SUPPORTING INFORMATION

Synthesis and Radical Polymerization of Adamantyl Methacrylate Monomers having Hemiacetal Moieties

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Section S1. Synthetic methods of adamantyl methacrylate monomers:

Section S1-1. Synthesis of 3-methacryloxyadamant-1-ylacetic acid (3). To a CH_2Cl_2 (15 mL) solution of 3-hydroxy-1-adamantane acetic acid (**1**) (2.0 g, 9.50 mmol), triethylamine (8.0 mL, 57 mmol) was added, followed by methacryloyl chloride (2.02 mL, 20.90 mmol) at 0 ^oC, and the mixture was stirred for 8 h. The resulting mixture was poured into aqueous HCl solution (0.25 M) at 0 ^oC, and the products were extracted with CH_2Cl_2, dried over anhydrous $MgSO_4$, and concentrated in vacuo to give a crude product of 3-methacryloxy-1-adamantane acetic acid methacrylic acid anhydride (**2**). This product (**2**) was dissolved in pyridine (5.0 mL) and H_2O (0.5 mL), and the solution was stirred overnight at room temperature. The resulting solution was poured into aqueous HCl (0.25 M) at 0 ^oC, and the products were extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$ and concentrated. Purification of the products with acidic silica-gel column chromatography (eluent: Hexane / AcOEt = 2 / 1) followed by recrystallization in hexane and ethyl acetate gave the title compound **3** (0.95g, 3.40 mmol) in 36 % yield. Mp: 118 ^oC.

IR (neat, KBr, cm^{-1}): 2570-3443 (br), 3110, 2988, 2928, 2851, 1700, 1640, 1455, 1416, 1333, 1312, 1174.

^1H NMR (DMSO-d6, 400 MHz) δ = 5.98 (s, 1H), 5.64 (s, 1H), 2.23 (s, 2H), 1.99-2.14 (m, 8H), 1.86 (s, 3H), 1.58 (m, 6H).

^{13}C NMR (DMSO-d6,100 MHz) δ = 178.20, 166.93, 138.14, 124.96, 80.76, 47.83, 45.96, 41.22, 40.65, 36.34, 35.63, 30.94, 18.62 .

Elemental Anal. Found: C, 68.87; H, 8.10 %. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97 %.

Section S1-2. Synthesis of 2-(1-propoxy)ethyl 3-methacryloxyadamant-1-ylacetate (4a).

Bis(2-ethylhexyl)hydrogen phosphate (10 μL, 0.03 mmol) was added to a mixture of 3-methacryloxyadamant-1-ylacetic acid (**3**) (0.95 g, 3.4 mmol) and n-propyl vinyl ether (1.52 mL, 13.6 mmol) and the resulting solution was stirred for 4 h at room temperature. Then, the crude reaction mixture was diluted with CH_2Cl_2 and purified by passing through a solid base ($Mg_6Al_2(OH)_{16}CO_3.4H_2O$) column. Concentration and drying of the obtained filtrate in vacuo gave the compound **4a** (1.11 g, 3.06 mmol) in 90 % yield.

IR (neat, KBr, cm^{-1}): 3111, 2923, 2862, 1715, 1648, 1458, 1182, 1126.

^1H NMR (DMSO-d6, 400 MHz, *J* in Hz) δ = 5.96 (s, 1H), 5.88 (q, 1H, *J* = 4), 5.64 (s, 1H), 3.57 (m, 1H), 3.45 (m, 1H), 2.22 (m, 4H), 1.97-2.13 (m, 6H), 1.86 (s, 3H), 1.58 (m, 8H), 1.40 (d, 3H, *J* = 4), 0.90 (t, 3H, *J* = 8).

^{13}C NMR ($CDCl_3$,100 MHz) δ = 170.94, 166.32, 137.88, 124.45, 96.20, 80.30, 70.84, 48.08, 45.95, 41.14, 40.47, 36.20, 35.50, 30.86, 23.17, 21.55, 18.86, 11.33.

Elemental Anal. Found: C, 69.04; H, 8.86 %. Calcd for $C_{21}H_{32}O_5$: C, 69.20; H, 8.85 %.

