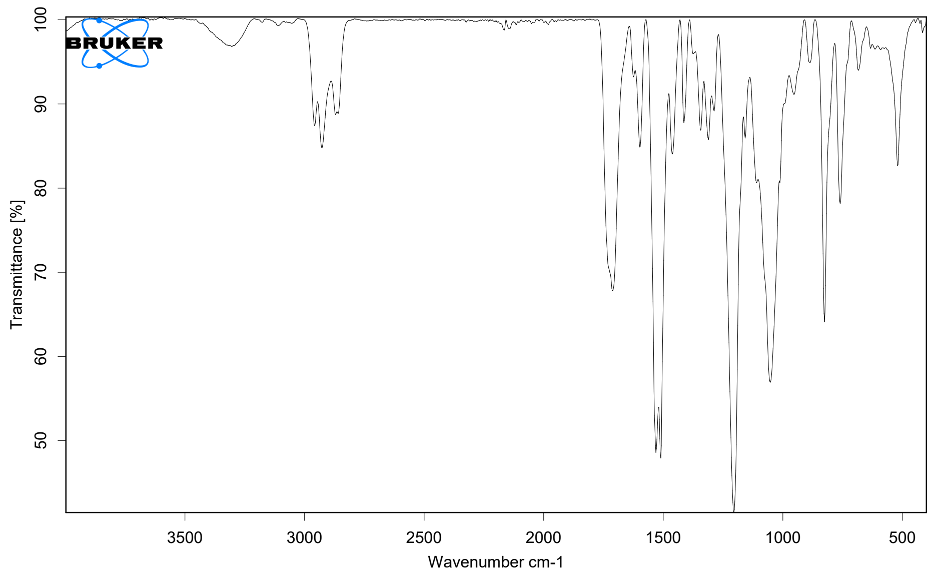
^{1}H -NMR (400 MHz, DMSO-d, 298K) spectrum of **poly(M1-*stat*-M2)c**.



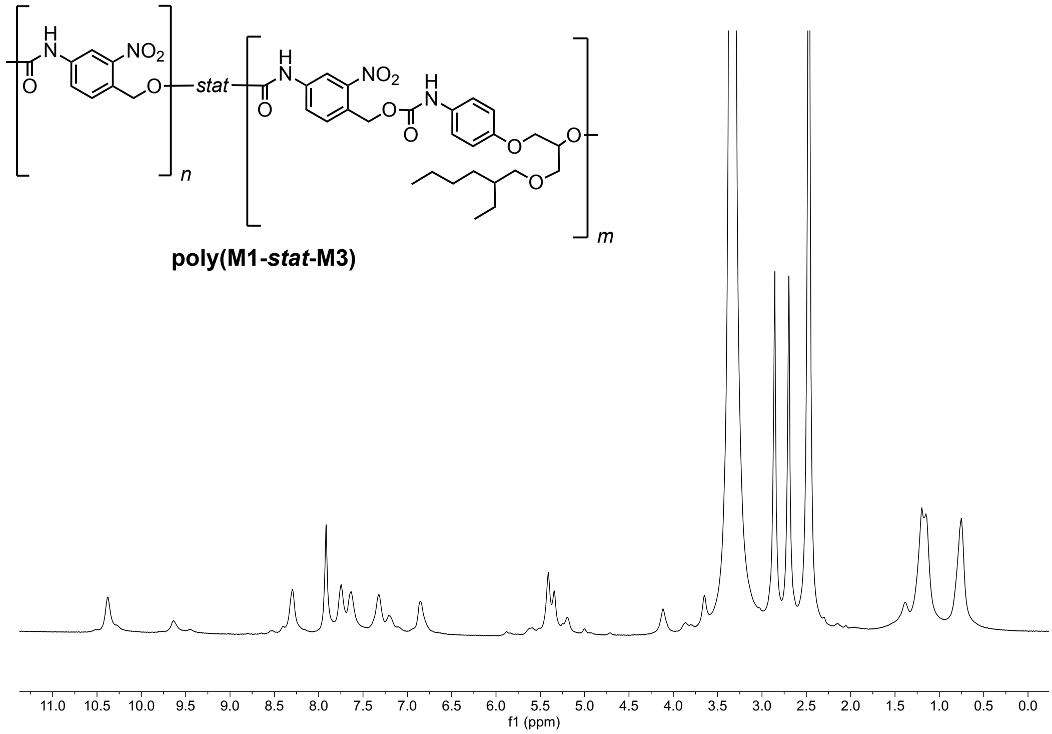
IR (ATR) spectrum of **poly(M1-*stat*-M2)c**.



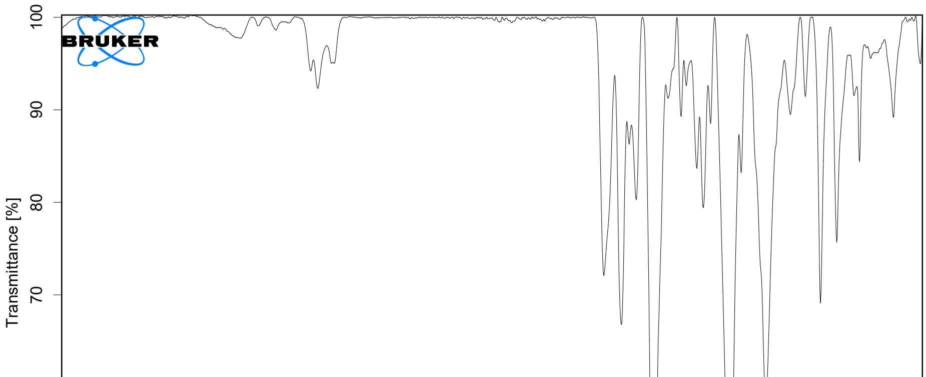
[1]H -NMR (400 MHz, DMSO-d, 298K) spectrum of **poly(M1-*stat*-M2)d**.



