

Supplementary Information

Functional of Polyesters Derived from Alternating Copolymerization of Norbornene Anhydride and Epoxides

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Experimental Section

Materials: All chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received unless otherwise specified. All polymerizations were mixed in an MBraun glovebox under argon. All liquid epoxides were stirred over powdered CaH₂ at RT for 24h, vacuum distilled, and stored in the glovebox. 4-(dimethylamino)pyridine (DMAP) was recrystallized from diethyl ether at -30°C. Aluminum isopropoxide was distilled under vacuum and stored in the glovebox. Anhydrous toluene was purchased from Sigma Aldrich and used as received. To dry NB for higher molecular weight polymers, NB was dissolved in THF with powdered calcium hydride and stirred overnight at RT. The slurry was transferred into the glovebox, filtered and evaporated to dryness. The chromium salen catalyst,¹ Grubbs 3rd generation catalyst,² and 2-((2-(2-methoxyethoxy)ethoxy)-methyl)oxirane (MEMO)³ were synthesized as previously reported.

Instrumentation: NMR spectra were all taken in CDCl₃ and recorded on a Varian U400, VXR500, or U500 NMR spectrometer. Gel Permeation Chromatography (GPC) was performed on a system equipped with an isocratic pump (Model 1200, Agilent Technology, Santa Clara, CA, USA) and an Optilab rEX refractive index detector (Wyatt Technology, Santa Barbara, CA, USA). Separations were performed using serially connected size exclusion columns (10² Å, 10³ Å, 10⁴ Å, 10⁵ Å Phenogel columns, 5 µm, 300 × 7.8 mm, Phenomenex, Torrance, CA, USA). The mobile phase consisted THF at a rate of 1 mL min⁻¹. Samples were filtered through a 0.45 µm PTFE filter before analysis. The molecular weight and polydispersity of polymers were determined by comparing to polystyrene standards. MALDI-TOF spectra were taken on a Bruker Ultra Flex extreme equipped with a 337 nm nitrogen laser. An accelerating voltage of 23 kV was applied, acquiring 1000 shots for each sample. Samples were prepared using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malonitrile (DCTB) as the matrix (10 mg mL⁻¹ in THF), and sodium trifluoroacetate as the cationization agent (10 mg mL⁻¹ in THF). Samples were dissolved in THF (10 mg mL⁻¹). Solutions of matrix, salt, and polymer were mixed in a volume ratio of 4 : 1 : 1,

respectively. The mixed solutions (0.5 μl) were hand spotted on a stainless steel MALDI target and allowed to dry completely. All spectra were recorded in reflectron mode. Thiol-ene reactions were performed using an Omnicure S1000 UV curing lamp (Lumen Dynamics, Mississauga, ON, Canada) equipped with an adjustable collimating adaptor. The lamp was adjusted to 100% power and positioned such that the measured intensity on the sample was $\sim 50 \text{ mW cm}^{-2}$. Differential scanning calorimetry (DSC) was conducted on a TA Instruments Q20 with a Liquid Nitrogen Cooling System. Tzero aluminum pan and lids were used to hold samples. Scans were conducted under nitrogen at a flow rate of 50 mL/min. Samples were run under a Heat/Cool/Heat Program with heating and cooling rates set to $10 \text{ }^\circ\text{C min}^{-1}$. First cooling and second heating curves are shown. The second heating curve was used to calculate T_g using TA Universal Analysis software.

General Polymerization Procedure: In a glovebox, anhydride (0.96 mmol), epoxide (0.96 mmol), catalyst (24 mg mL^{-1} in toluene, 100 μl , 0.004 mmol), DMAP (12 mg mL^{-1} in toluene, 38.5 μl , 0.004 mmol), and toluene (246 μl) were added to a 3 mL crimp vial with a magnetic stir bar, sealed, and heated outside the glovebox on an aluminum heating block at 110°C for 5 hours. Dissolution of the resulting polymer reaction in DCM or CHCl_3 (1 mL), precipitating into hexanes (12 mL), and drying gave the final product as a light red powders or as hard clear red solids depending upon the T_g of the polymer. Yields were typically $>70\%$.

Conversion of Monomer

Reactions were removed from heating block and allowed to cool. A small aliquot was removed and dissolved in CDCl_3 . Conversion monitored by ^1H NMR spectroscopy, comparing the methylene bridging protons of NB monomer at $\sim \delta 1.5$ and $\sim \delta 1.8$ to those of the polymer which appear at $\delta 1.2 - 1.5$.

Thiol-ene Click of 2-phenylethanethiol with NB-*alt*-SO

In a quartz reaction flask, NB-*alt*-SO (30 mg, 0.1 mmol NB) was mixed with 2-phenylethanethiol (54 μl , 0.4 mmol) and 2,2-dimethoxy-2-phenylacetophenone (5 mg, 0.02 mmol) in 2 mL THF. The flask was purged with nitrogen for 5 minutes, sealed, and placed under UV irradiation (365nm , 50 mW cm^{-2}) for 1 hour. The reaction was directly precipitated into hexanes (12 mL), followed by dissolution in minimal DCM, and re-precipitation into hexanes. Drying of polymer gave the final product as a yellow solid (41.2 mg, 94 %).

Tetrazine Click of 3,6-Di-2-pyridyl-1,2,4,5-tetrazine with NB-*alt*-SO

A solution of NB-*alt*-SO (20 mg, 0.067 mmol NB) and 2,6-dipyridyl-1,2,4,5-tetrazine (19 mg, 0.08 mmol) in 1.5 mL of a 2:1 v/v solution of DCM/DMSO was stirred overnight at room temperature. The resulting solution was clear and slightly pink in color due to excess tetrazine. The remaining solution was diluted in DCM, washed five times with water, then dried over sodium sulfate, concentrated, then precipitated into hexanes (12 mL) to give a yellow solid upon drying (17 mg, 47%).

ROMP Crosslinking of NB-*alt*-SO

In a glovebox, 150mg of NB-*alt*-SO was dissolved into 1 mL of DCM, followed by the addition of 2.5 mg of Grubbs 3rd generation catalyst. After allowing the solution to sit for 2-3 hours, gelation was observed.

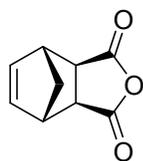
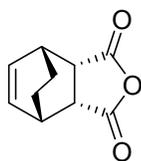
LCST behavior of polymer

A 0.5 mg mL⁻¹ solution of (NB-*alt*-MEMO) in water was placed in a temperature controlled cell. Once the solution has reached the desired temperature, the cuvette was quickly placed into a UV-Vis spectrophotometer and % transmittance was read at 500nm.

