

Well-Defined Renewable Polymers Derived from Gum Rosin

Yijun Zheng,[†] Kejian Yao,[†] James Lee,[†] David Chandler,[†]
Jifu Wang,[‡] Chunpeng Wang,[‡] Fuxiang Chu,[‡] and
Chuanbing Tang^{*,†}

[†]Department of Chemistry and Biochemistry and Nanocenter,
University of South Carolina, 631 Sumter Street, Columbia,
South Carolina 29208, and [‡]Chinese Academy of Forestry,
Wan Shou Shan, Beijing, China 100091

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Synthesis of new polymeric materials from renewable natural resources has become a rapidly growing area, as these materials could potentially replace or partially replace environmentally and energy unfavorable plastics derived from petroleum chemicals.^{1–6} However, applications of renewable polymers are significantly behind petroleum-derived polymers, partially because of relative high cost and limitations in the monomer resources and therefore derived polymers. Thus, the development of novel low-cost and scalable monomers from renewable resources is essential.^{7–12}

We have focused on developing a new class of renewable polymers using gum rosin due to its abundance, low cost, and its potential ability to be derivatized into polymerizable monomers. Produced more than 1 million tons annually, crude rosin and gum rosin, whose major components are resin acids (primarily abietic acid) with characteristic hydrophenanthrene rings, are exudates from pine trees and are generally used as ingredients for inks, vanishes, adhesives, cosmetics, medicines, chewing gums, etc.^{13–15} However, the use of rosin as renewable resources has been mostly focused on step-growth polymerization to prepare low molecular weight polymeric materials.^{16–21} Controlled radical polymerization (CRP) of monomers derived from gum rosin has not been studied, partially due to the absence of highly pure polymerizable vinyl monomers.^{22–24} CRP allows to prepare well-defined polymers with controlled molecular weight, functionality, and architectures, which can enable one to develop more advanced materials such as thermoplastic elastomers and composites.^{25–27} Herein we report the synthesis of high-quality rosin-derived vinyl monomers and the first preparation of well-defined rosin-derived polymers using atom transfer radical polymerization (ATRP).

We chose commercial dehydroabietic acid (DHAA, a racemic mixture) as our starting rosin materials since the aromatic ring in the hydrophenanthrene ring structure makes it more stable than abietic acid, while the functional carboxylic acid group allows the derivatization of various vinyl monomers.^{22–24} However, most DHAA from commercial sources contain ~5–10% unknown impurities (GS-MS data, Figures S1–S4), which turned out to be difficult to separate out. However, after derivatization of DHAA into vinyl monomers, we were able to remove all impurities readily through simple column chromatography. Under this scenario, four rosin-based acrylate and methacrylate monomers were synthesized (Scheme 1). Different spacers were placed between the vinyl group and dehydroabietic group in order to vary the steric effect imparted onto the vinyl group, which could have significant influence on the control of polymerization. Moreover, thermal

properties (e.g., glass transition temperature (T_g)) of resulting polymers can be finely tuned. For dehydroabietic acrylate (DAA),²⁸ the dehydroabietic group is connected directly to the vinyl ester group, while dehydroabietic butyl acrylate (DABA) has the longest spacer in between.

DAA was prepared from acryloyl chloride and dehydroabietic alcohol, which was obtained by reduction of dehydroabietic acid with sodium borohydride. For other monomers (dehydroabietic ethyl acrylate (DAEA), DABA, dehydroabietic ethyl methacrylate (DAEMA)), dehydroabietic acid was first converted into acyl chloride under oxalyl chloride followed by in-situ esterification reaction with hydroxyl groups of corresponding (meth)acrylates. Impurities were removed by column chromatography. The structures of all monomers were confirmed by ¹H NMR, ¹³C NMR, and mass spectra (see Supporting Information). Figure 1 shows clear evidence of high purity of vinyl monomers, as confirmed from chemical shifts of vinyl, aromatic, methylene protons, and those protons next to the aromatic ring. All integrations of NMR spectra matched very well. From the two-dimensional correlation spectroscopy (COSY) study of ¹H NMR (Figures S5 and S6), the region between 1 and 2.5 ppm is also clearly assigned to the proton on the hydrophenanthrene ring. To the best of our knowledge, this is the first report on the synthesis of highly pure vinyl monomers derived from gum rosin.

Copper-catalyzed ATRP of all vinyl monomers was carried out in various conditions, and the results are summarized in Table 1. Gel permeation chromatography (GPC) traces of poly(dehydroabietic acrylate) (PDAA) were broad and multimodal with high polydispersity index (PDI = 3.65) (run 1 in Table 1, Figure S7), suggesting an uncontrolled polymerization, most likely due to dominating steric hindrance of side groups. The polymerizations of DAEA and DABA were first carried out in anisole with the use of copper(I) bromide and tris[2-(dimethylamino)ethyl]amine (Me₆Tren) as the catalyst and ligand. However, both polymerizations resulted in low molecular weight (< 7000 g/mol) after 48 h (not shown). The use of the more polar solvent tetrahydrofuran (THF) significantly increased the polymerization rate while maintaining PDI < 1.3. After 16 h, the molecular weight was 11 500 and 21 500 g/mol for poly(dehydroabietic ethyl acrylate) (PDAEA) and poly(dehydroabietic butyl acrylate) (PDABA), respectively (runs 2 and 3 in Table 1). The higher molecular weight of PDABA was consistent with less hindrance due to longer spacer between rosin moiety and vinyl group. The representative GPC traces are shown in Figure 2. The acrylate rosin polymers had a monomodal symmetric elution curve, indicating well-controlled polymerization. The rate enhancement in more polar solvents could be due to improved solubility of catalysts, which has been observed in different systems.^{25,29,30}

We then carried out ATRP of methacrylate monomers (DAEMA) derived from rosin. Under the use of the same solvent (THF) as used for acrylate monomers, the polymerization of DAEMA was much faster than that of acrylate. 80% conversion was achieved within 24 h with a molecular weight of 32 900 g/mol for poly(dehydroabietic ethyl methacrylate) (PDAEMA) (run 4 in Table 1). However, the polymerization was not controlled as the PDI was as high as 1.6. Then we performed the polymerization with the use of less polar solvent: anisole. The reaction was slower but with much better control (run 5 in Table 1). The PDI was about 1.33. The GPC trace showed a symmetric single peak throughout the polymerization (Figure 2). Although the role of the solvent in the polymerization system is currently under

*Corresponding author: Ph 803-777-3628; Fax 803-777-9521; e-mail tang.c@chem.sc.edu.

investigation, some solvent-assisted side reactions such as elimination of HBr from poly(methacrylic halide)s could occur in more polar solvents.^{25,29,30} It is worth noting that most of the molecular weight determined by GPC was much lower than that obtained by ^1H NMR analysis, suggesting that rosin-derived polymers may have significantly different hydrodynamic volume compared to polystyrene calibration standards, probably due to large dehydroabietic side groups.