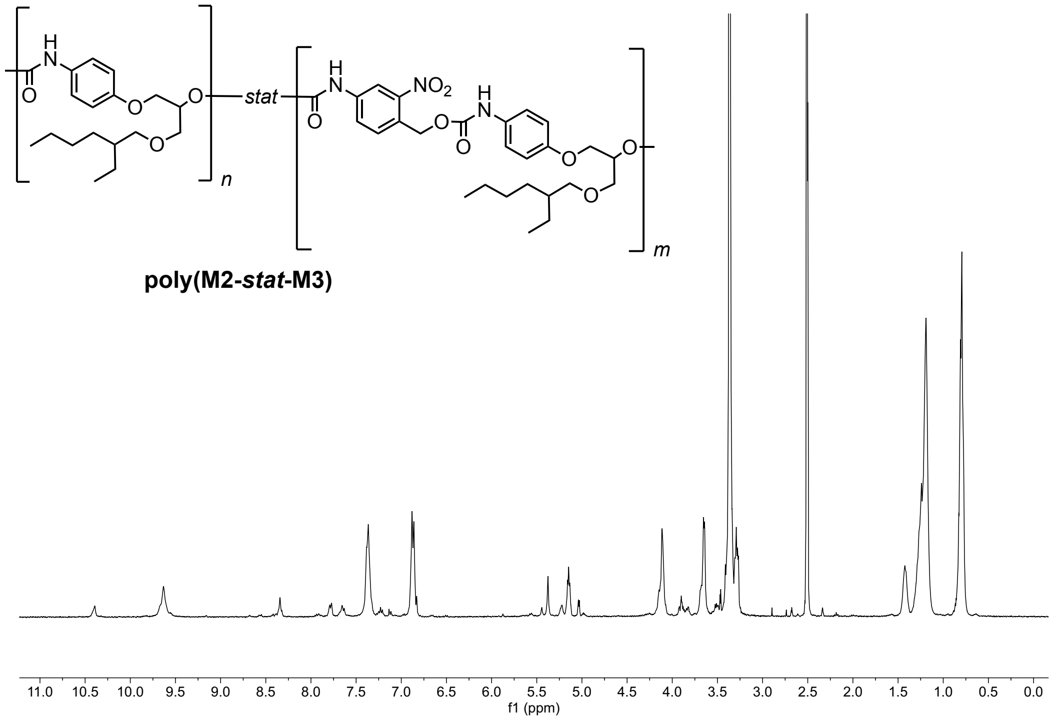
IR (ATR) spectrum of **poly(M1-*stat*-M2)d**.



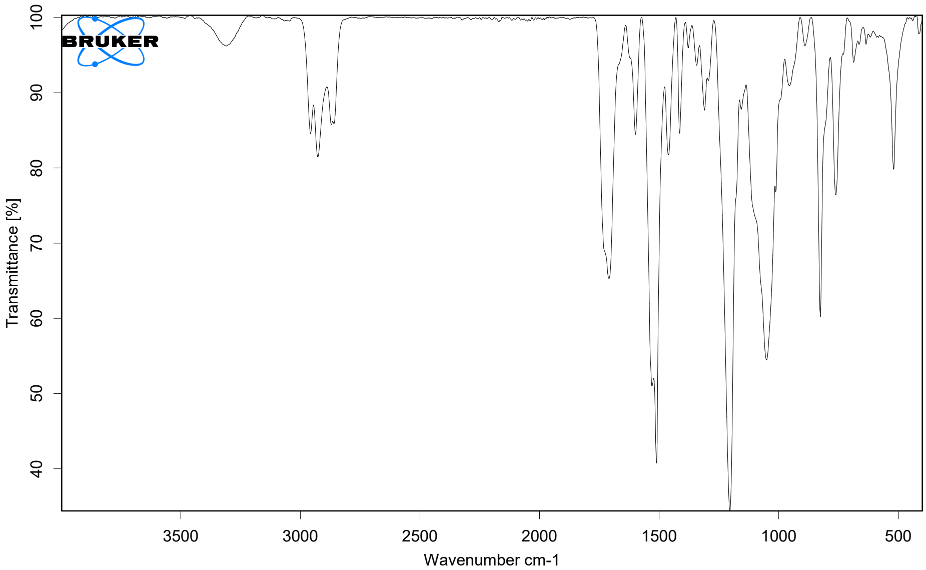
[1]H -NMR (400 MHz, DMSO-d, 298K) spectrum of **poly(M1-*stat*-M3)**.



IR (ATR) spectrum of **poly(M1-*stat*-M3)**.