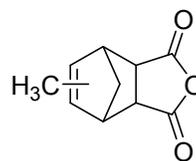
Table S1. Various characteristics of NB containing or related polymers

Entry	Anhydride	Epoxide	Catalyst	Conv (%)	M_n (kDa)	M_w/M_n	T_g
1 ^a	NB	SO	Al(OiPr) ₃	55	5.5	1.96	--
2 ^a	NB	SO	Mg(OEt) ₂	58	4.7	1.73	--
3	<i>exo</i> -NB	AGE	Chromium(III) salen + DMAP	100	8.2	1.15	13
4	BHA	AGE	Chromium(III) salen + DMAP	100	8.2	1.41	29
5	MNB	AGE	Chromium(III) salen + DMAP	--	12.6	1.39	28
6	NB + 2-phenylethanethiol	SO	--	--	3.2	1.09	68
7	NB + 3,6-Di-2-pyridyl-1,2,4,5-tetrazine	SO	--	--	3.2	1.19	183

Reaction conditions: [anhydride]:[epoxide]:[1]:[DMAP] = 250:250:1:1 in toluene, 110°C, 5 h. ^a Reaction performed for 48h. *exo*-NB = *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride; BHA = *cis*-endo-Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride; MNB = methyl-5-norbornene-2,3-dicarboxylic anhydride.

*exo*-NB

BHA



MNB

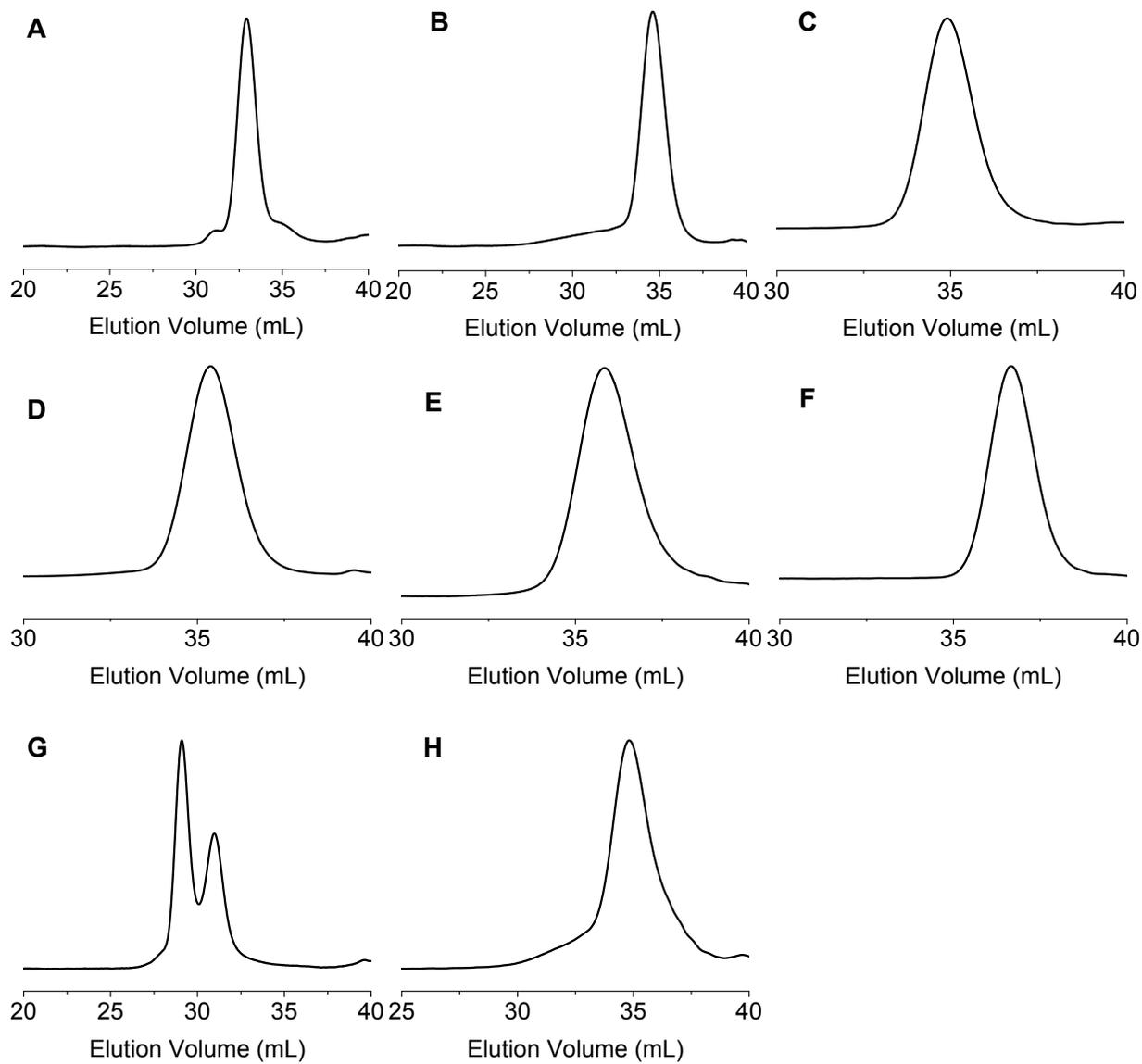


Figure S1. GPC-dRI traces of polymers from Table 1. (A) NB-*alt*-ECH (B) NB-*alt*-AGE (C) NT-*alt*-PGE (D) NB-*alt*-CHO (E) NB-*alt*-SO (F) NB-*alt*-BO (G) NB-*alt*-PGE dry NB (H) NB-*alt*-MEMO.