^1H NMR spectra (Figure 3) of acrylate and methacrylate polymers show that the characteristic signals of vinyl protons from monomers at 5.4–6.5 ppm disappeared, accompanied by

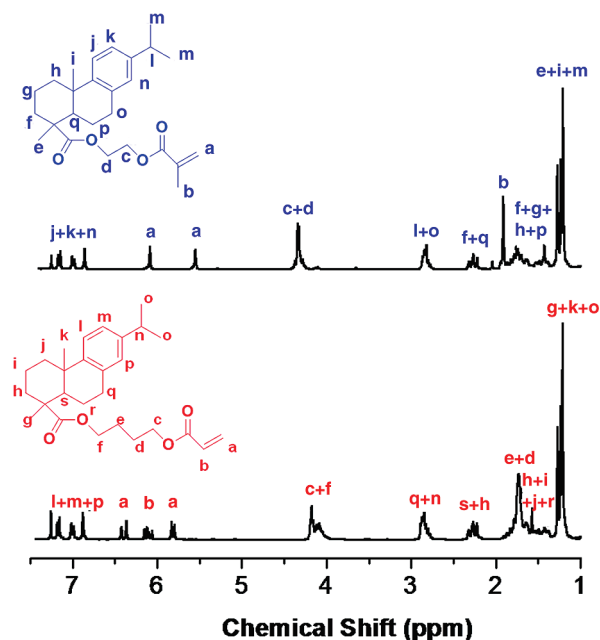


Figure 1. ^1H NMR spectra of vinyl monomers derived from rosin.

the appearance of broad peaks at 1–2.5 ppm corresponding to $-\text{CH}_2-\text{CH}-$ protons from the polymer backbone. All other peaks of dehydroabietic side groups were broader with nearly same chemical shifts as those of the monomers.

The thermal properties of PDAEA, PDABA, and PDAEMA polymers were characterized with the aid of differential scanning calorimetry (DSC) (Figure 4). All polymers exhibited typical thermoplastic behaviors, with no melting observed. The glass transition temperatures (T_g) showed a dependence of chemical structures of backbone and side groups. The methacrylate polymer (PDAEMA) showed highest $T_g \sim 90^\circ\text{C}$, while lowest $T_g (\sim 22^\circ\text{C})$ was observed from acrylate polymers with longest spacers between side groups and backbone (PDABA), about 20°C lower than that of PDAEA. This was in agreement with the concept that the longer spacer reduced the rotation barriers of acrylate polymers and decreased the T_g . Thermogravimetric analysis (TGA) of these different polymers was carried out under N_2 (Figure S8). All polymers showed two-stage weight loss behavior.

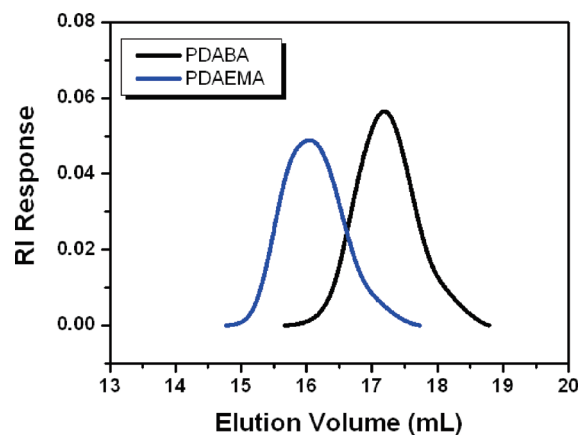


Figure 2. GPC traces of PDABA and PDAEMA prepared by ATRP (corresponding to runs 3 and 5 from Table 1, respectively).

Scheme 1. Synthesis of Vinyl Monomers from Gum Rosin

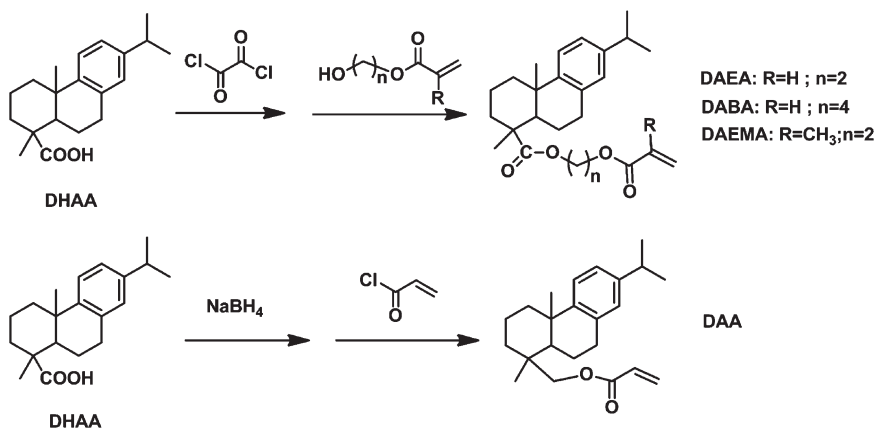


Table 1. ATRP of Vinyl Monomers Derived from Gum Rosin^a

run	monomer	[M]/[I]/[C]/[L]	solvent	ligand	time (h)	conv (%)	M_n (NMR)	M_n (GPC)	M_w/M_n
1	DAA	100/1/0.5/0.5	THF	Me_6Tren	24	30	10 200	5 600	3.65
2	DAEA	100/1/0.5/0.5	THF	Me_6Tren	16	29	11 500	4 300	1.20
3	DABA	100/1/0.5/0.5	THF	Me_6Tren	16	54	21 500	7 700	1.25
4	DAEMA	100/1/0.5/0.5	THF	Me_6Tren	24	80	32 900	36 000	1.60
5	DAEMA	100/1/0.5/0.5	Anisole	Me_6Tren	20	75	31 000	19 000	1.33

^a Initiator: ethyl 2-bromoisobutyrate; catalyst: CuBr ; ligand: Me_6Tren ; [M]/[I]/[C]/[L]: molar concentration ratio of monomer/initiator/catalyst/ligand; M_n (GPC): molecular weight obtained from GPC using PSt as standards; M_n (NMR): molecular weight obtained from ^1H NMR. Me_6Tren = tris[2-(dimethylamino)ethyl]amine; THF = tetrahydrofuran.