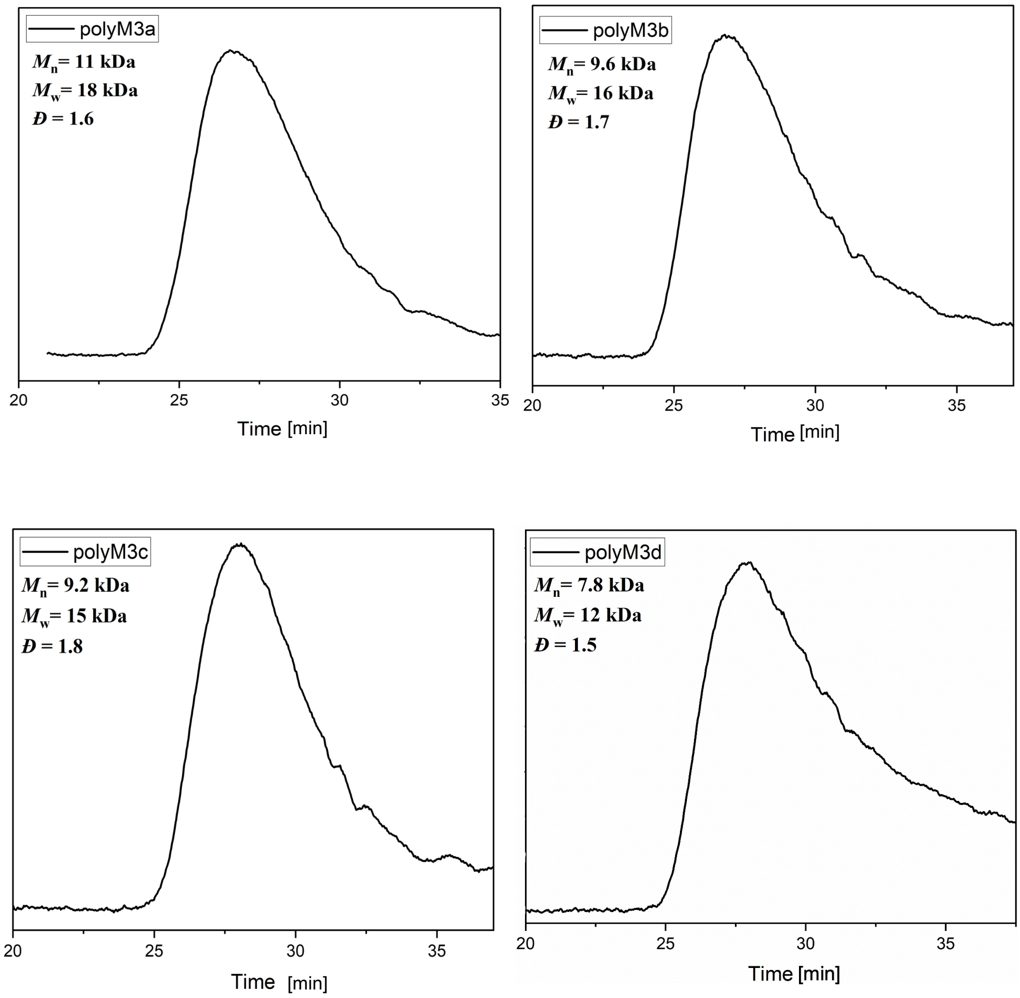


[1]H -NMR (400 MHz, DMSO-d, 298K) spectrum of **poly(M2-*stat*-M3)**.

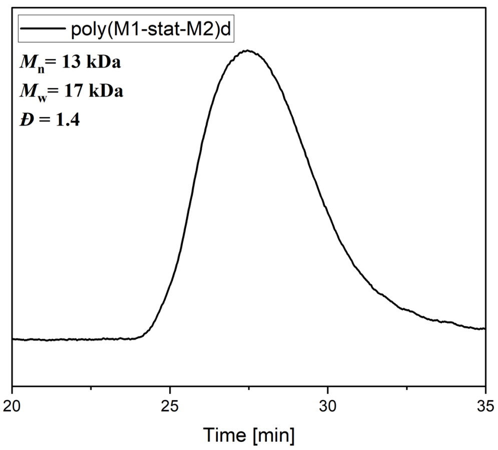


IR (ATR) spectrum of **poly(M2-*stat*-M3)**.

Size-Exclusion Chromatography (SEC)



SEC profiles of **polyM3a-d** (DMAc).

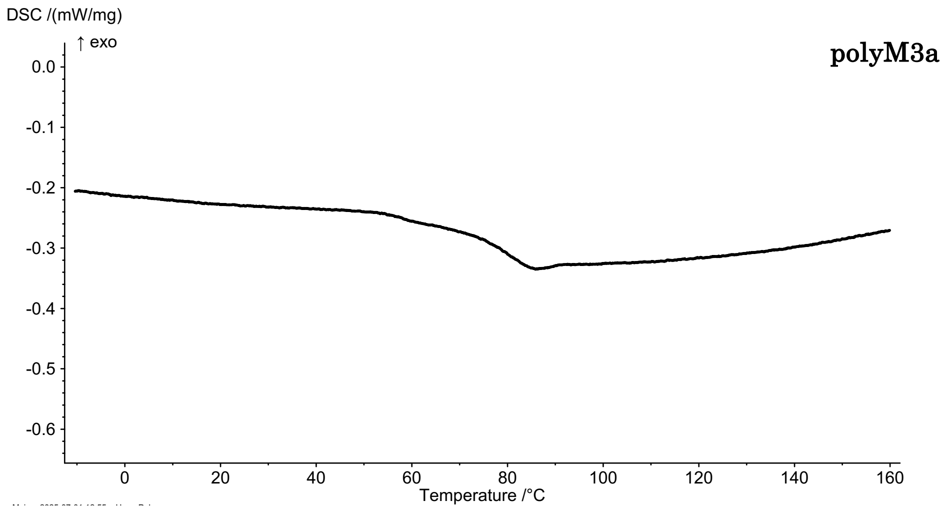


SEC profile of **poly(M1-*stat*-M2)d** (DMAc).

