Supplementary Information (SI) for Materials Advances.

Supporting Information

Tuning the Mechanical Performance of Polydicyclopentadiene Copolymers Through Dicyclopentadienone Monomer Incorporation

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Contents

Experimental Details

General Considerations

All commercial materials were used as received. Dicyclopentadiene (DCPD), 5-ethylidene-2-norbornene (ENB), and 4-dimethylaminopyridine (DMAP) were obtained from Millipore Sigma. Dichloromethane (DCM), pyridine (Py), and acetic anhydride (Ac_2O) were obtained from Fisher Scientific. Meso-tetraphenylporphyrin (TPP) was obtained from AK scientific. Tri-*n*-butyl-phosphite (TBP) was obtained from Alfa Aesar. Grubbs second generation catalyst (GC2) was obtained from Chem-Impex.

^{1}H and ^{13}C NMR spectra were obtained using a Bruker AVANCE 300 (300.27 MHz for ^{1}H, 75.51 MHz for ^{13}C) or a Bruker AVANCE NEO 500 (500.27 MHz for ^{1}H, 125.81 MHz for ^{13}C). Data were processed using MestReNova. Singlet = s, d = doublet, t = triplet, br = broad, app = apparent.

Melting points were taken on an SRS digimelt and a Gallenkamp melting point apparatus.

IR spectra were recorded using an Agilent Cary 630 FTIR spectrometer with diamond ATIR attachment. Samples were measured as solids and pressed into the crystal using the supplied press.

Differential scanning calorimetry samples were run on a TA instruments DSC25 using TZero aluminum DSC pans with hermetic lid. A pin hole was added for solid samples using the tip of a 21 ½ gauge needle. An empty TZero aluminum DSC pan with TZero aluminum hermetic lid and pin hole was used as a reference. Samples were measured from 40°C to 250°C then cooled to −30 °C at 20 °C/min to erase thermal history then ramped at 10 °C/min from −30 °C to 250 °C. The T_g was obtained from the second trace.

Thermogravimetric analysis was done on a TA instruments SDT Q600. Samples were heated at 20 °C per minute to a maximum temperature of 600°C, under a nitrogen atmosphere.

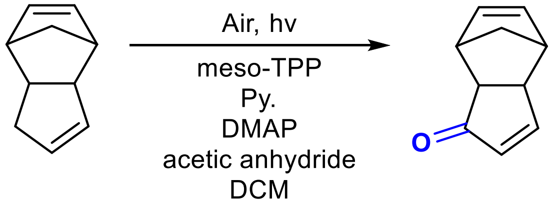
Dynamic mechanical thermal analysis was done on an Anton Paar Modular Compact Rheometer 302 fitted with an Anton Paar SRF-12 geometry and CTD 600 oven. Samples were measured through 25°C-T_g + 40 °C or 250 °C over a period of 85 minutes. A logarithmic strain of 0.01–0.1 % at 1 Hz and a normal force of −0.1 N was used. Regular dimensioned 25 x 10 x 3 mm (Length x width x height) bar type samples were machined by the University of Victoria Science Machine Shop from reaction injection molded rectangular plaques. Glass transition temperatures were obtained from the peak of the loss factor and storage modulus at 25 °C or the closest next point. DMTA data is displayed in stack plots with each component having its own scale.

Tensile testing was performed using an Admet MtestQuattro machine. ASTM Type V dog bone samples were machined by the University of Victoria Science Machine Shop from reaction injection molded rectangular plaques. The ends of the samples were fixed between the grips and subjected to a loading rate of 10 mm/min. Force-displacement curves were obtained and converted to stress-strain curves. Stress is defined as the force on the cross-section area of the sample (MPa) while strain represents the displacement to the initial length of the specimen (mm/mm, presented as dimensionless). Strain was obtained as recorded from the instrument. Young's modulus was obtained from the slope of the linear region of the stress–strain curve. Modulus of toughness was determined as the area under the stress–strain curve. Ultimate tensile strength was determined from the maximum of the stress–strain curve.