Section S1-3. Synthesis of 2-(cyclohexyloxy)ethyl 3-methacryloxyadamant-1-ylacetate (4b)

Bis(2-ethylhexyl)hydrogen phosphate (10 μL, 0.03 mmol) was added to a mixture of 3-methacryloyladamant-1-ylacetic acid (**3**) (0.95 g, 3.40 mmol) and cyclohexyl vinyl ether (1.93 mL, 13.60 mmol) and the resulting solution was stirred for 4 h at room temperature. Then, the crude reaction mixture was diluted with CH_2Cl_2 and purified by passing through a solid base ($Mg_6Al_2(OH)_{16}CO_3.4H_2O$) column. Concentration and drying of the obtained filtrate in vacuo gave the compound **4b** (1.03 g, 2.55 mmol) in 75 % yield.

IR (neat, KBr, cm^{-1}): 2996, 2934, 2859, 1717, 1637, 1457, 1181, 1130.

^1H NMR ($CDCl_3$, 400 MHz, *J* in Hz) δ = 6.04 (q, 1H, *J* = 4), 6.01 (s, 1H), 5.49 (s, 1H), 3.55 (m, 1H), 2.14-2.32 (m, 4H), 2.01-2.10 (m, 4H), 1.90 (s, 5H), 1.61 (m, 10H), 1.42 (d, 3H, *J* = 4), 1.28 (m, 6H).

^{13}C NMR ($CDCl_3$,100 MHz) δ = 171.55, 166.85, 138.35, 124.62, 94.39, 80.51, 48.78, 46.55, 41.59, 40.86, 36.94, 35.90, 33.55, 32.29, 31.03, 25.84, 24.58, 21.89, 18.67.

ESI/HRMS: $[M+H]^+$; Calcd for $C_{24}H_{36}O_5$, 404.2563; found 405.2600.

Section S1-4. Synthesis of 2-(t-butoxy)ethyl 3-methacryloxyadamant-1-ylacetate (4c)

Bis(2-ethylhexyl)hydrogen phosphate (10 μL, 0.03 mmol) was added to a mixture of 3-methacryloyladamant-1-ylacetic acid (**3**) (0.95 g, 3.40 mmol) and t-butyl vinyl ether (1.79 mL, 13.60 mmol) and the resulting solution was stirred for 4 h at room temperature. Then, the crude reaction mixture was diluted with CH_2Cl_2 and purified by passing through a solid base ($Mg_6Al_2(OH)_{16}CO_3.4H_2O$) column. Concentration and drying of the obtained filtrate in vacuo gave the compound **4c** (1.09 g, 2.89 mmol) in 85 % yield.

IR (neat, KBr, cm^{-1}): 2984, 2918, 2867, 1718, 1638, 1458, 1181, 1130.

^1H NMR ($CDCl_3$, 400 MHz, *J* in Hz) δ = 6.15 (q, 1H, *J* = 4), 6.02 (s, 1H), 5.50 (s, 1H), 2.28 (s, 2H), 2.07-2.23 (m, 8H), 1.92 (s, 3H), 1.65 (m, 6H), 1.43 (d, 3H, *J* = 4), 1.30 (s, 9H).

^{13}C NMR ($CDCl_3$,100 MHz) δ = 170.70, 166.51, 137.86, 124.52, 91.74, 80.38, 75.95, 48.04, 46.09, 41.20, 40.75, 36.30, 35.56, 30.88, 28.49, 23.05, 18.69.

Elemental Anal. Found: C, 69.77; H, 9.26 %. Calcd for $C_{22}H_{34}O_5$: C, 69.81; H, 9.05 %.

Section S2. Free radical polymerizations of 4a, 4b and 4c.

Section S2-1. Polymerization of 2-(1-propoxy)ethyl-3-methacryloxyadamant-1-ylacetate (4a)

A mixture of the monomer **4a** (150 mg, 0.41 mmol) and AIBN (2.0 mg, 0.012 mmol) in methyl ethyl ketone (MEK) were degassed by three freeze / thaw cycles, sealed under vacuum, and heated to 60 ^{o}C for 16 h. The reaction mixture was precipitated with hexane. The white solid precipitate was collected and dried to give the desired **poly-4a** (130 mg) in 87 % yield.