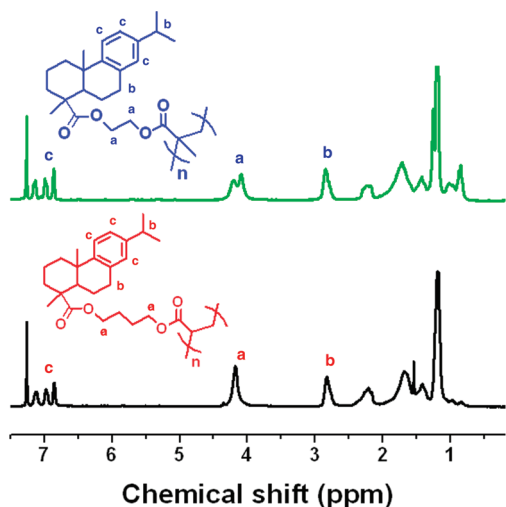


Figure 3. ^1H NMR spectra of PDABA and PDAEMA prepared by ATRP (corresponding to runs 3 and 5 from Table 1, respectively).

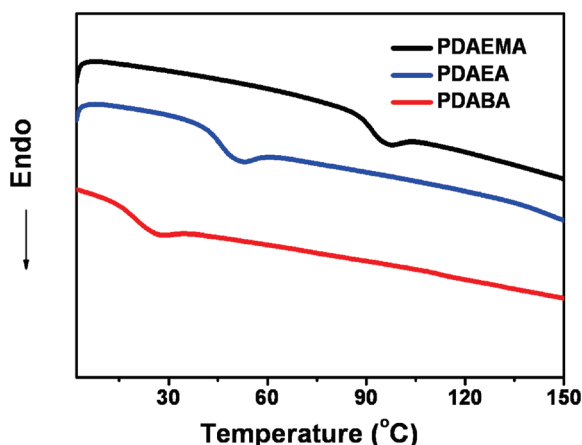


Figure 4. DSC traces of PDAEA, PDABA, and PDAEMA prepared by ATRP (corresponding to runs 2, 3, and 5 from Table 1, respectively).

The first stage exhibited a slight weight loss with similar onsets at 220 °C, although PDAEA showed noticeable higher loss (~15 wt %) than that of PDABA and PDAEMA (~5 wt %). TGA traces of the second stage were similar to onsets at nearly 325 °C followed by almost complete weight loss due to full decomposition of polymer backbones.

In conclusion, we have developed a strategy to synthesize a new class of monomers and well-defined renewable polymers from abundant low-cost natural resources: gum rosin. Highly pure rosin-derived acrylate and methacrylate monomers were prepared through simple esterification with dehydroabietic acid. The first well-defined rosin-derived polymers with low polydispersity and controlled molecular weight were obtained using ATRP. These polymers exhibited tunable thermal properties (e.g., glass transition temperature) by simple manipulation of monomer structures. The successful synthesis of rosin-derived monomers and well-defined polymers opens a new avenue toward development of a variety of rosin-derived renewable polymeric materials (e.g., thermoplastic elastomers, hybrids, composites) as potential competing replacement for petroleum-derived plastics.

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Supporting Information Available: Experimental details, GC-MS data, 2D-COSY ^1H NMR spectra, GPC data, and TGA traces of polymers (Figures S1–S8). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Williams, C. K.; Hillmyer, M. A. *Polym. Rev.* **2008**, *48*, 1–10.
- (2) Corma, A. I. S.; Velt, A. *Chem. Rev.* **2007**, *107*, 2411–2502.
- (3) Dodds, D. R.; Gross, R. A. *Science* **2007**, *318*, 1250–1251.
- (4) Mecking, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1078–1085.
- (5) Okada, M. *Prog. Polym. Sci.* **2002**, *27*, 87–133.
- (6) Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederick, W. J.; Hallett, J. P.; Leak, D. L.; Liotta, C. L.; Mielenz, J. R.; Murphy, R.; Templer, R.; Tschaplinski, T. *Science* **2006**, *311*, 484–489.
- (7) Gunera, F. S.; Yagci, Y.; Erçiyas, A. T. *Prog. Polym. Sci.* **2006**, *31*, 633–670.
- (8) Meier, M. A. R.; Metzger, J. O.; Schubert, U. S. *Chem. Soc. Rev.* **2007**, *36*, 1788–1802.
- (9) Wool, R. P.; Knot, S. N.; LaScala, J. J.; Bunker, S. P.; Lu, J.; Thieleman, W.; Can, E.; Morry, S. S.; Williams, G. I. In *Advancing Sustainability through Green Chemistry and Engineering*; Lankey, R. L., Ed.; American Chemical Society: Washington, DC, 2002; Vol. 823, pp 177–204.
- (10) U.S. Biobased Products: Market Potential and Projections Through 2025. Office of the Chief Economist, Office of Energy Policy and New Uses, U.S. Department of Agriculture 2008, <http://www.usda.gov/oce/reports/energy/BiobasedReport2008.pdf>.
- (11) Lowe, J. R.; Tolman, W. B.; Hillmyer, M. A. *Biomacromolecules* **2009**, *10*, 2003–2008.
- (12) Kobayashi, S.; Lu, C.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2009**, *131*, 7960–7961.
- (13) Maiti, S.; Das, S.; Maiti, M.; Ray, A. In *Polymer Application of Renewable-Resource Materials*; Carraher, C. E., Sperling, L. H., Eds.; Plenum Press: New York, 1983; p 129.
- (14) Maiti, S.; Ray, S. S.; Kundu, A. K. *Prog. Polym. Sci.* **1989**, *14*, 297–338.
- (15) Pine Chemical Association, Newsletter, February 2010, http://www.pinechemicals.org/clientuploads/Publications/No2020_FEB2010_PCA_Newsletter.pdf.
- (16) Roy, S. S.; Kundu, A. K.; Maiti, S. *Eur. Polym. J.* **1990**, *26*, 471–474.
- (17) Atta, A. M.; Nassar, I. F.; Bedawy, H. M. *React. Funct. Polym.* **2007**, *67*, 617–626.
- (18) Zhang, Y.; Heath, R. J.; Hourston, D. J. *J. Appl. Polym. Sci.* **2000**, *75*, 406–416.
- (19) Bicu, I.; Mustata, F. *Macromol. Mater. Eng.* **2000**, *280–281*, 47–53.
- (20) Bicu, I.; Mustata, F. *J. Polym. Sci., Polym. Chem.* **2005**, *43*, 6308–6322.
- (21) Mustata, F.; Bicu, I. *Eur. Polym. J.* **2010**, *46*, 1316–1327.
- (22) Do, H.-S.; Park, J.-H.; Kim, H.-J. *J. Appl. Polym. Sci.* **2009**, *111*, 1172–1176.
- (23) Wang, J.-F.; Lin, M.-T.; Wang, C.-P.; Chu, F.-X. *J. Appl. Polym. Sci.* **2009**, *113*, 3757–3765.
- (24) Lee, J. S.; Hong, S. *Eur. Polym. J.* **2002**, *38*, 387–392.
- (25) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921–2990.
- (26) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661–3688.
- (27) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379–410.
- (28) For simplicity, the names of monomers are not strictly followed the IUPAC nomenclature system.
- (29) Matyjaszewski, K.; Nakagawa, K.; Jasieczek, C. G. *Macromolecules* **1998**, *31*, 1535–1541.
- (30) Pascual, S.; Coutin, B.; Tardi, M.; Polton, A.; Vairon, J. P. *Macromolecules* **1999**, *32*, 1432–1437.