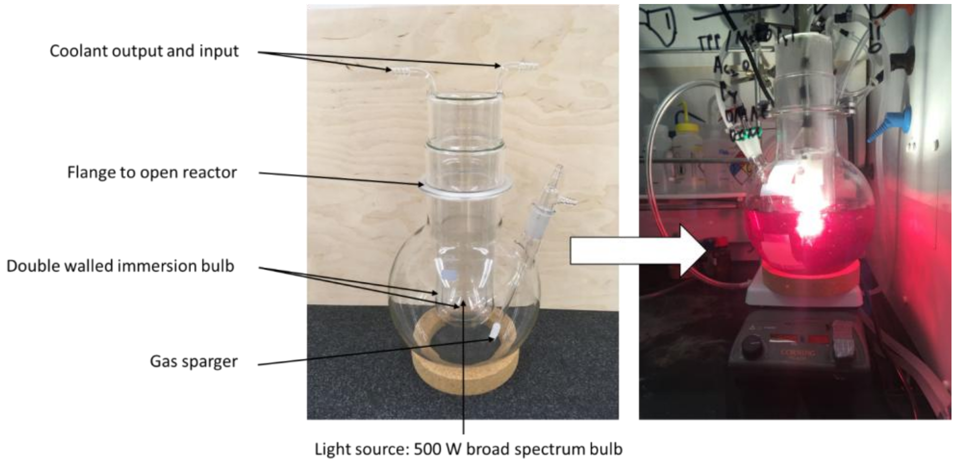
Swelling experiments were performed by subjecting polymer chunks to high vacuum at 0.15 mmHg for 2 hours prior to weighing. Samples were weighed then submerged in 10 mL of either methanol or toluene in a sealed vial. After the desired interval, samples were removed from the solvent, dabbed dry and weighed. Samples were then placed back into the solvent.

Vickers microhardness testing was performed using a Buehler Wilson VH 3100 instrument with a Vickers diamond-shaped indenter using a dwell time of 10 seconds and a 1 kg load. Regular dimensioned 25 x 10 x 3 mm (Length x width x height) bar type samples were machined by the University of Victoria Science Machine Shop from reaction injection molded rectangular plaques and were sent for hardness testing at the University of British Columbia Okanagan Campus Survive and Thrive Applied Research Laboratory.

Synthesis of Monomer



This compound was prepared as described in the literature.[1] *meso*-Tetraphenylporphyrin (*meso*-TPP; 0.01 mol %) and DMAP (5.6 g, 46 mmol) were dissolved in DCM (2.2 L). Acetic anhydride (230 mL; 2.4 mol), pyridine (94 mL; 1.2 mol) and dicyclopentadiene (DCPD; 300 g; 2.2 mol) were subsequently added. The mixture was irradiated in a 5 L photoreactor using a Boryli BTL P28S 500W halogen bulb contained in a cold finger. The mixture was sparged with air and reacted for 27 days. The reaction mixture was washed with 2 M HCl and then with saturated sodium bicarbonate. The aqueous extracts were back extracted with DCM. All DCM fractions were combined and concentrated in vacuo yielding a black oil. The crude reaction mixture was adhered to a silica gel plug and washed with hexanes then eluted with 3:1 hexane to ethyl acetate. The resulting concentrate was then purified via vacuum distillation (70°C at 0.15 mmHg) in a 90°C water bath. Yields up to 50.5 % yield of oxaDCPD as a white crystalline solid. MP: 54–59 °C. ^{1}H NMR (300.27 MHz, Chloroform-*d*) δ 7.38 (dd, *J* = 5.8, 2.6 Hz, 1H), 5.98 – 5.92 (m, 2H), 5.78 (dd, *J* = 5.4, 2.9 Hz, 1H) 3.45 – 3.39 (m, 1H), 3.22 (br s, 1H), 2.97 (app s, 1H), 2.80 (app t, *J* = 5.1, 1H), 1.76 (dd, *J* = 8.4, 1.0 Hz, 1H), 1.63 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (125.81 MHz, Chloroform-*d*) δ 209.12, 163.79, 135.93, 131.76, 131.52, 51.84, 49.29, 47.36, 44.17, 43.28.

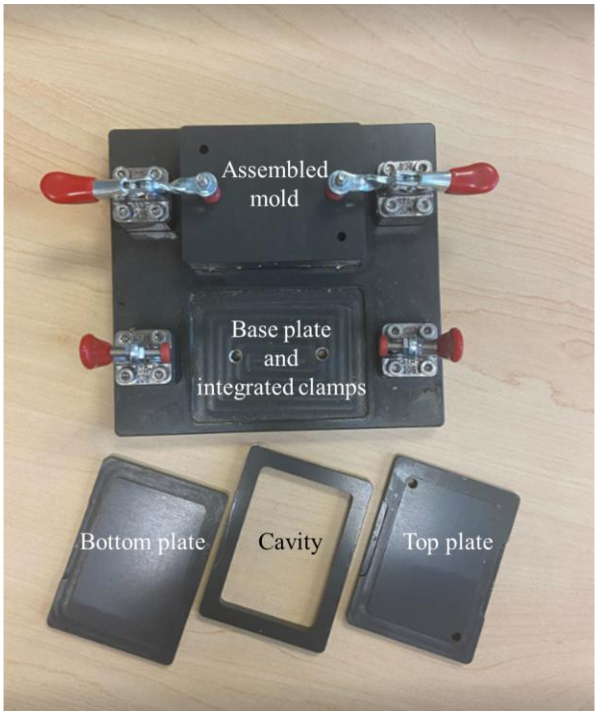


Scheme S-1. Five-liter custom photoreactor used to produce monomer on large scale.