IR (neat, KBr, cm^{-1}): 2920, 1726, 1175.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 5.80 (1H), 3.5 (1H), 3.3 (1H), 0.8-2.2 (29 H).

Section S2-2. Polymerization of 2-(cyclohexyloxy)ethyl 3-methacryloxyadamant-1-ylacetate (4b)

A mixture of the monomer **4b** (150 mg, 0.37 mmol) and AIBN (1.8 mg, 0.011 mmol) in methyl ethyl ketone (MEK) were degassed by three freeze / thaw cycles, sealed under vacuum, and heated to 60 ^{o}C for 16 h. The reaction mixture was precipitated into hexane. The white solid precipitate was collected and dried to give the desired **poly-4b** (110 mg) in 73 % yield.

IR (neat, KBr, cm^{-1}): 2950, 1740, 1450, 1180.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 6.00 (1H), 3.5 (1H), 1.0-2.4 (34H).

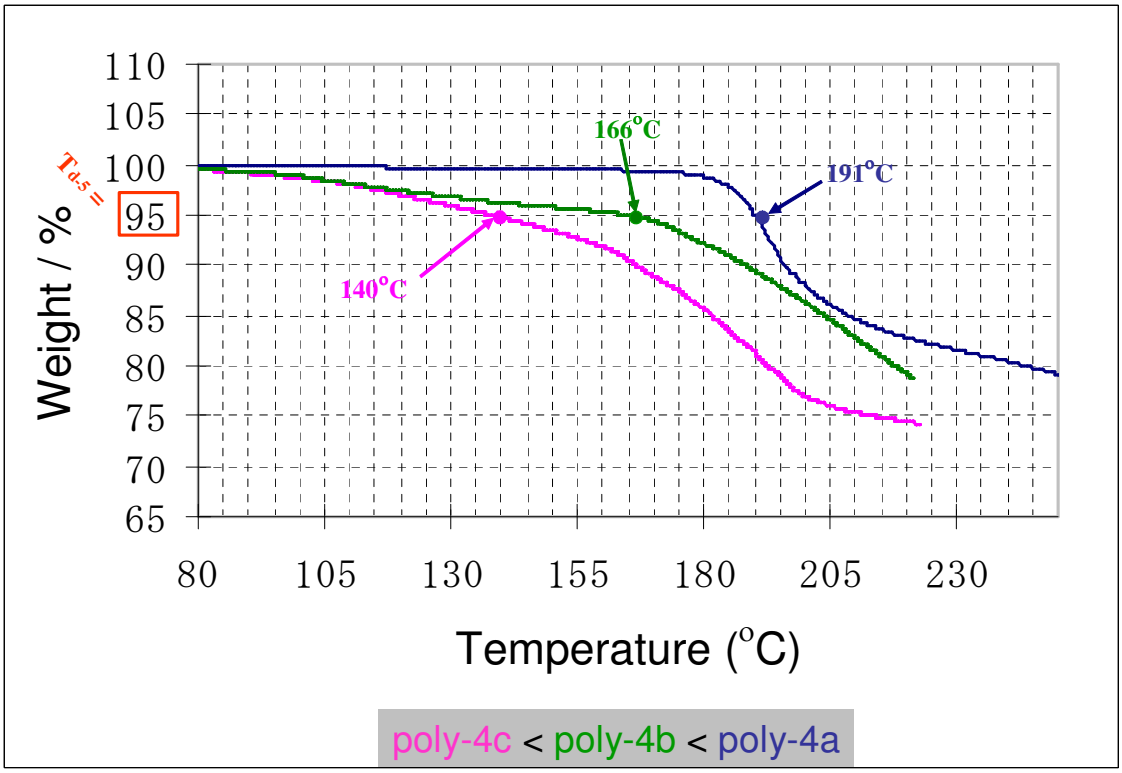
Section S2-3. Polymerization of 2-(t-butoxy)ethyl 3-methacryloxyadamant-1-ylacetate (4c)

A mixture of the monomer **4c** (150 mg, 0.40 mmol) and AIBN (2.0 mg, 0.012 mmol) in methyl ethyl ketone (MEK) were degassed by three freeze / thaw cycles, sealed under vacuum, and heated to 60 ^{o}C for 16 h. The reaction mixture was precipitated into hexane. The white solid precipitate was collected and dried to give the desired **poly-4c** (119 mg) in 79 % yield.