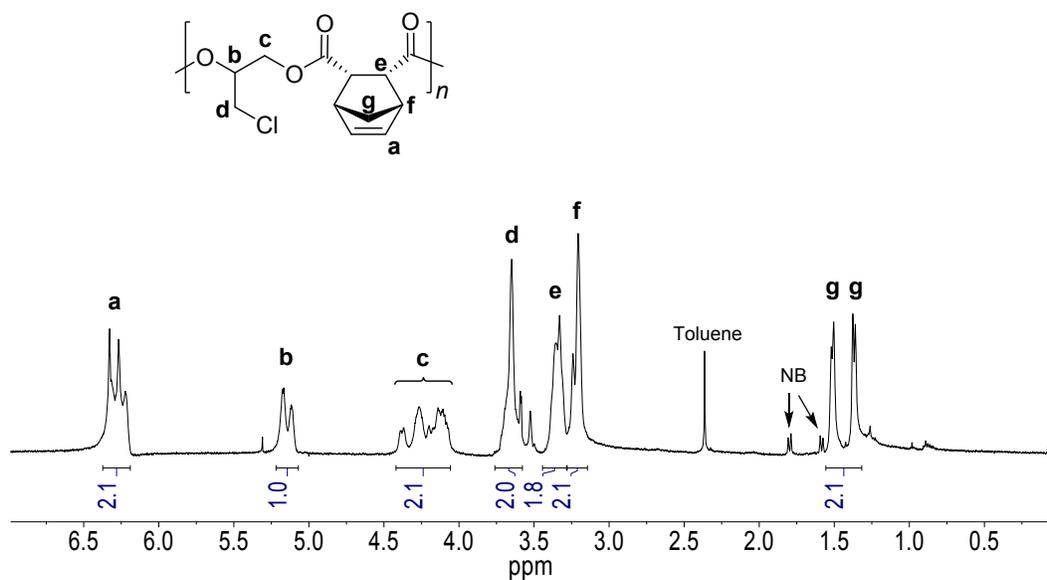


Figure S2. ^1H NMR spectrum of poly(*cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride-*alt*-epichlorohydrin) (NB-*alt*-ECH) (Table 1, entry 1). Yield = 97%, conversion = 89%.

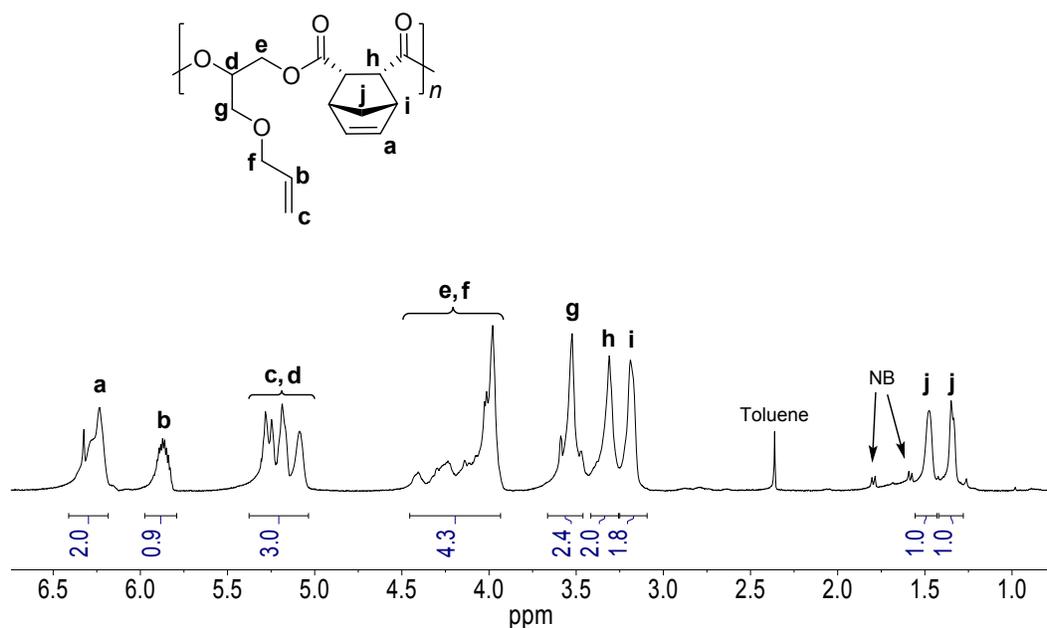


Figure S3. ^1H NMR spectrum of poly(*cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride-*alt*-allyl glycidyl ether) (NB-*alt*-AGE) (Table 1, entry 2). Yield = 95%, conversion = 95%.

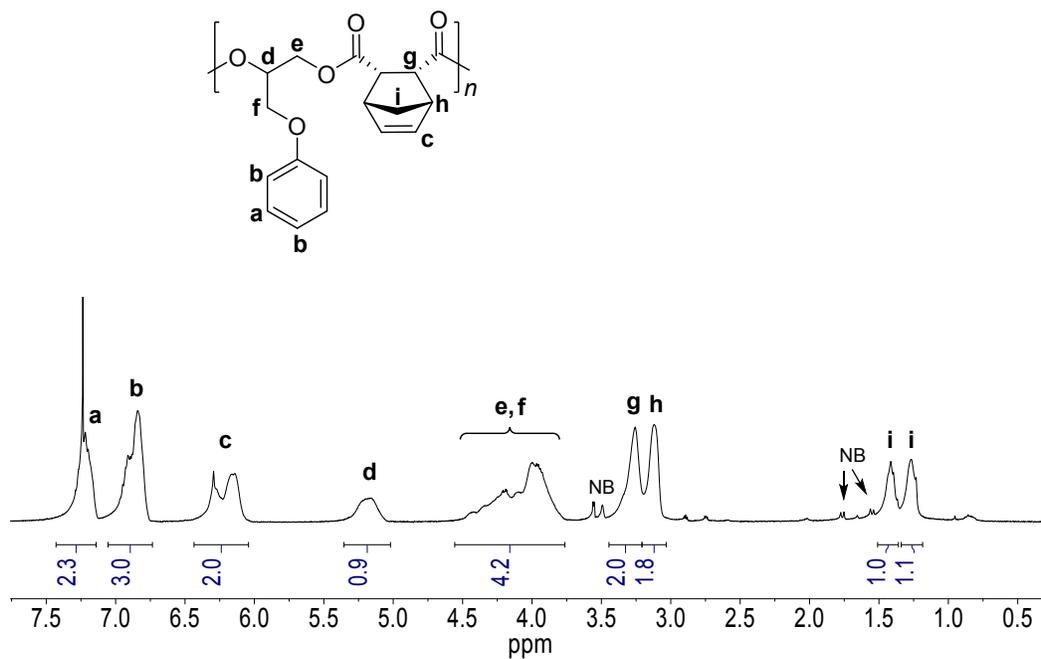


Figure S4. ¹H NMR spectrum of poly(*cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride-*alt*-phenyl glycidyl ether) (NB-*alt*-PGE) (Table 1, entry 3). Yield = 74%, conversion = 98 %.