This 5-liter photoreactor (Scheme S-1) was blown at the University of Victoria glass shop by scientific glassblower Sean Adams. The reactor flask is fitted with a double walled immersion well. This houses a 500-watt broad spectrum sunlite P28s BASE 120 V light bulb centered in the reactants using an aluminum jig heatsink, made by the Science Machine Shop at the University of Victoria. Water from a chiller is pumped through the immersion well removing heat generated by the light source. Additional air cooling was also utilized by blowing a stream of air into the well with the light bulb. This setup offers substantially better photon penetration through the reactants as compared to external lights. Additionally, this reactor significantly reduces solvent consumption through evaporation and maintained the reaction at a constant temperature.

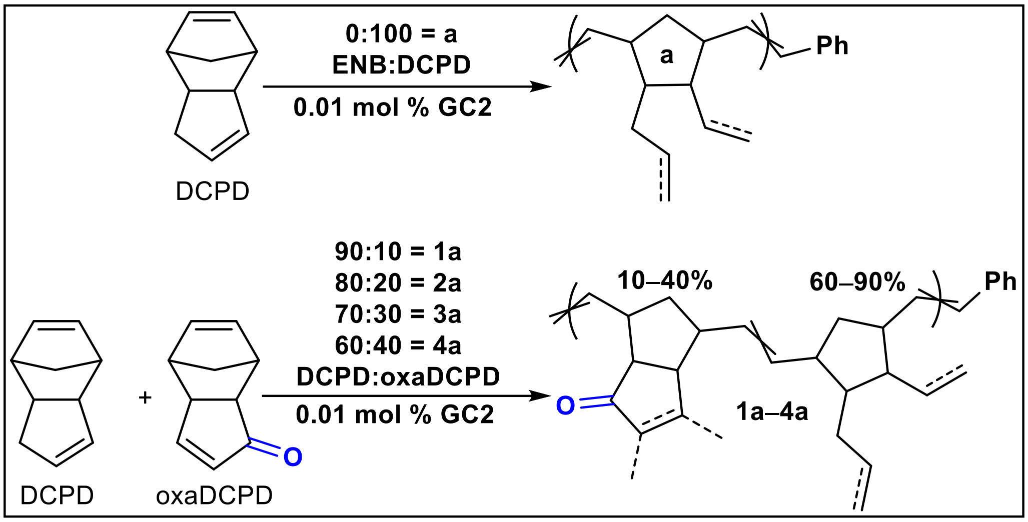
General Reaction Injection Molding Protocol

Monomer(s) were melted together at ~60°C and Tri-n-butyl-phosphite inhibitor was mixed into the liquid monomers. Grubbs 2nd generation catalyst was then added, and the mixture was sonicated to obtain a homogenous resin. The resin was poured into an aluminum 3 piece mold through a plastic syringe until resin flowed back out through both sprue holes. The mold was tapped, tilted, and rotated from side to side and end to end to ensure the removal of all air bubbles. The mold was transferred to a 110°C oven and allowed to cure for 40 minutes.