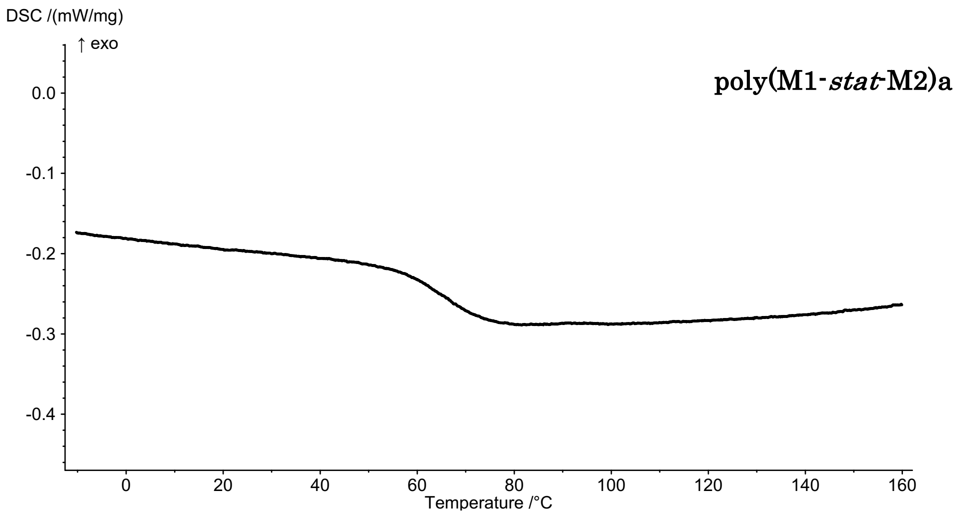
Thermal analysis of synthesized compounds

Thermal parameters were obtained by following profiles and summarized in Table 3 in the main text.

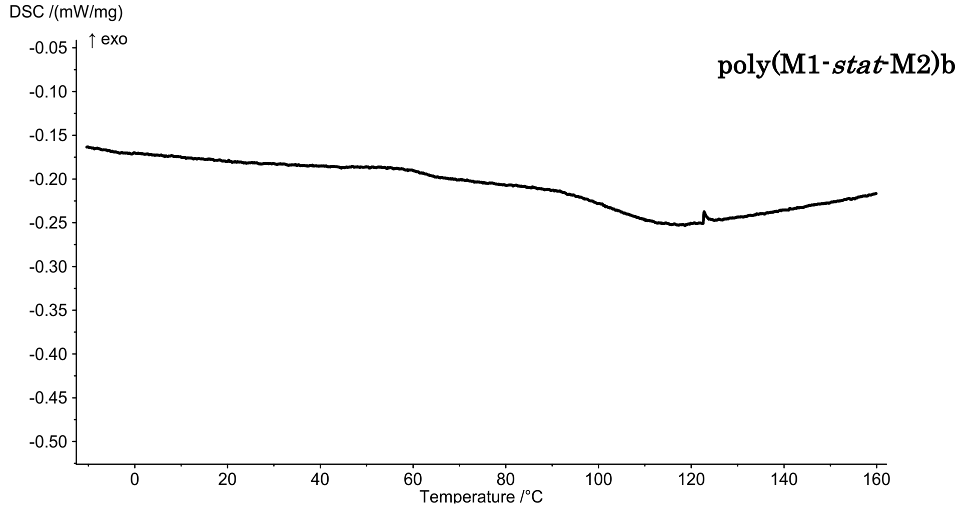
Differential Scanning Calorimetry (DSC)



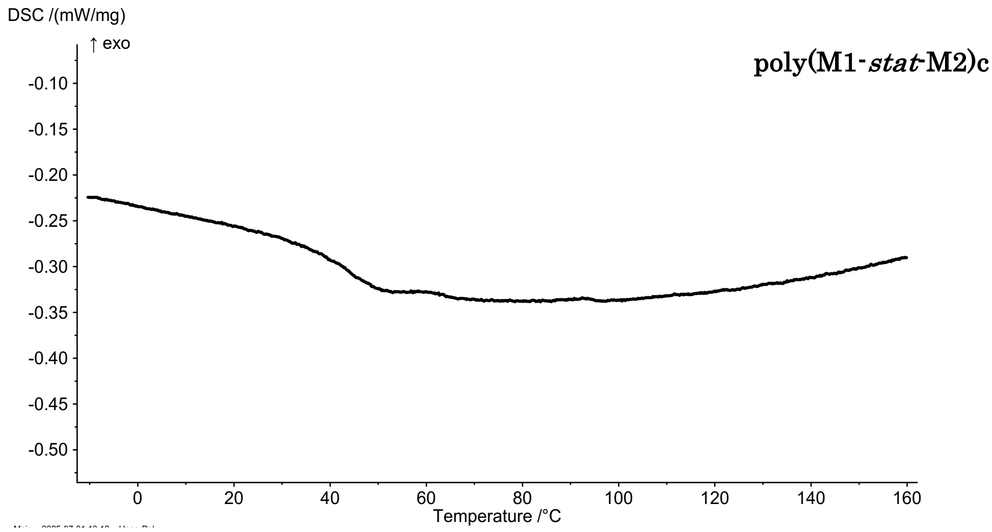
DSC profile of **polyM3a**.