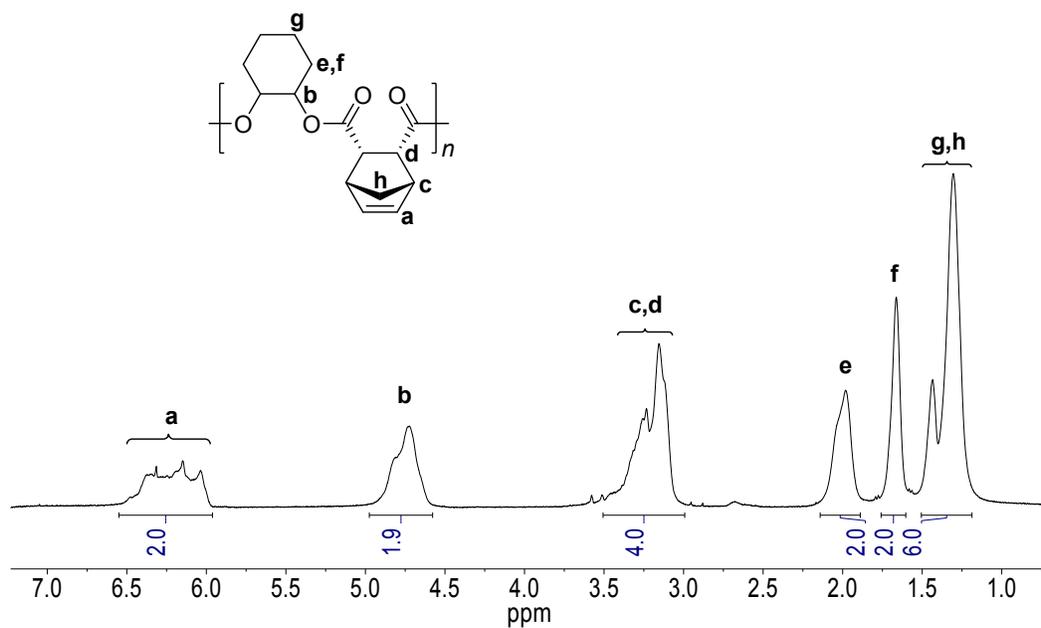


Figure S5. ¹H NMR spectrum of poly(*cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride-*alt*-cyclohexene oxide) (NB-*alt*-CHO) (Table 1, entry 4). Yield = 78%, conversion = 97%.

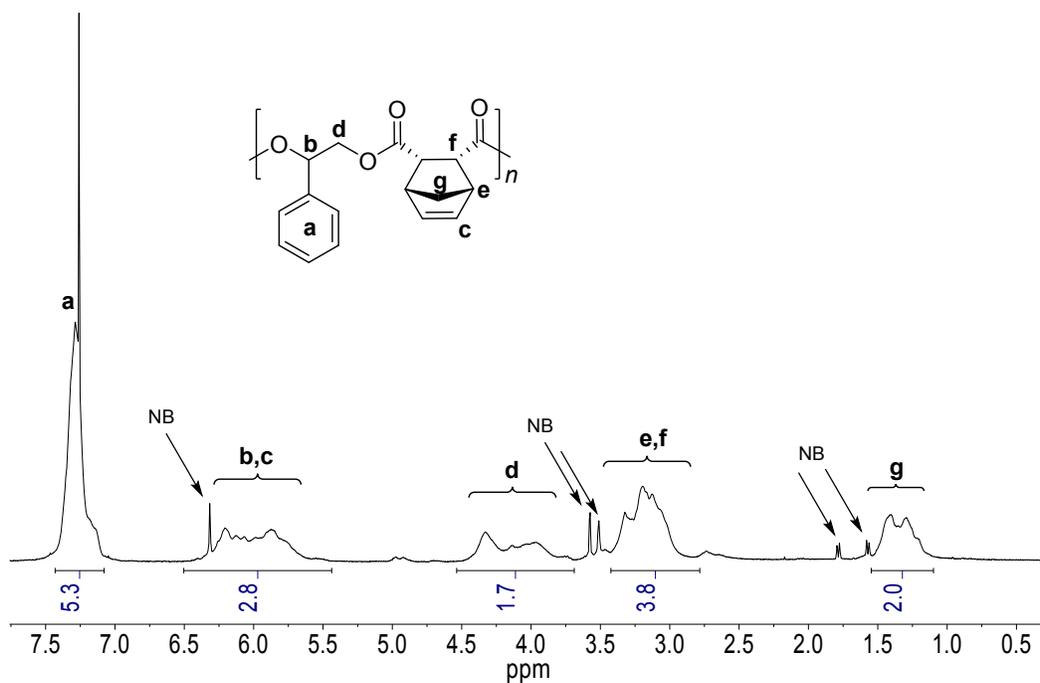


Figure S6. ¹H NMR spectrum of poly(*cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride-*alt*-styrene oxide) (NB-*alt*-SO) (Table 1, entry 5). Yield = 75%, conversion = 94%.

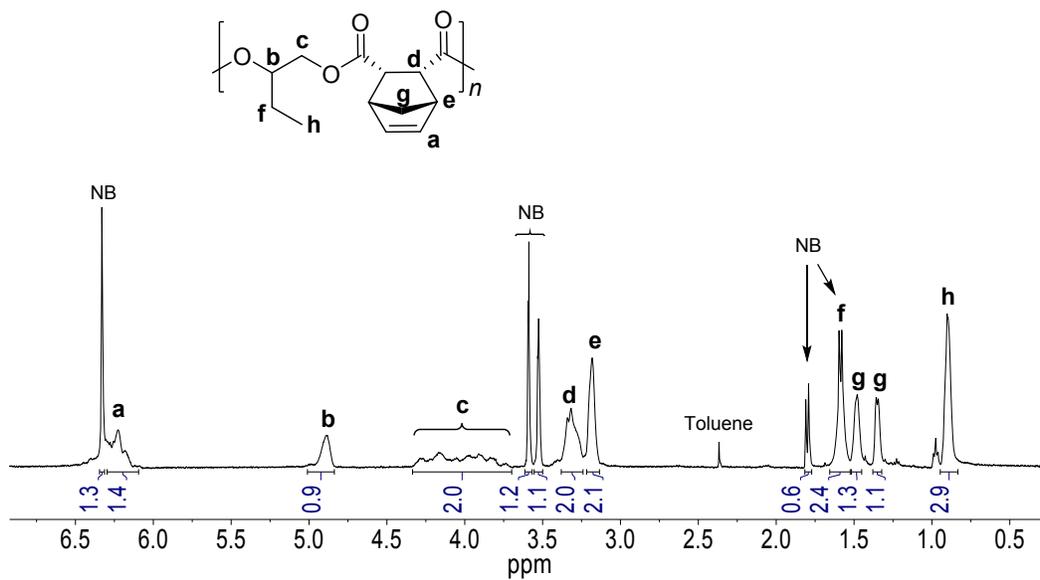


Figure S7. ¹H NMR spectrum of poly(*cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride-*alt*-butane oxide) (NB-*alt*-BO) (Table 1, entry 6). Yield = 69%, conversion = 67%.