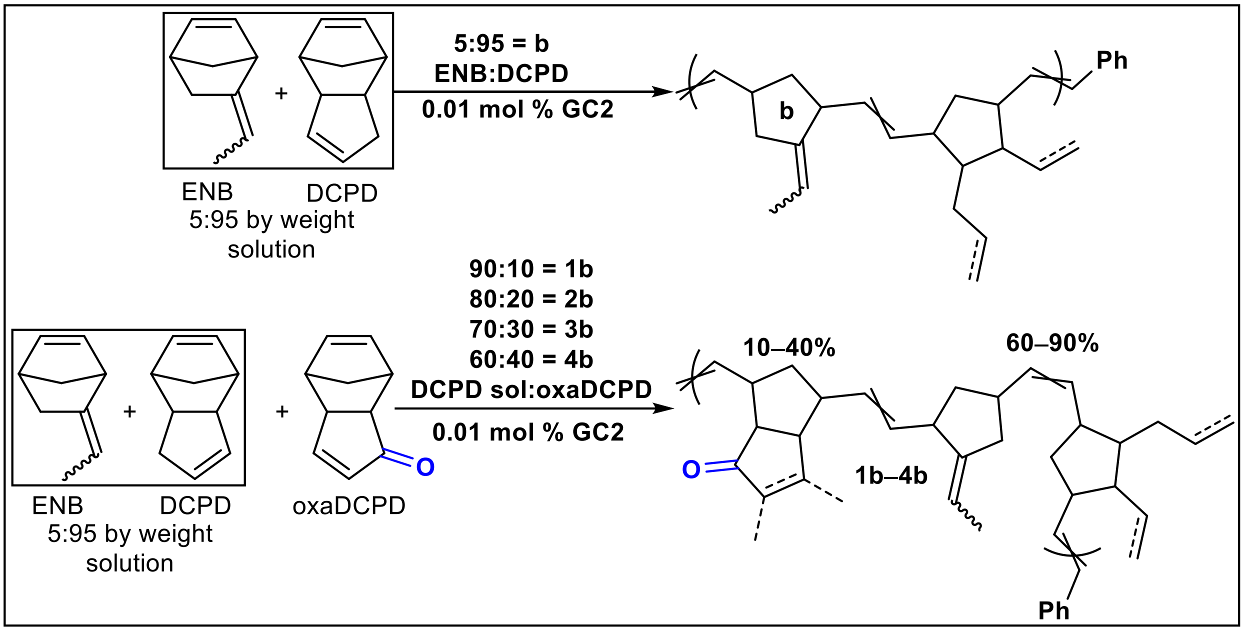
Scheme S-2. Three-piece aluminum mold for lab scale reaction injection molding of plaques.

a-type Reaction Injection Molding Protocol



OxaDCPD (14.4091 g; 0.098 mol) and dicyclopentadiene (DCPD; 21.6284 g; 0.20 mol) were melted together until liquid. Tri-n-butyl-phosphite (15.6 mg; 0.062 mmol) was mixed in as an inhibitor. Grubbs 2nd generation catalyst (GC2; 22.0 mg; 0.026 mmol; ~0.01 mol %) was then added. The mixture was sonicated to obtain ~36 g of homogenous resin, 40 % oxaDCPD by weight. This procedure was repeated for all weight fractions of 0, 10, 20, and 30 weight % of oxaDCPD. The resin was then injected through the barrel of a plastic syringe into a preheated (50 °C) aluminum mold until resin emerged from the opposite sprue hole. The mold was then tilted and tapped to ensure the removal of all air bubbles. The mold was transferred to a 110°C oven and allowed to cure for 40 minutes.

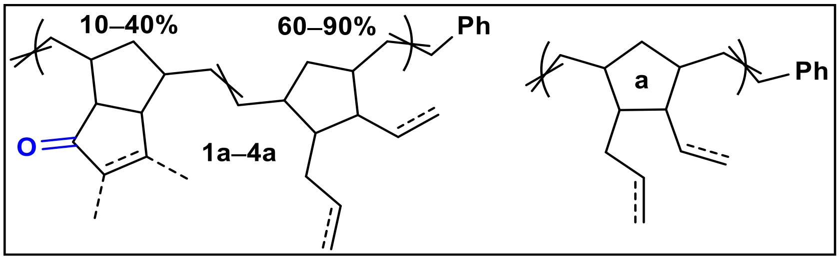
b-type Reaction Injection Molding Protocol



DCPD (151.44 g; 1.14 mol) was melted and ethylidene norbornene (ENB; 7.97 g; 0.066 mol) was added to obtain a liquid 95 % DCPD, 5 % ENB solution by weight. OxaDCPD (14.4159 g; 0.098 mol) was melted and added to a 21.6176 g aliquot of this solution. Tri-n-butyl-phosphite (17.5 mg; 0.069 mmol) was mixed in as an inhibitor. Grubbs 2nd generation catalyst (GC2; 21.5 mg; 0.025 mmol; ~0.01 mol %) was then added. The mixture was sonicated to obtain 36 g of homogenous 40 % oxaDCPD by weight resin. This procedure was repeated for all weight fractions of 0, 10, 20, and 30 weight % of oxaDCPD. The resin was then injected through the barrel of a plastic syringe into an aluminum mold until resin emerged from the opposite sprue hole. The mold was then tilted and tapped to ensure the removal of all air bubbles. The mold was transferred to a 110°C oven and allowed to cure for 40 minutes.