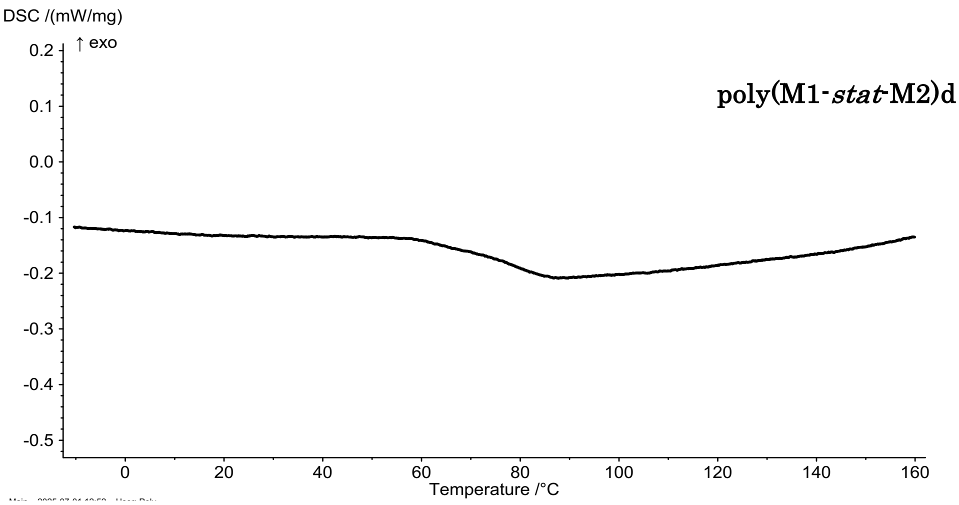
DSC profile of **poly(M1-*stat*-M2)a**.



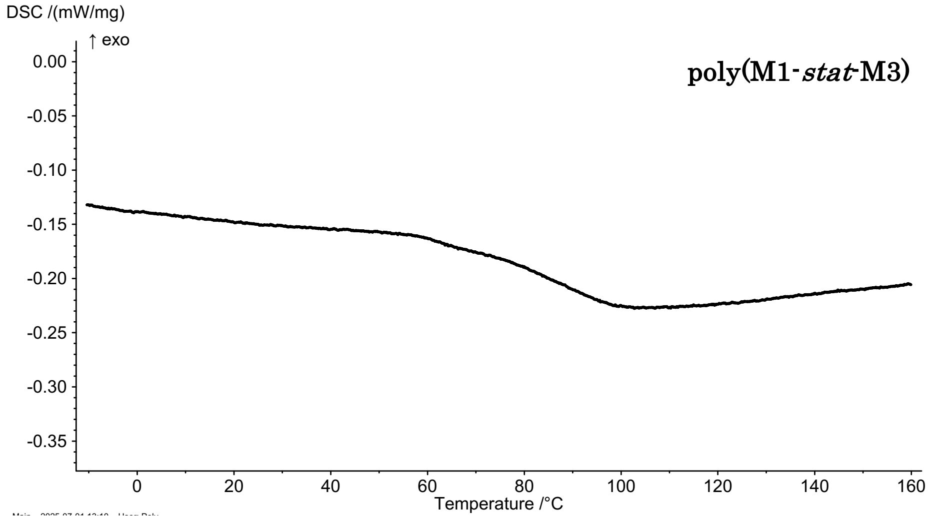
DSC profile of **poly(M1-*stat*-M2)b**.



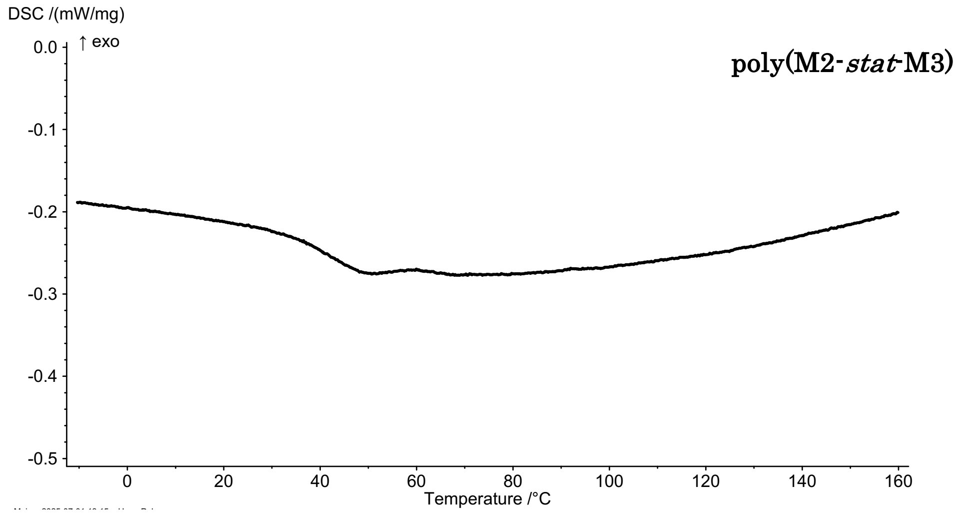
DSC profile of **poly(M1-*stat*-M2)c**.