IR (neat, KBr, cm^{-1}): 2980, 1730,1458, 1151.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 6.10 (1H), 0.8-2.4 (33H).

Figure S1. Comparative TGA curve of **poly-4a**, **poly-4b** and **poly-4c**.



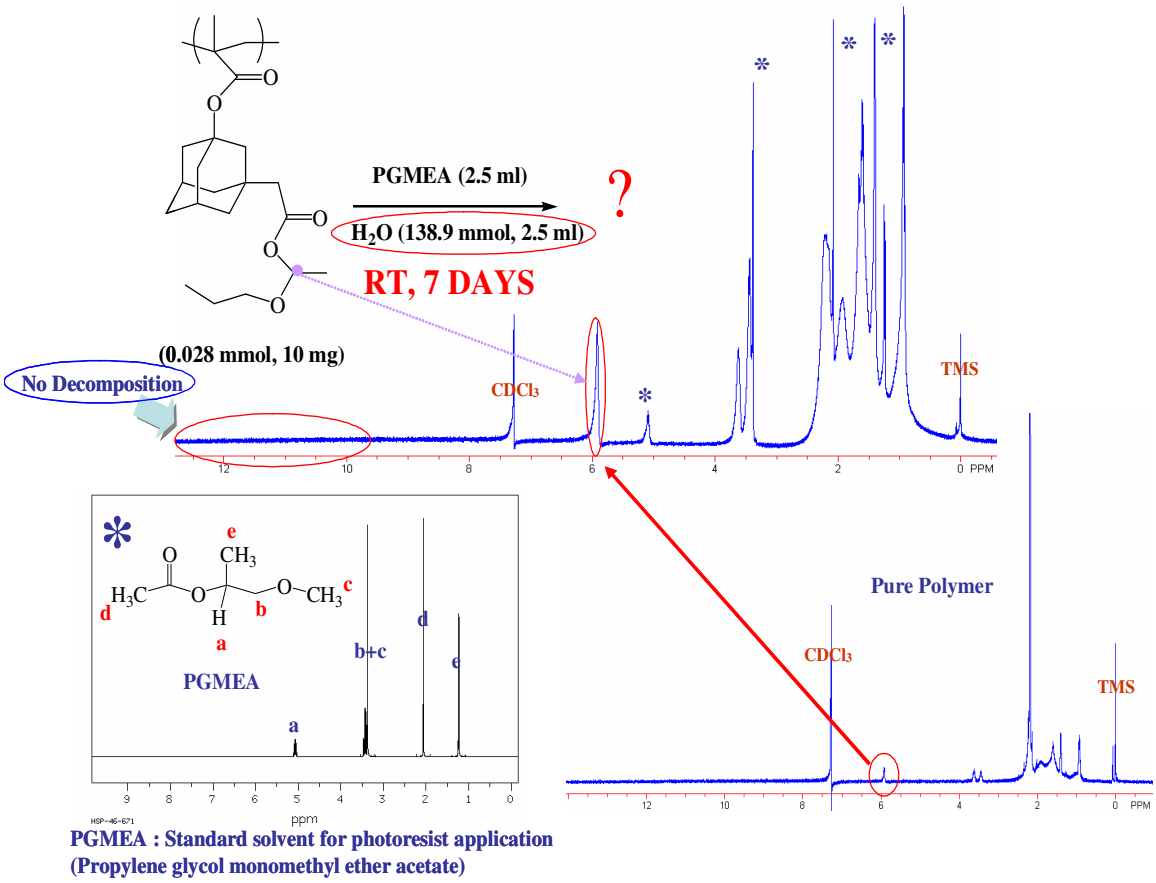


Figure S2. ^{1}H NMR analyses to determine the stability of of **poly-4a** in presence of high moisture content.