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Yijun Zheng¹, Kejian Yao¹, Sangmin Lee¹, David Chandler¹,
Jifu Wang², Chunpeng Wang², Fuxiang Chu², Chuanbing Tang^{1*}

¹University of South Carolina, Department of Chemistry and Biochemistry,
631 Sumter Street, Columbia, South Carolina 29208

²Chinese Academy of Forestry, Beijing, China 100086

Email: tang.c@chem.sc.edu

Supporting Information

Materials.

Dehydroabietic acid (DHAA, ~90%) was obtained from Wuzhou Chemicals, China and used as received. Tetrahydrofuran (THF, Aldrich) and anisole (Aldrich) were refluxed with sodium and distilled just before use under nitrogen atmosphere. Tris(2-(dimethylamino)ethyl)amine (Me₆Tren) was prepared according to the literature.¹ 2-Hydroxyethyl acrylate (2-HEA) (stabilized, 97%, Aldrich), 2-hydroxyethyl methacrylate (2-HEMA) (stabilized, 97%, Aldrich) and 4-hydroxybutyl acrylate (4-HBA) (stabilized, 97%, Aldrich) were passed through basic alumina column. Oxalyl chloride, triethylamine, sodium borohydride (NaBH₄), acryloyl chloride, ethyl-2-bromoisobutyrate (EBiB) and copper(I) bromide (99.999%) were used as received (Aldrich).

Characterization.

Gas Chromatography-Mass Spectrometry (GC/MS) analysis of DHAA raw materials was carried out on Agilent 6890N Network GC system and Agilent 5973 mass selective detector. Prior to GC/MS analysis, DHAA was transformed into methyl DHAA by using TMAH (tetramethyl ammonium hydroxide) in the solution of methanol because DHAA was not gasified due to the presence of the carboxylic acid group. GC was performed on Agilent HP-5

capillary column (30m×0.25mm×0.25μm) with an oven temperature of 250 °C. Carrier gas was He at a flow-rate of 1.0 mL/min. The temperature of injection port was 250 °C. 0.2 μL of sample was injected into the GC system. The mass spectrometer was operated in electron ionization mode. The temperature of ion source was 230 °C.

¹H NMR and ¹³C NMR spectra were recorded on Bruker ARX 300 and ARX 400 spectrometers. The chemical shifts were recorded in ppm (δ) relative to tetramethylsilane. Mass spectra were measured on a VG S70 mass spectrometer. Gel permeation chromatography (GPC) was performed at room temperature on a Varian system equipped with a Varian 356-LC refractive index detector and a Prostar 210 pump. The columns were STYRAGEL HR1, HR2 (300×7.5 mm) from Varian. HPLC grade THF was used as eluent at a flow rate of 1 ml/min. THF and samples were filtered over microfilters with pore size of 0.2μm (Nylon, Millex-HN 13 mm Syringes Filters, Millipore, USA). The columns were calibrated using polystyrene standards. The thermal transitions of the copolymers were recorded using differential scanning calorimetry (DSC) on a TA Q200 calorimeter in a temperature range from 0 to 180 °C at a heating rate of 10 °C min⁻¹ under a continuous nitrogen flow. All the data were collected during the second heating process after cooling at 2 °C min⁻¹ from 180 °C. The average sample mass was about 5 mg, and the nitrogen flow rate was 50 mL min⁻¹. Thermogravimetric analysis (TGA) data were collected on TA SDT Q600 using a heating rate of 5 °C/min from 25 to 600°C under helium.

Synthesis.

Dehydroabietic ethyl acrylate (DAEA): dehydroabietic acid (10 g, 33 mmol) was dissolved in dichloromethane (60 mL). Oxalyl chloride (5.66 g, 36.3 mmol) was added slowly. After the solution was stirred at 0°C for 3 h, excessive oxalyl chloride was removed by distillation. Triethylamine (5.0 g, 57 mmol) and 2-HEA (4.39 g, 37 mmol) were subsequently added. The reaction mixture was stirred at 0°C overnight and then washed with 5% NaCO₃ solution followed by drying over anhydrous Na₂SO₄ and evaporated to dryness. The product was further purified by silica gel chromatography (ethyl acetate /hexane: 1/9 (v/v)) to afford white powder (5.0 g) in 45% yield. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.26-7.14 (d, *J* = 8.21 Hz,

1H; Ar), 7.01-6.99 (d, J = 8.51 Hz, 1H; Ar), 6.91-6.87(s, 1H; Ar), 6.43-6.38 (d, J = 17.14 Hz, 1H; vinyl), 6.16-6.06(dd, J = 10.52, 10.41 Hz, 1H; vinyl), 5.85-5.82 (d, J = 10.00 Hz, 1H; vinyl), 4.36-4.27 (m, 4H; OCH₂), 2.93-2.80(m, 3H), 2.34-1.21 (m, 21H). ¹³C NMR (400 MHz, CDCl₃, δ , ppm):16.49, 18.59, 21.76, 24.00, 25.19, 30.12, 33.48, 36.55, 36.95, 37.96, 44.77, 47.71, 62.01, 62.16, 123.96, 124.21, 126.91, 128.00, 131.34, 134.66, 145.76, 146.86, 165.86, 178.32. MS (ESI, m/z) for C₂₅H₃₄O₄: 398 (M⁺).