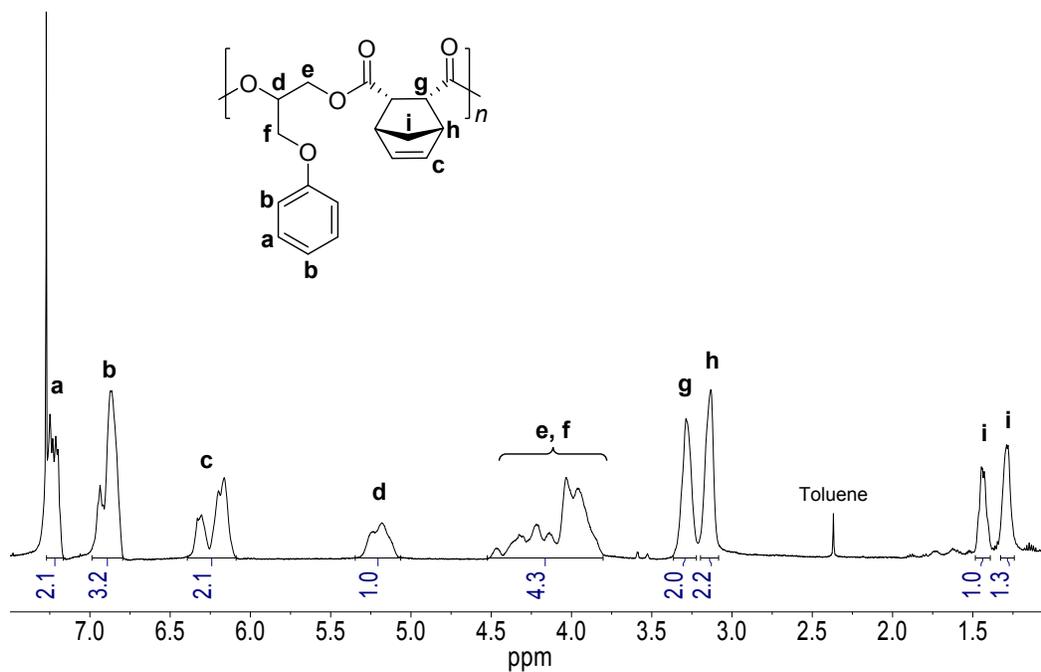


Figure S8. ¹H NMR spectrum of poly(*cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride-*alt*-phenyl glycidyl ether) (NB-*alt*-PGE) with NB dried over CaH₂ (Table 1, entry 7). Yield = 95%, conversion >99%.

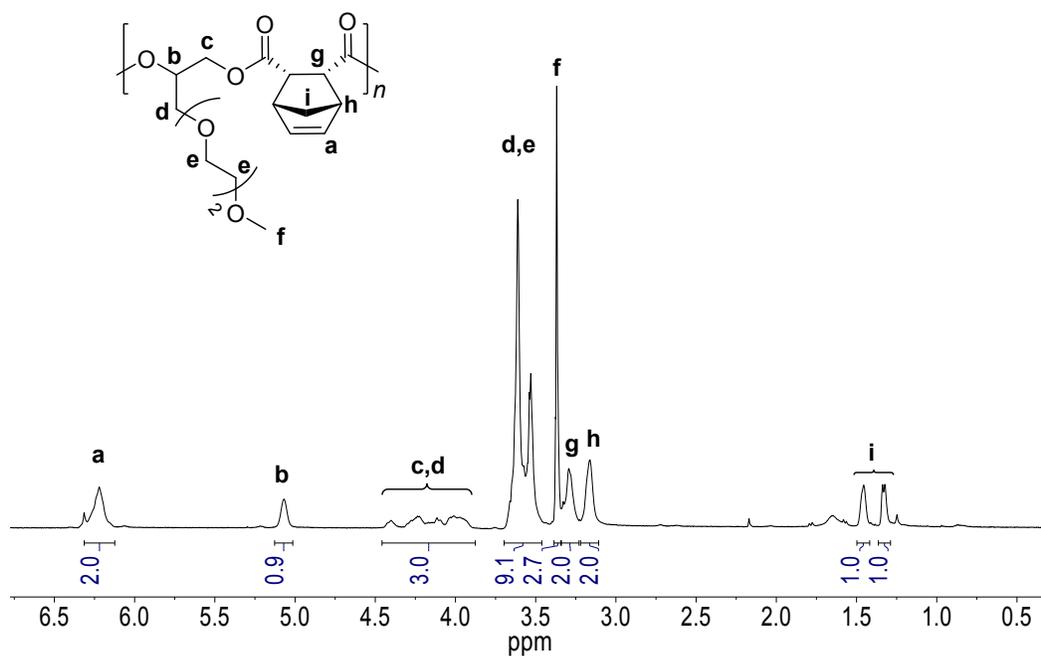


Figure S9. ^1H NMR spectrum of poly(*cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride-*alt*-2-((2-(2-methoxyethoxy)-ethoxy)methyl)oxirane) (NB-*alt*-MEMO) (Table 1, entry 8). Conversion = 93%, Yield = 93%.

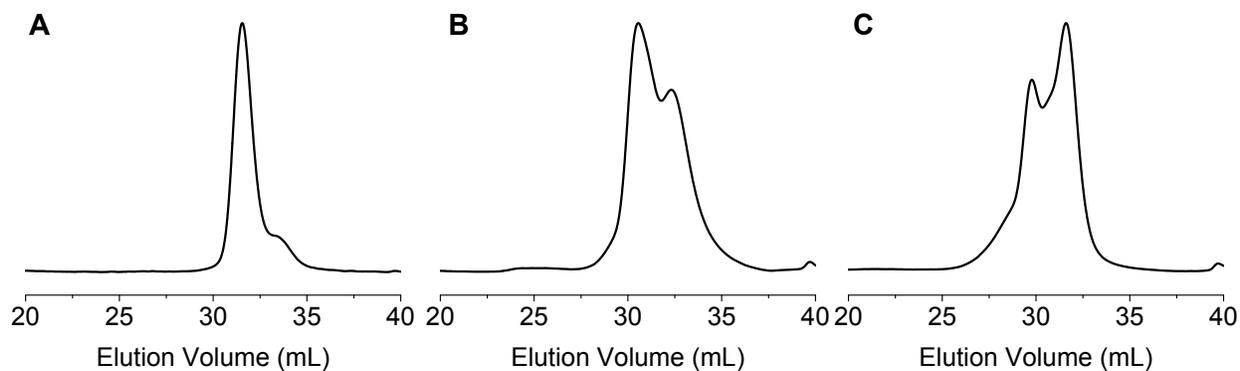


Figure S10. GPC-dRI elution profiles of polymers listed in Table S1. (A) *exo*-NB-*alt*-AGE (B) BHA-*alt*-AGE (C) MNB-*alt*-AGE.