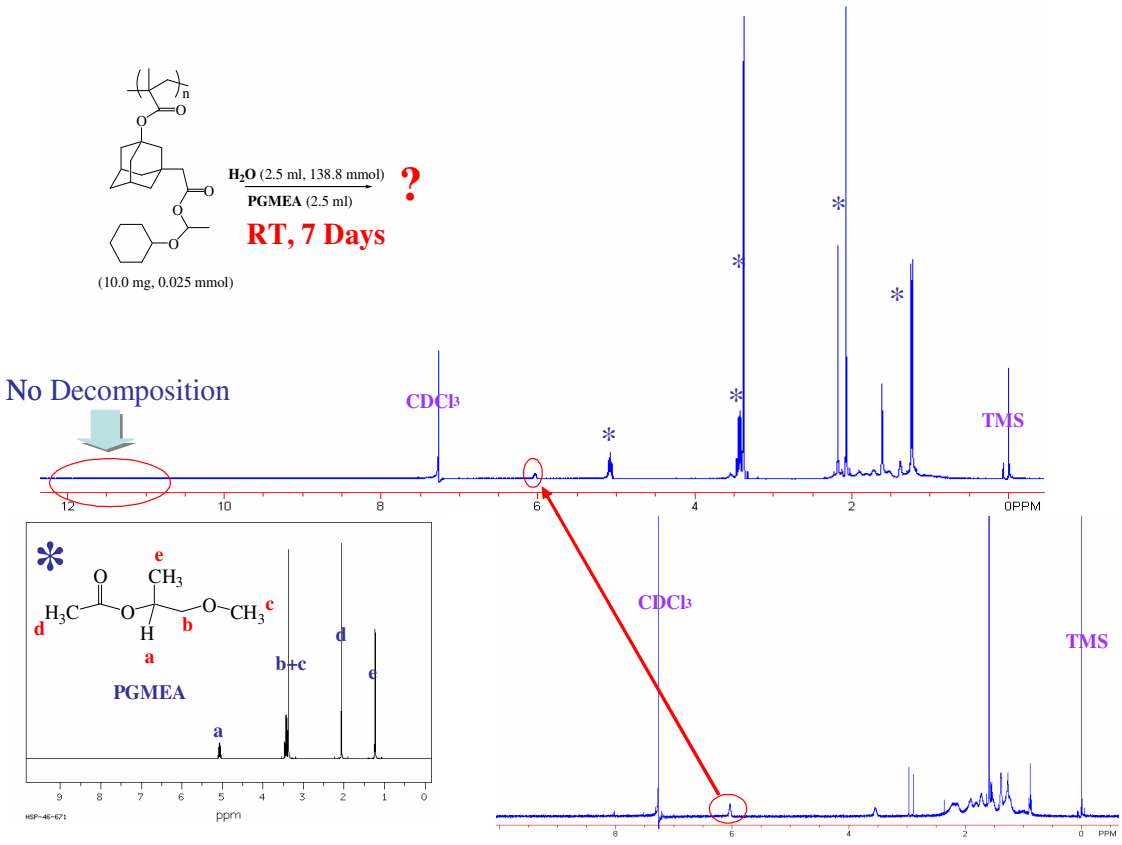


Figure S3. ^{1}H NMR analyses to determine the stability of of **poly-4b** in presence of high moisture content.