Dehydroabietic ethyl methacrylate (DAEMA): The synthesis was similar to DAEA synthesis, using 2-HEMA instead of 2-HEA. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 7.17-7.15 (d, J = 8.16 Hz, 1H; Ar), 7.00-6.98 (d, J = 7.79 Hz, 1H; Ar), 6.87-6.85(s, 1H; Ar), 6.17-6.09 (s, 1H; vinyl), 5.58-5.55 (s, 1H; vinyl), 4.38-4.26 (m, 4H; OCH₂), 2.84-2.77(m, 3H), 1.91-1.16 (m, 23H). ¹³C NMR (400 MHz, CDCl₃, δ , ppm):16.49, 18.26, 18.58, 21.74, 23.99, 24.02, 25.15, 30.06, 33.48, 36.57, 36.95, 37.97, 44.77, 62.22, 62.51, 123.95, 124.17, 126.03, 126.90, 134.64, 135.94, 145.75, 146.85, 167.09, 178.31. MS (ESI, m/z) for C₂₆H₃₆O₄: 412 (M⁺).

Dehydroabietic ethyl methacrylate (DABA): The synthesis was similar to DAEA synthesis, using 4-HBA instead of 2-HEA. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 7.12-7.09 (d, J = 7.83 Hz, 1H; Ar), 6.95-6.92 (d, J = 7.42 Hz, 1H; Ar), 6.83-6.81(s, 1H; Ar), 6.35-6.30 (d, J = 16.49 Hz, 1H; vinyl), 6.08-5.99 (dd, J = 10.31, 10.80 Hz, 1H; vinyl), 5.76-5.73 (d, J = 10.26 Hz, 1H; vinyl), 4.13-3.98 (m, 4H; OCH₂), 2.82-2.71(m, 3H), 1.80-1.14 (m, 25H). ¹³C NMR (400 MHz, CDCl₃, δ , ppm):14.00, 16.81, 19.30, 22.35, 23.82, 25.30, 25.45, 26.93, 30.16, 31.62, 33.31, 36.10, 37.47, 37.97, 45.00, 47.86, 64.65, 123.66, 124.00, 124.22, 126.64, 126.95, 127.94, 145.75, 146.85, 167.09, 178.31. MS (ESI, m/z) for C₂₇H₃₈O₄: 426 (M⁺).

Dehydroabietic acrylate (DAA): dehydroabietic acid (6.6 g, 22 mmol) was dissolved in diethyl ether (100 mL). NaBH₄ (4.54 g, 0.120 mol) in 40 mL diethyl ether were added in 30 min. After the solution was stirred at room temperature overnight, excessive NaBH₄ was destroyed by adding 120 mL methanol slowly. The reaction mixture was washed with 5% H₂SO₄ and the organic layer was collected and washed with 5% NaHCO₃ solution followed by drying over anhydrous Na₂SO₄ and evaporated to dryness, yielding dehydroabietic alcohol,

which was used immediately for next step reactions. Triethylamine (26 mL) and acryloyl chloride (4 g, 44 mmol) were added slowly to the above dehydroabietic alcohol in dichloromethane (150 mL). The reaction mixture was stirred at 0°C overnight and the solution was washed with 5% NaCO₃ solution followed by drying over anhydrous Na₂SO₄ and evaporated to dryness. The product was further purified by silica gel chromatography (ethyl acetate /hexane: 1/9 (v/v)) to afford white powder (3.29g) in 46% yield. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.20-7.17 (d, *J* = 8.78 Hz, 1H; Ar), 7.01-6.99 (d, *J* = 8.78 Hz, 1H; Ar), 6.90-6.87(s, 1H; Ar), 6.41-6.35 (d, *J* = 17.39 Hz, 1H; vinyl), 6.14-6.05 (dd, *J* = 10.30, 10.44 Hz, 1H; vinyl), 5.82-5.78 (d, *J* = 9.57 Hz, 1H; vinyl), 4.09-3.78 (dd, 2H; OCH₂), 2.93-2.74(m, 3H), 1.83-1.17 (m, 21H). ¹³C NMR (400 MHz, CDCl₃, δ, ppm): 17.54, 18.58, 19.03, 24.02, 25.45, 30.30, 33.44, 35.60, 36.97, 37.49, 37.75, 44.32, 68.00, 72.47, 123.91, 124.22, 126.91, 128.54, 130.70, 134.79, 145.62, 147.12, 166.40. MS (ESI, *m/z*) for C₂₃H₃₂O₂: 340 (M⁺).

ATRP: use **PDAEA** synthesis as an example. A mixture of monomer DAEA (0.5 g, 1.2 mmol), Me₆Tren (2.76mg, 0.012 mmol), EBiB (1.84 μl, 0.012 mmol) and THF (3 mL) was introduced into a polymerization tube. After three freeze-pump-thaw cycles, CuBr (1.8 mg, 0.012 mmol) was added to the flask while the contents were at a solid state and deoxygenated by vacuum followed by back-filling with nitrogen three times. The tube was heated at 90 °C for 16 hours. The polymerization was stopped by diluting the reaction mixture with THF. The products were precipitated in methanol three times and dried to constant weight, yielding white powder. The conversion of monomers was 29% as determined from ¹H NMR analysis. M_n (PDAEA) = 11500 g/mol, PDI (PDAEA) = 1.20. ¹H NMR (300 MHz, CDCl₃, δ): 6.7-7.2 (broad, aromatic); 3.9-4.4 (d, OCH₂CH₂O); 2.6-2.8 (protons next to aromatic ring); 1-2.5 (broad, -CH₂CH- and all other protons from hydrophenanthrene ring).