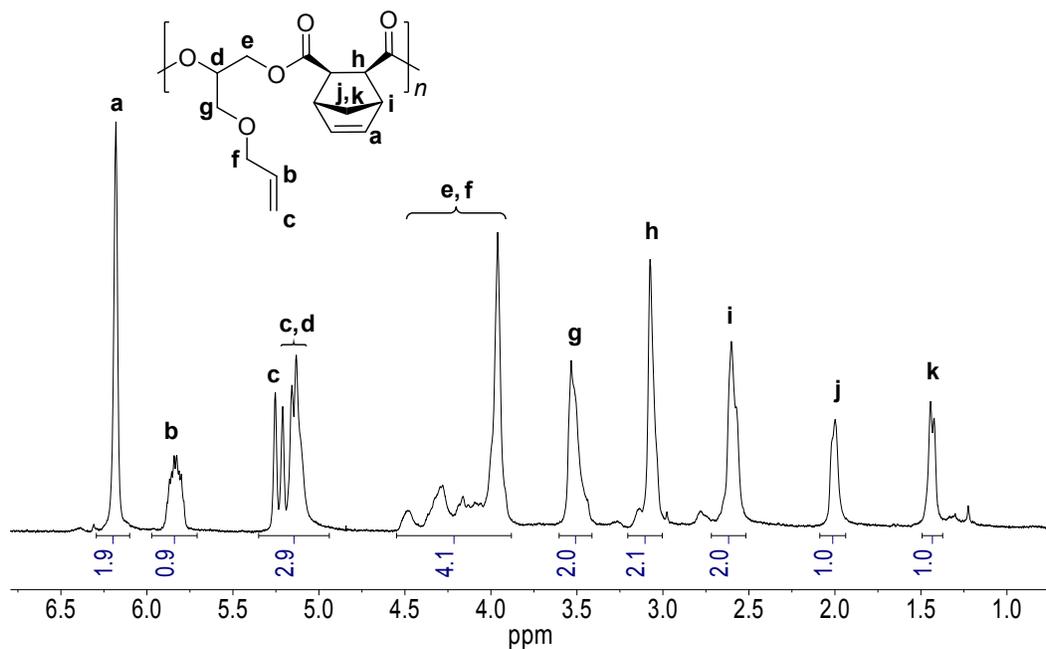


Figure S11. ^1H NMR spectrum of poly(*cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride-*alt*-allyl glycidyl ether) (*exo*-NB-*alt*-AGE) (Table S1, entry 1). Yield = 73%, conversion >99%.

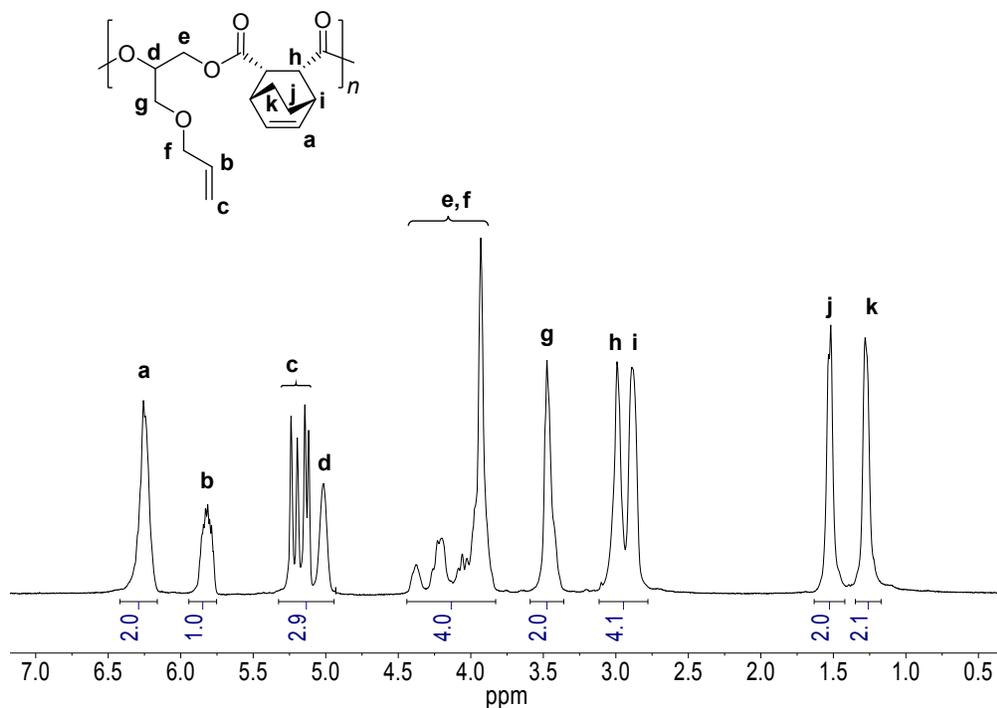


Figure S12. ^1H NMR spectrum of poly(*cis*-*endo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride-*alt*-allyl glycidyl ether) (BHA-*alt*-AGE) (Table S1, entry 2). Yield = 83%, conversion >99%.