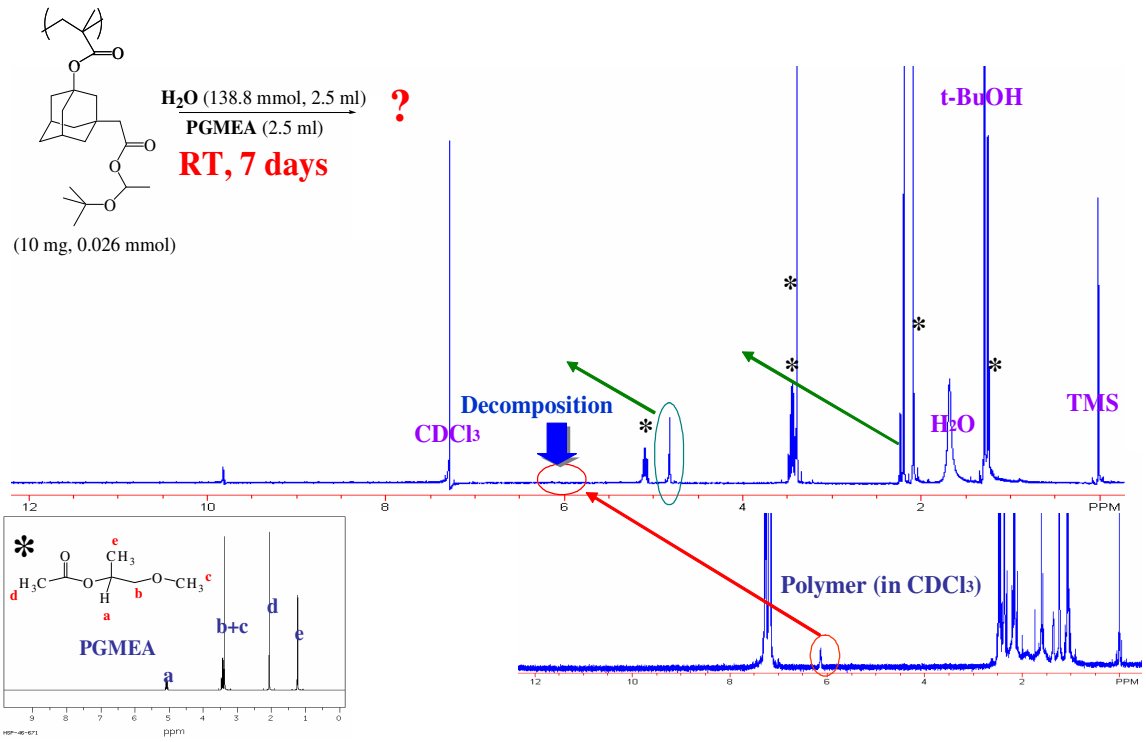


Figure S4. ^{1}H NMR analyses to determine the stability of of **poly-4c** in presence of high moisture content.

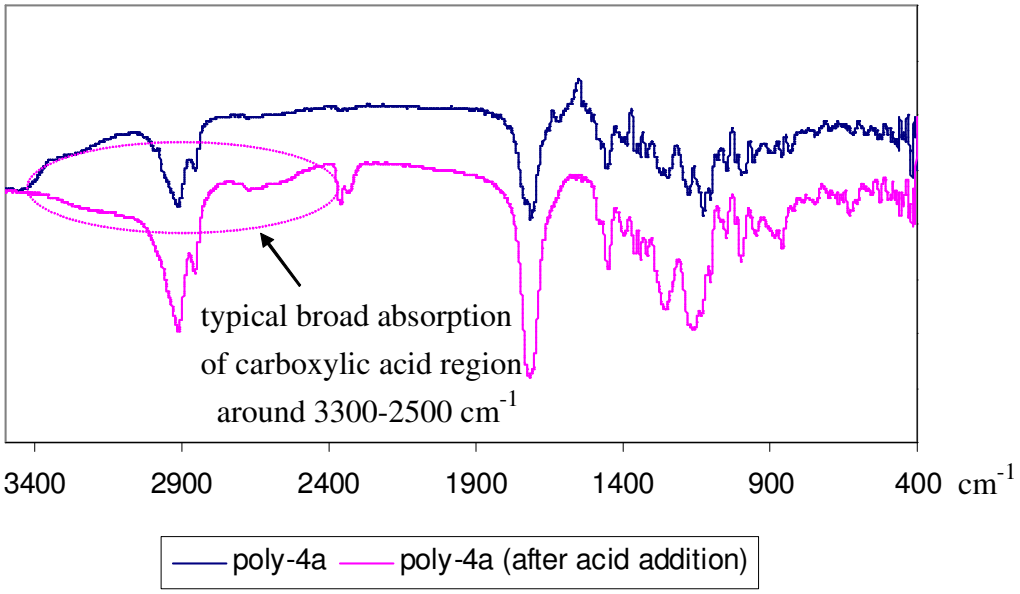


Figure S5. FTIR of **poly-4a** before and after acid addition.