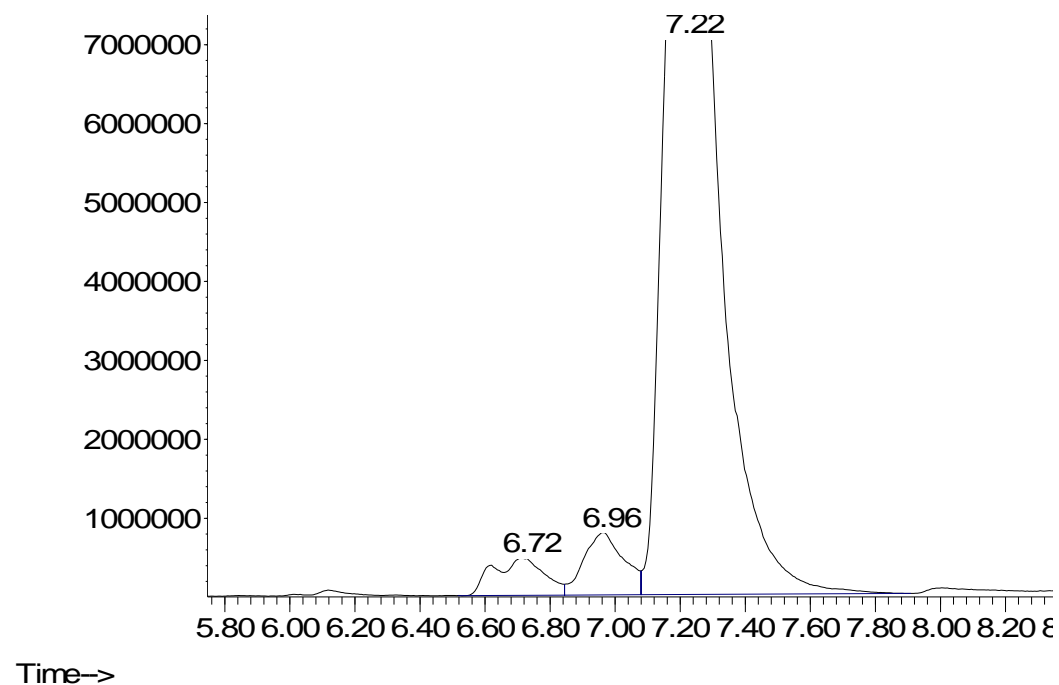


Figure S1. GC traces of DHAA.

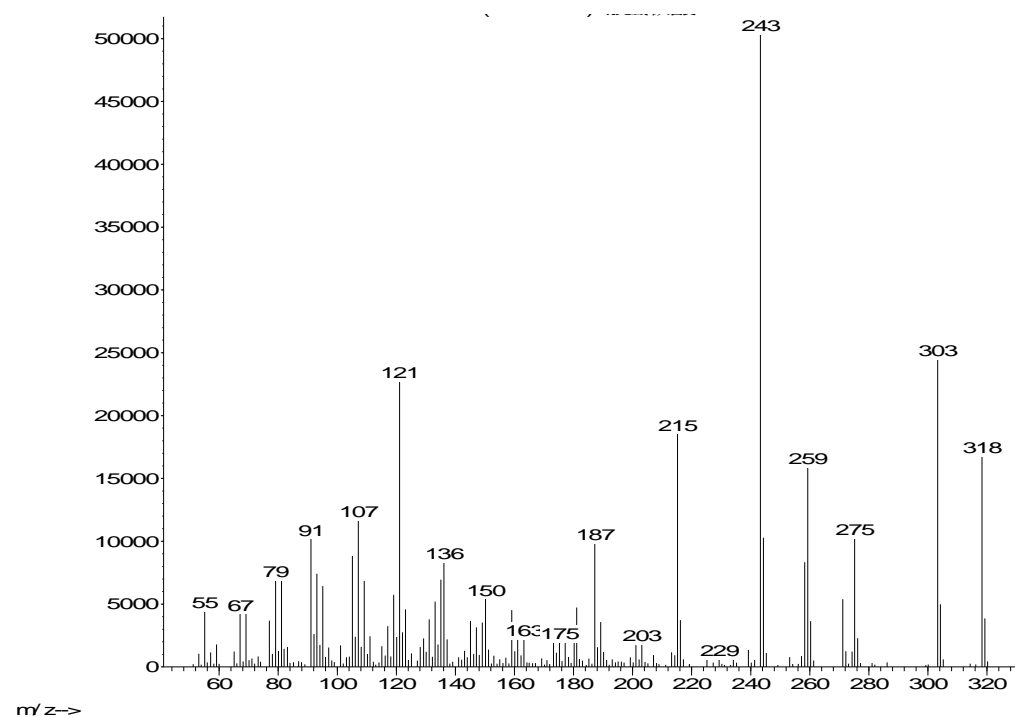


Figure S2. Mass spectrum of DHAA at 6.72 min.

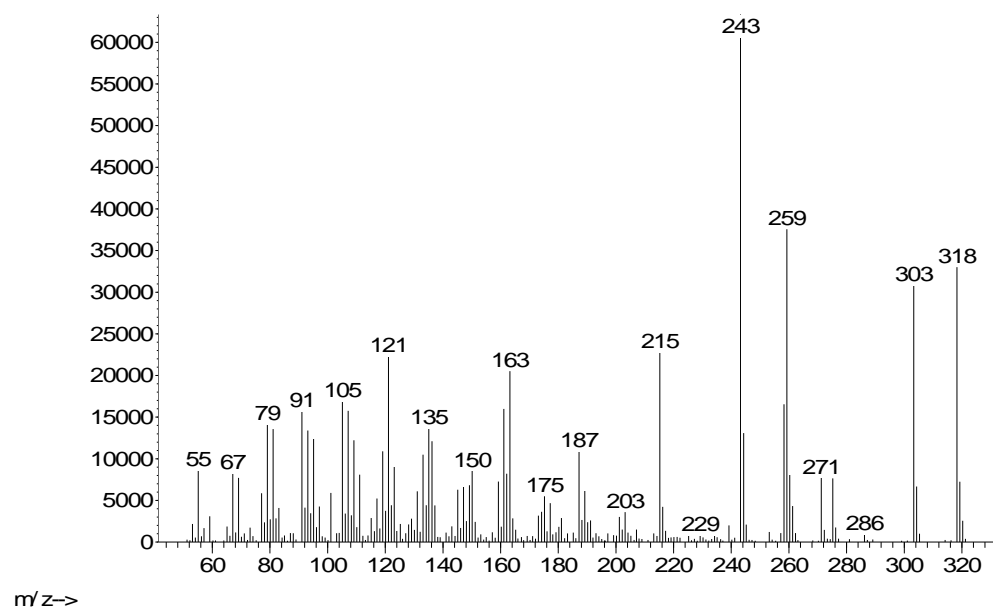


Figure S3. Mass spectrum of DHAA at 6.93 min.