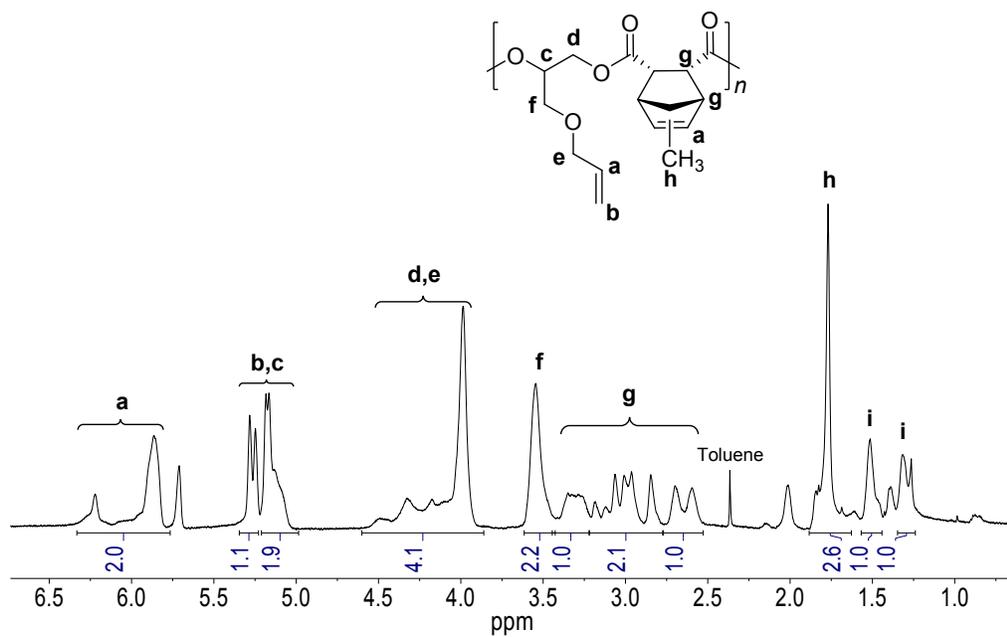


Figure S13. ^1H NMR spectrum of poly(methyl-5-norbornene-2,3-dicarboxylic anhydride-*alt*-allyl glycidyl ether) (MNB-*alt*-AGE) (Table S1, entry 4). Yield = 86%, conversion > 99%.

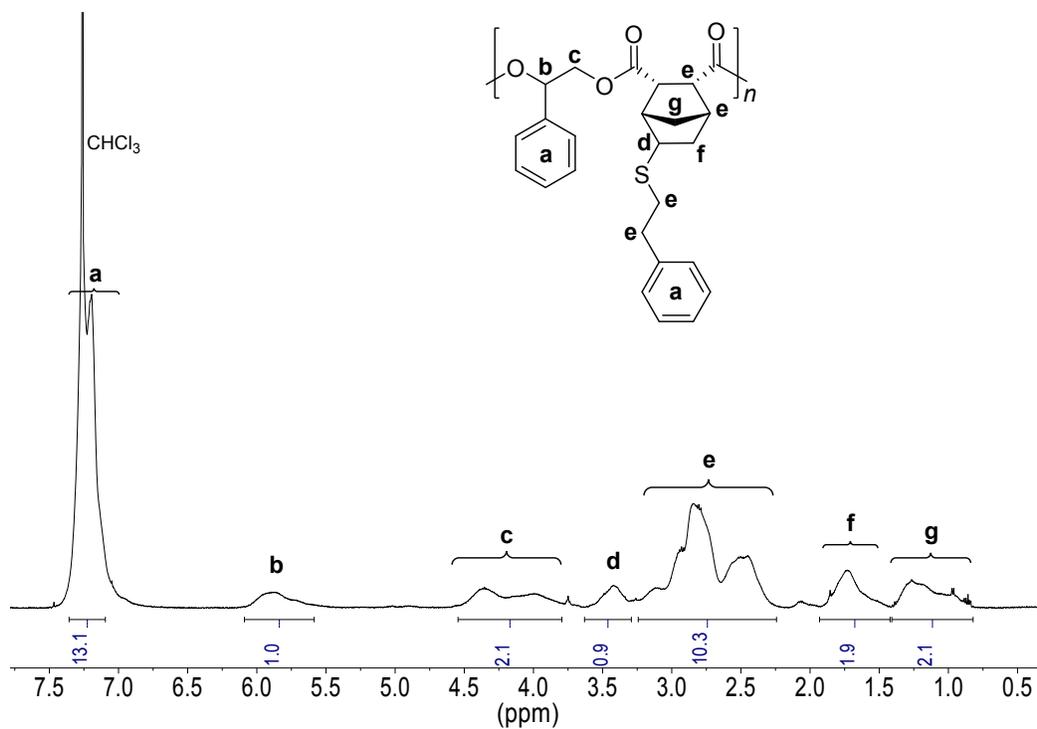


Figure S14. ^1H NMR spectrum of 2-phenylethanethiol modified NB-*alt*-SO.

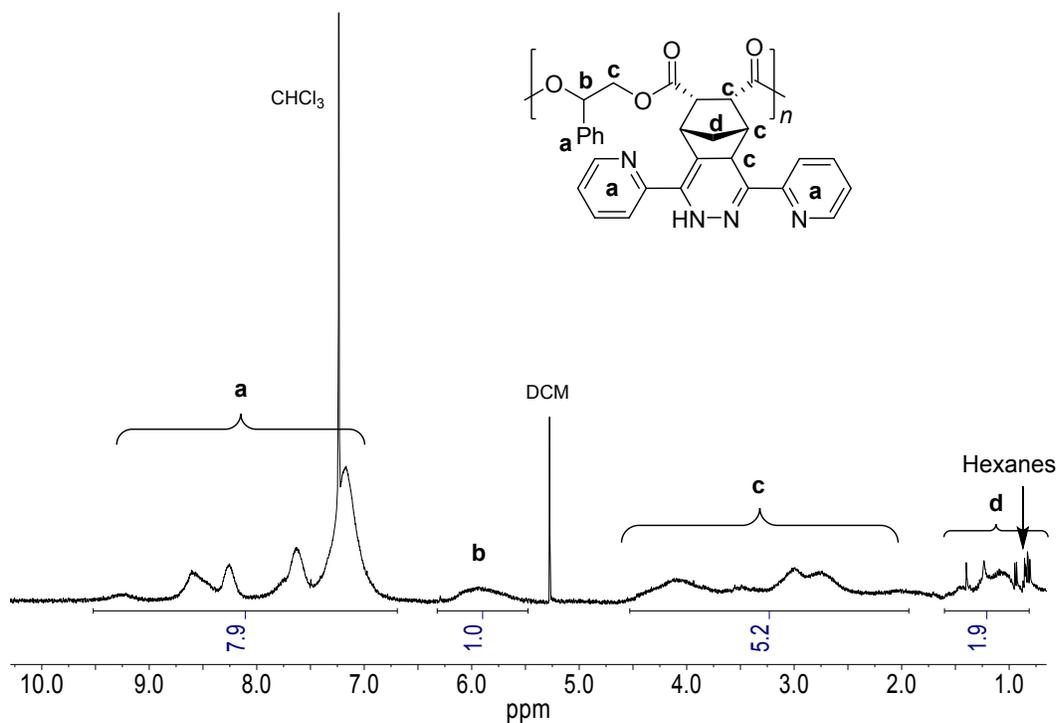


Figure S15. ^1H NMR spectrum of 3,6-di-2-pyridyl-1,2,4,5-tetrazine modified NB-*alt*-SO.