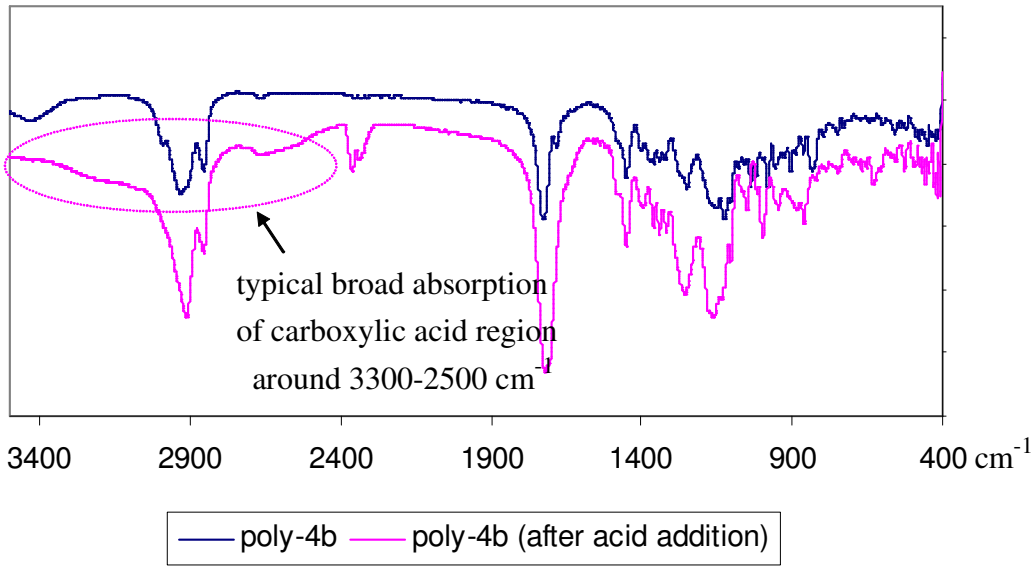


Figure S6. FTIR of **poly-4b** before and after acid addition.

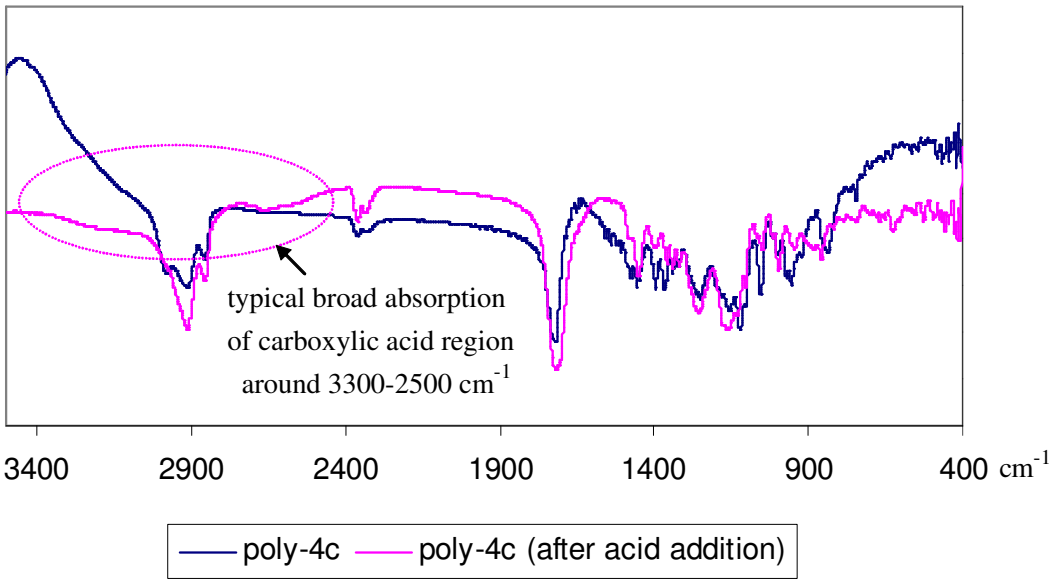


Figure S7. FTIR of **poly-4c** before and after acid addition.