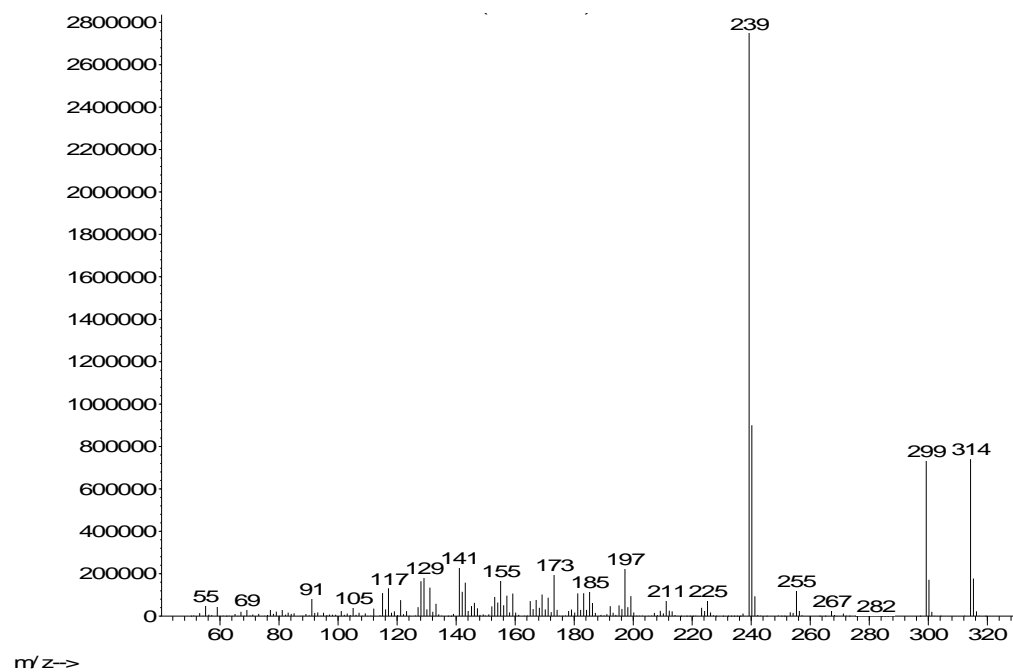


Figure S4. Mass spectrum of DHAA at 7.22 min.

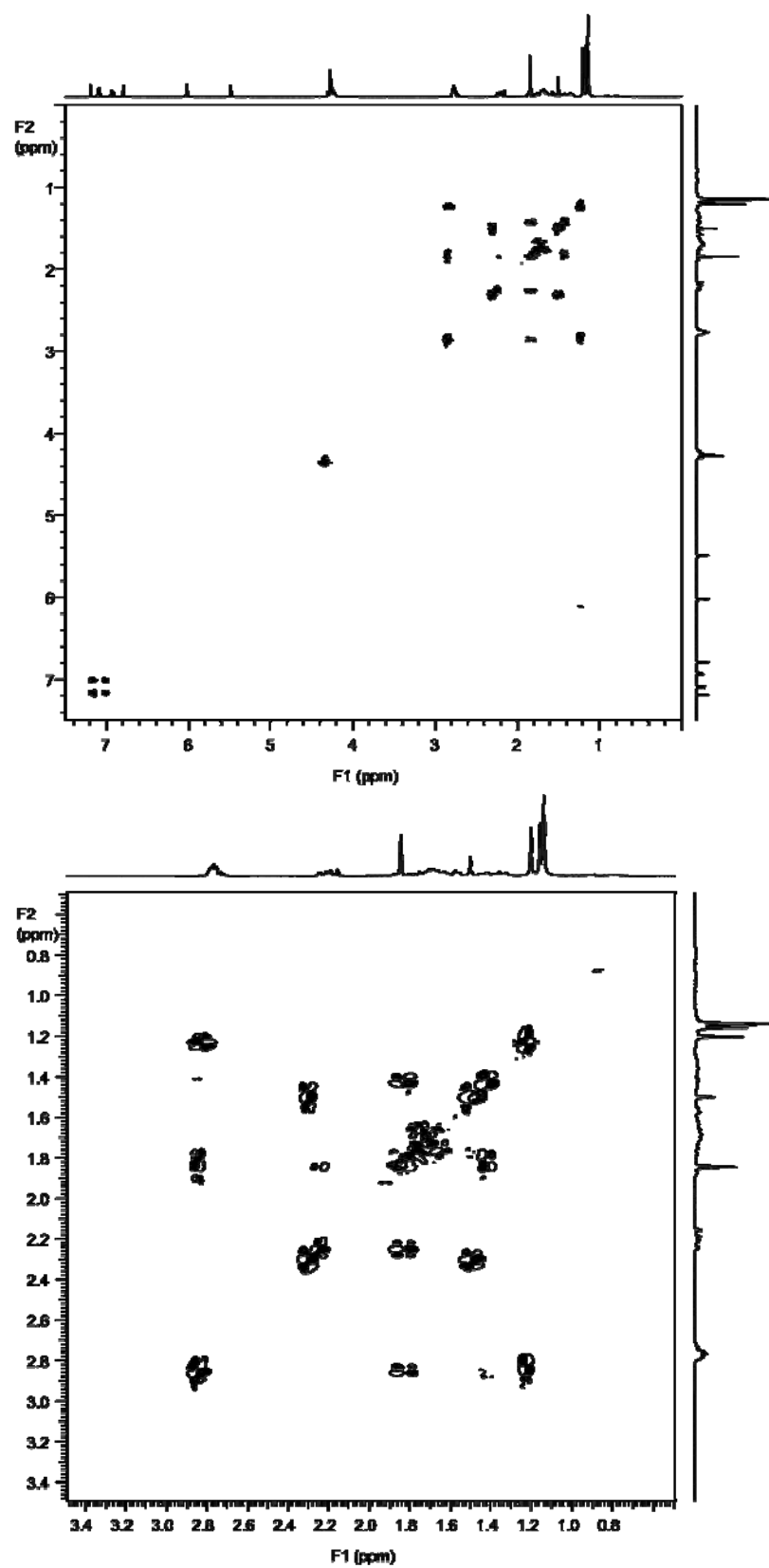


Figure S5. ^1H NMR 2D-COSY spectra of vinyl monomer DAEMA.