DSC profile of **poly(M1-*stat*-M2)d**.

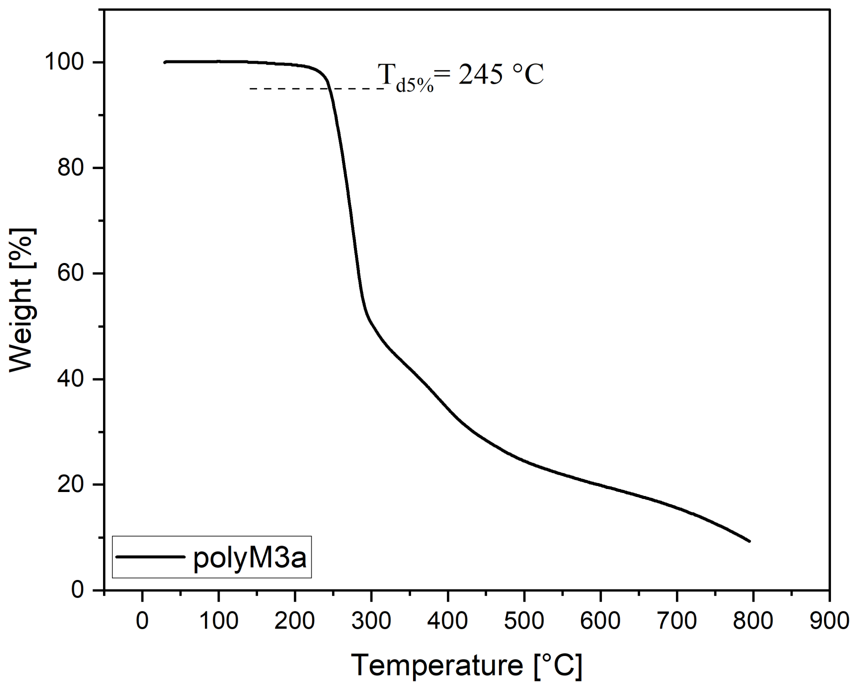


DSC profile of **poly(M1-*stat*-M3)**.

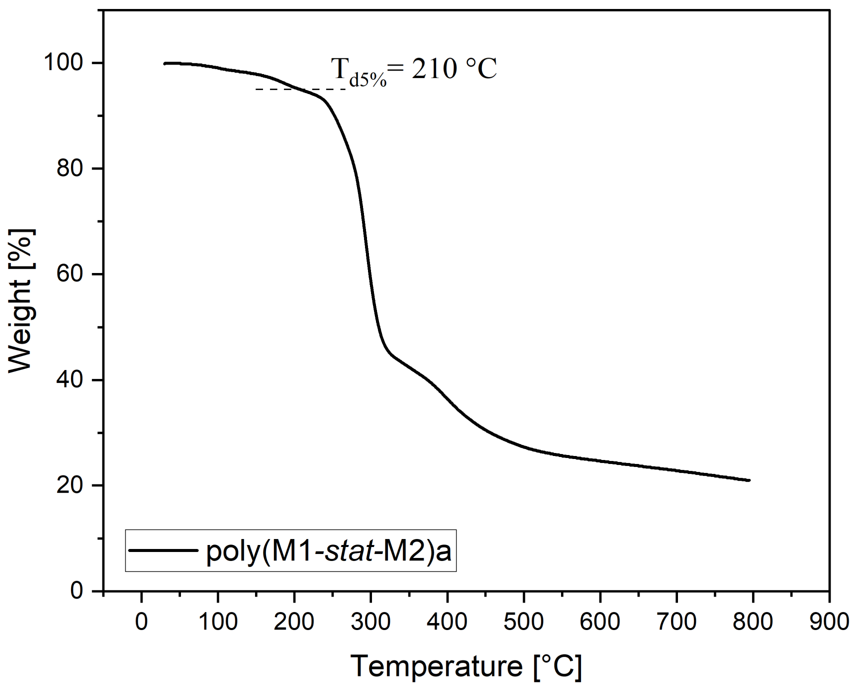


DSC profile of **poly(M2-*stat*-M3)**.