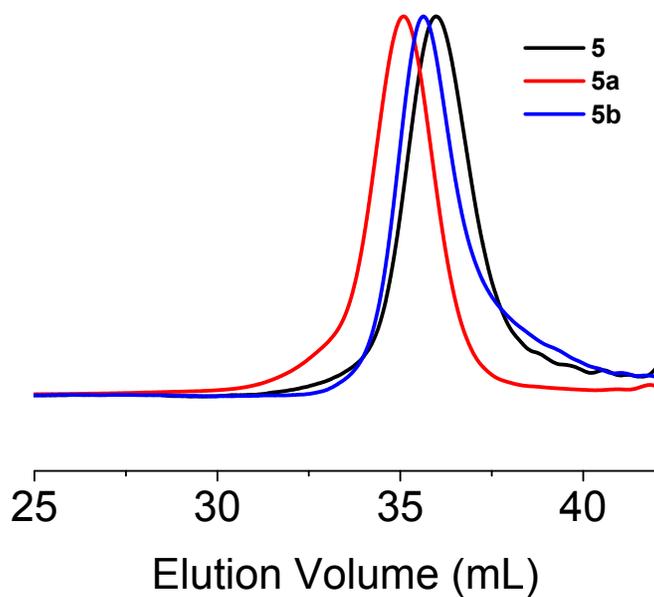


Figure S16. GPC trace of NB-*alt*-SO (5) after modification with 2-phenylethanethiol (5a) or with 3,6-di-2-pyridyl-1,2,4,5-tetrazine (5b). The shift in peak 5b is less substantial as significant compaction of the polymer structure is likely, given that the ^1H NMR spectrum shows broad peaks likely due to π - π interactions of the added tetrazine units.

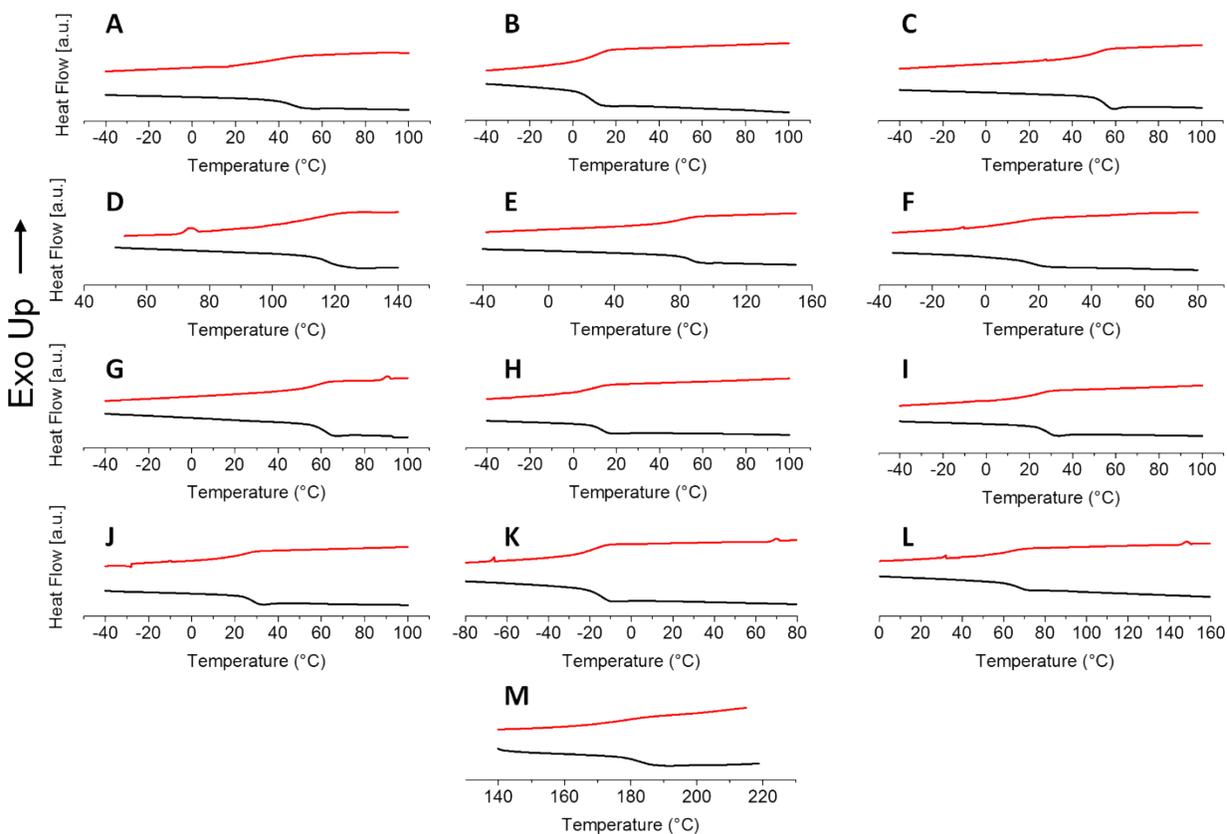


Figure S17. DSC traces for various polymers. Black = 2nd heating, red = 1st cooling. (A) NB-*alt*-ECH (B) NB-*alt*-AGE (C) NB-*alt*-PGE_{3.1k} (D) NB-*alt*-CHO (E) NB-*alt*-SO (F) NB-*alt*-BO (G) NB-*alt*-PGE_{17k} (H) *exo*-NB-*alt*-AGE (I) BHA-*alt*-AGE (J) MNB-*alt*-AGE (K) NB-*alt*-MEMO (L) **5a** (M) **5b**.

(1) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Fang, C. C.; Billodeaux, D. R.; Reibenspies, J. H. *Inorg. Chem.* **2004**, *43*, 6024-6034.

(2) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics* **2001**, *20*, 5314-5318.

(3) Jungk, S. J.; Moore, J. A.; Gandour, R. D. *J. Org. Chem.* **1983**, *48*, 1116-1120.