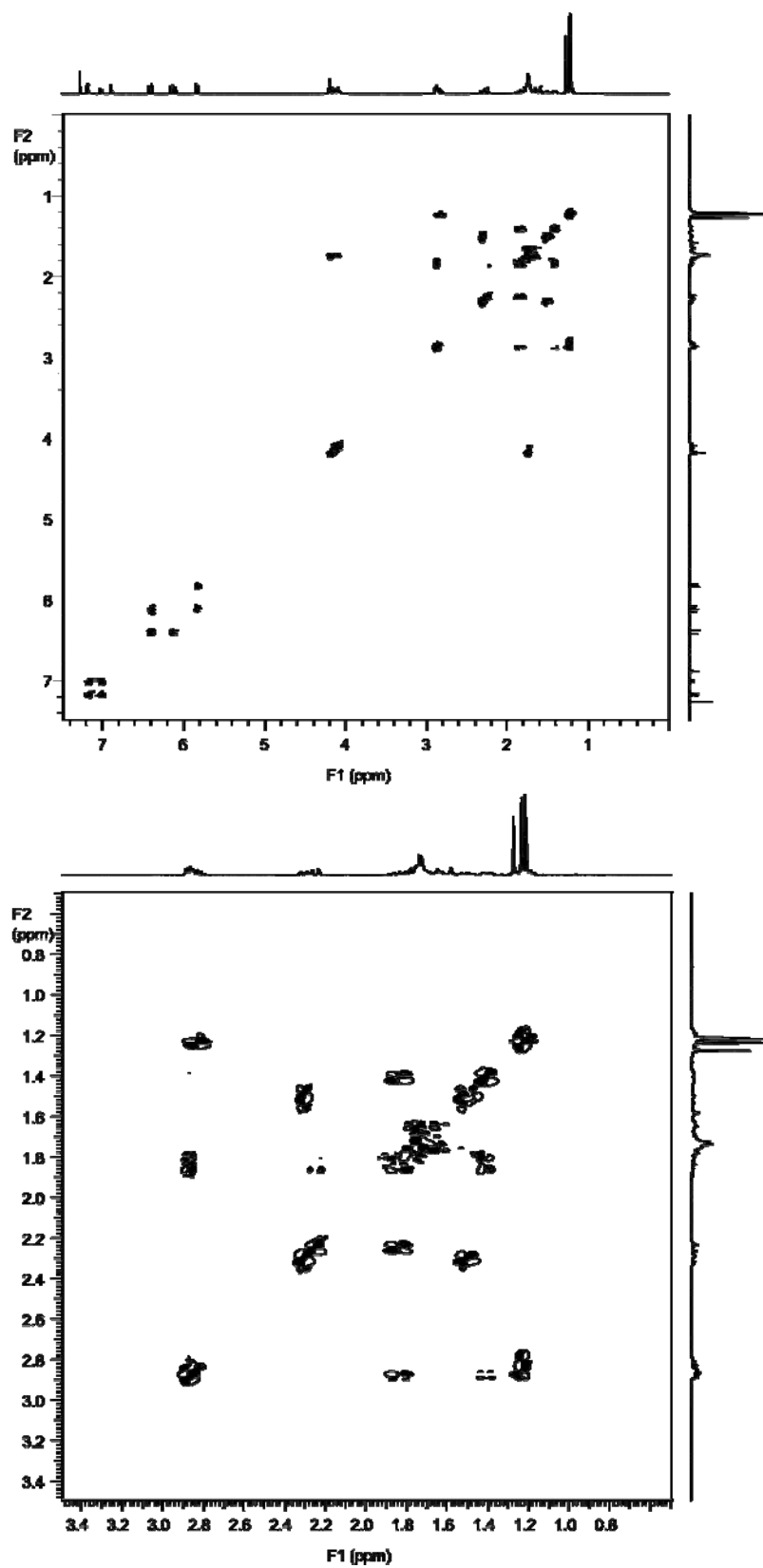


Figure S6. ^1H NMR 2D-COSY spectra of vinyl monomer DABA.

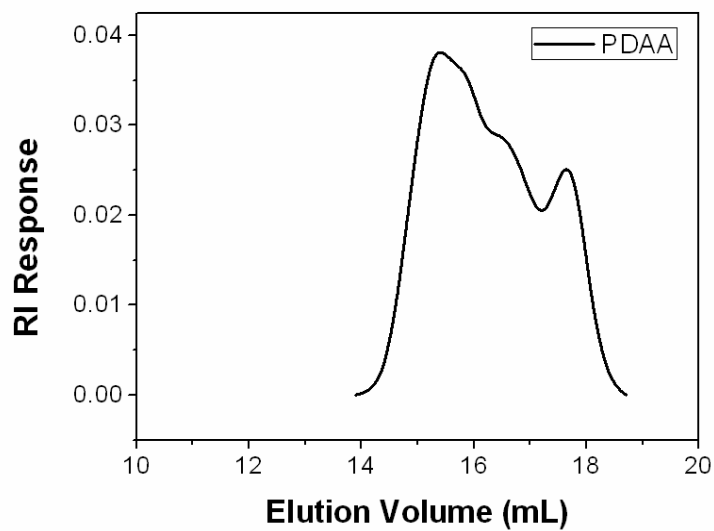


Figure S7. GPC trace of PDAA prepared by ATRP (Run 1 from Table 1).

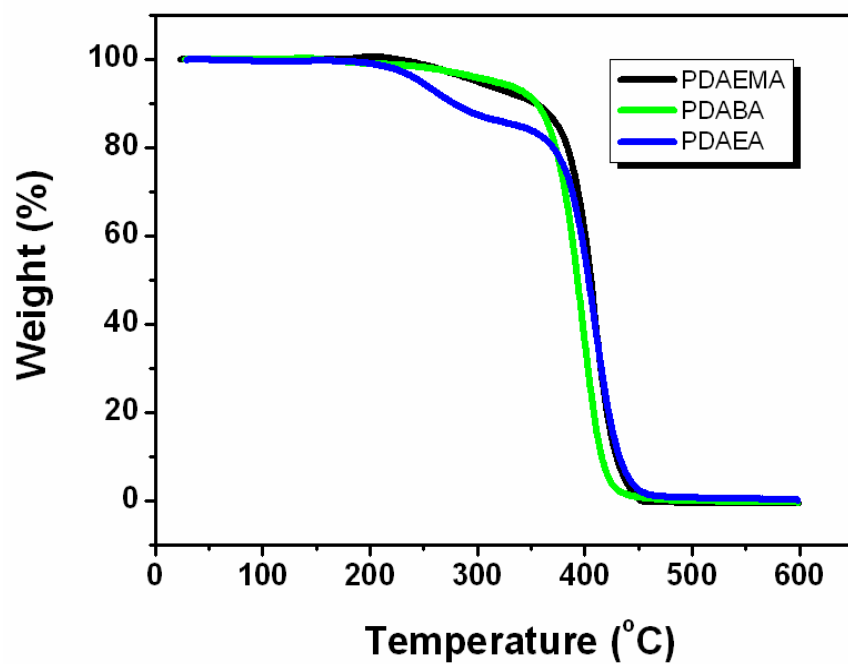


Figure S8. TGA traces of PDAAEA, PDABA and PDAEMA polymers prepared by ATRP (Runs 2, 3 and 5 from Table 1).

References:

1. Xia, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules*, **1998**, 31, 5958–5959