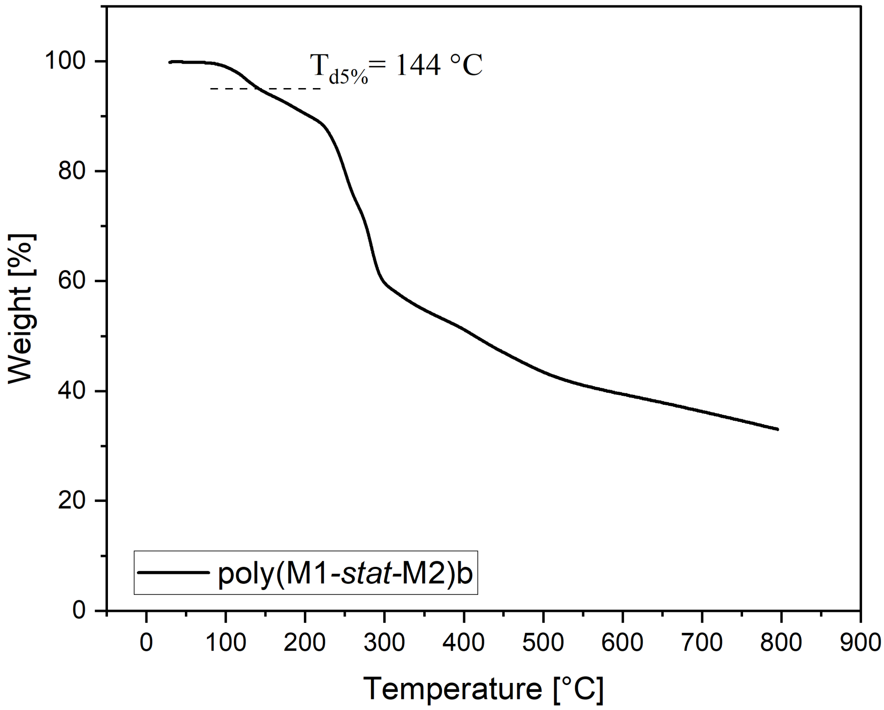
Thermal Gravimetric Analysis (TGA)



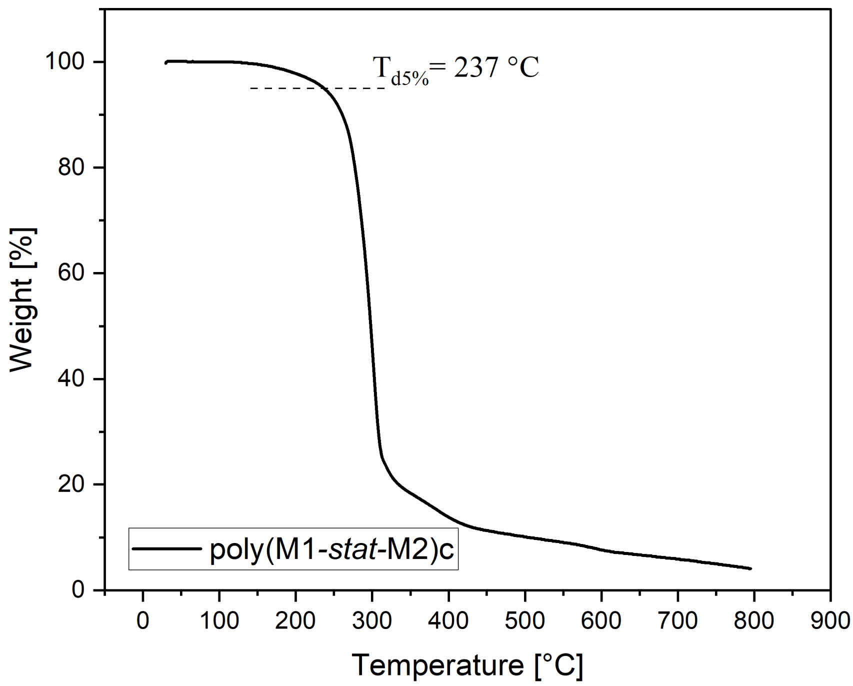
TGA profile of **polyM3a**.



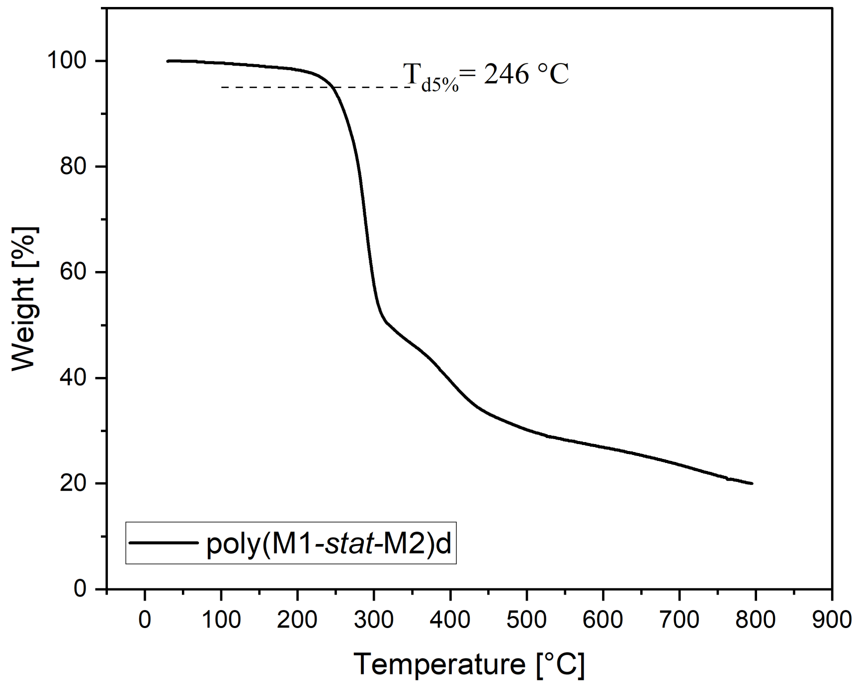
TGA profile of **poly(M1-*stat*-M2)a**.



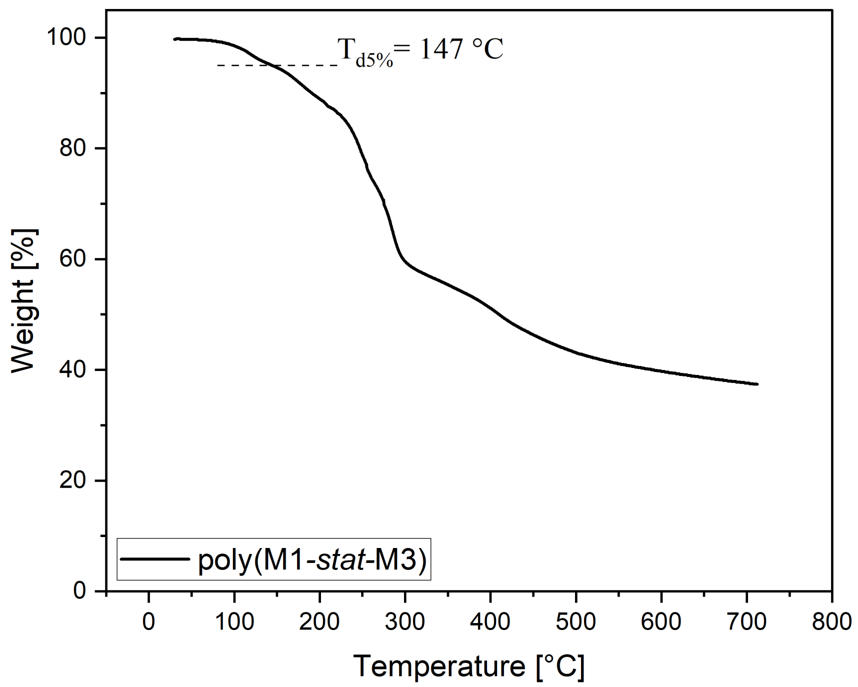
TGA profile of **poly(M1-*stat*-M2)b**.



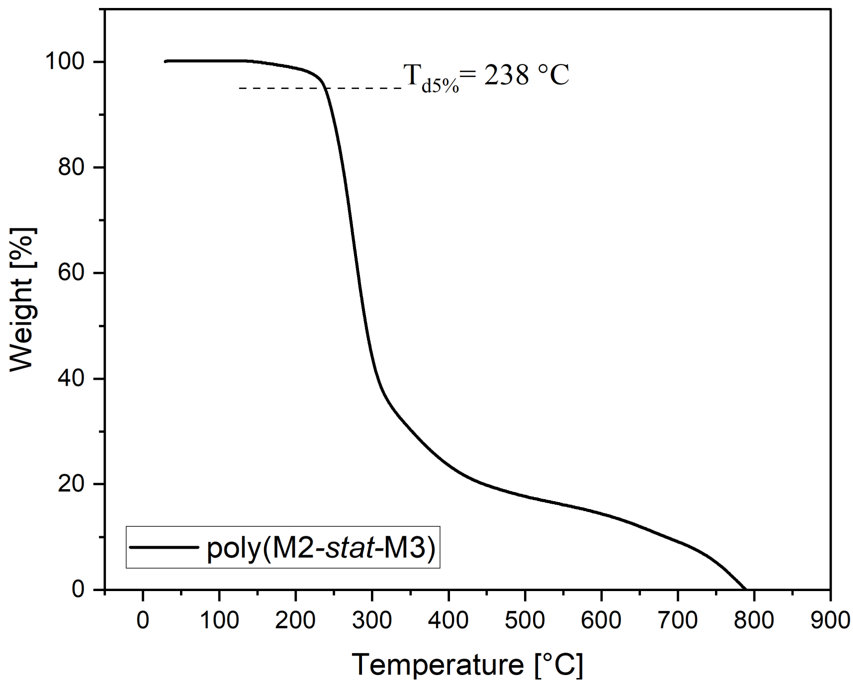
TGA profile of **poly(M1-*stat*-M2)c**.



TGA profile of **poly(M1-*stat*-M2)d**.



TGA profile of **poly(M1-*stat*-M3)**.



TGA profile of **poly(M2-*stat*-M3)**.

5. References

[1] (a) J. Reeb, Y. Shen, P. Theato, Y. Akae, *Macromolecules* **2025**, *58*, 2701-2708; (b) X. Kneidl, L. Forkel, T. Cui, P. Theato, Y. Akae, *J. Polym. Sci.* **2026***, 64,* 366-375.

[2] Y. Shen, P. Theato, Y. Akae, *Macromolecules* **2024**, *57*, 8162-8175.

[3] (a) Y. Akae, H. Okamura, Y. Koyama, T. Arai, T. Takata, *Org. Lett*. **2012**, *14*, 2226-2229; (b) Y. Akae, Y. Koyama, S. Kuwata, T. Takata, *Chem. Eur. J.* **2014**, *20*, 17132-17136; (c) Y. Akae, H. Sogawa, T. Takata, *Angew. Chem. Int. Ed. Engl.* **2018**, *57*, 11742-11746; *Angew. Chem.* **2018**, *130*, 11916-11920.