Characterization

Polymer Characterization



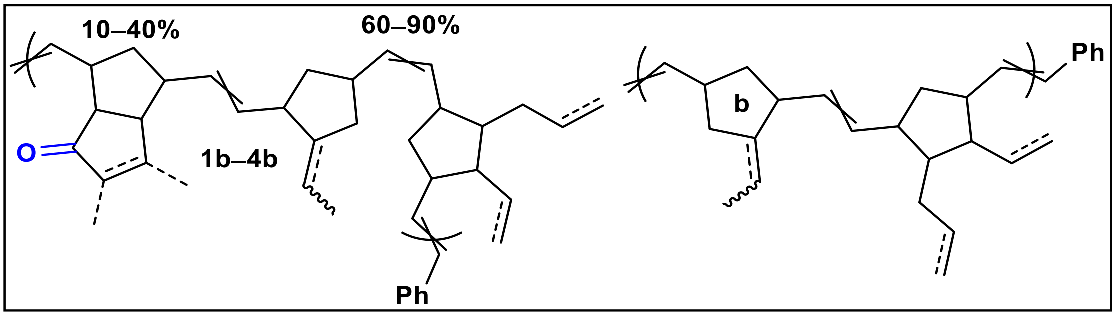


Table S1. Summary of thermal properties, densities and mol% of polymers and copolymers. n = 3

Material	Glass Transition Temperature (DMTA, °C)	Glass Transition Temperature (DSC, °C)	Density	oxaDCPD mol%	DCPD mol%	ENB mol%
a	186.1 ± 0.8	167.28	1.07 ± 0.005	0	100	0
1a	186.0 ± 0.8	174.12	1.08 ± 0.003	9.129834	90.87017	0
2a	106.1 ± 0.4	124.84	1.10 ± 0.001	18.43794	81.56206	0
3a	131.4 ± 2.5	128.26	1.12 ± 0.016	27.92958	72.07042	0
4a	129.7 ± 3.1	137.59	1.12 ± 0.012	37.61024	62.38976	0
b	173.4 ± 3.0	161.96	1.06 ± 0.007	0	94.52793	5.472069
1b	181.8 ± 11.7	149.76	1.09 ± 0.015	9.08859	85.93667	4.974736
2b	157.4 ± 0.7	129.56	1.11 ± 0.003	18.36314	77.16963	4.467226
3b	140.0 ± 8.9	147.91	1.11 ± 0.008	27.82941	68.22136	3.949225
4b	182.1 ± 0.4	158.27	1.11 ± 0.001	37.49342	59.08617	3.420403

Table S2. Summary of mechanical properties of polymers and copolymers. n = 3

Material	Tensile Strength (Mpa)	Strain at Break (%)	Toughness (MPa)	Young's Modulus (GPa)	Storage Modulus (MPa)	Loss Modulus
a	64.4 ± 0.8	0.19 ± 0.01	8.5 ± 0.5	0.99 ± 0.05	1929.8 ± 49.3	18.4 ± 3.2
1a	66.5 ± 1.5	0.20 ± 0.04	9.1 ± 2.4	0.97 ± 0.05	2082.6 ± 72.9	19.5 ± 1.3
2a	48.7 ± 5.8	0.13 ± 0.04	4.1 ± 1.3	1.27 ± 0.1	2153.8 ± 78.5	34.6 ± 0.8
3a	51.8 ± 1.7	0.08 ± 0.02	2.6 ± 0.8	1.29 ± 0.03	2180.7 ± 78.5	46.1 ± 0.2
4a	63.0 ± 1.3	0.21 ± 0.02	8.2 ± 0.8	0.91 ± 0.04	2170.8 ± 132.8	54.7 ± 2.9
b	59.8 ± 1.6	0.19 ± 0	7.3 ± 0.3	0.83 ± 0.03	2058.7 ± 13.1	23.6 ± 3.5
1b	77.3 ± 7.0	0.49 ± 0.2	29.3 ± 16.7	1.62 ± 0.1	1975.9 ± 65.9	22.4 ± 5.6
2b	51.6 ± 3.6	0.22 0.2	8.9 ± 9.9	1.29 ± 0.1	2146.8 ± 27.8	36.3 ± 1.0
3b	76.6 ± 5.9	0.69 ± 0.4	39.6 ± 22.7	1.54 ± 0.08	2137.9 ± 54.2	47.1 ± 1.8
4b	53.7 ± 1.2	0.16 ± 0.07	5.2 ± 2.6	0.84 ± 0.01	2330.4 ± 76.9	30.2 ± 1.5

NMR Spectra

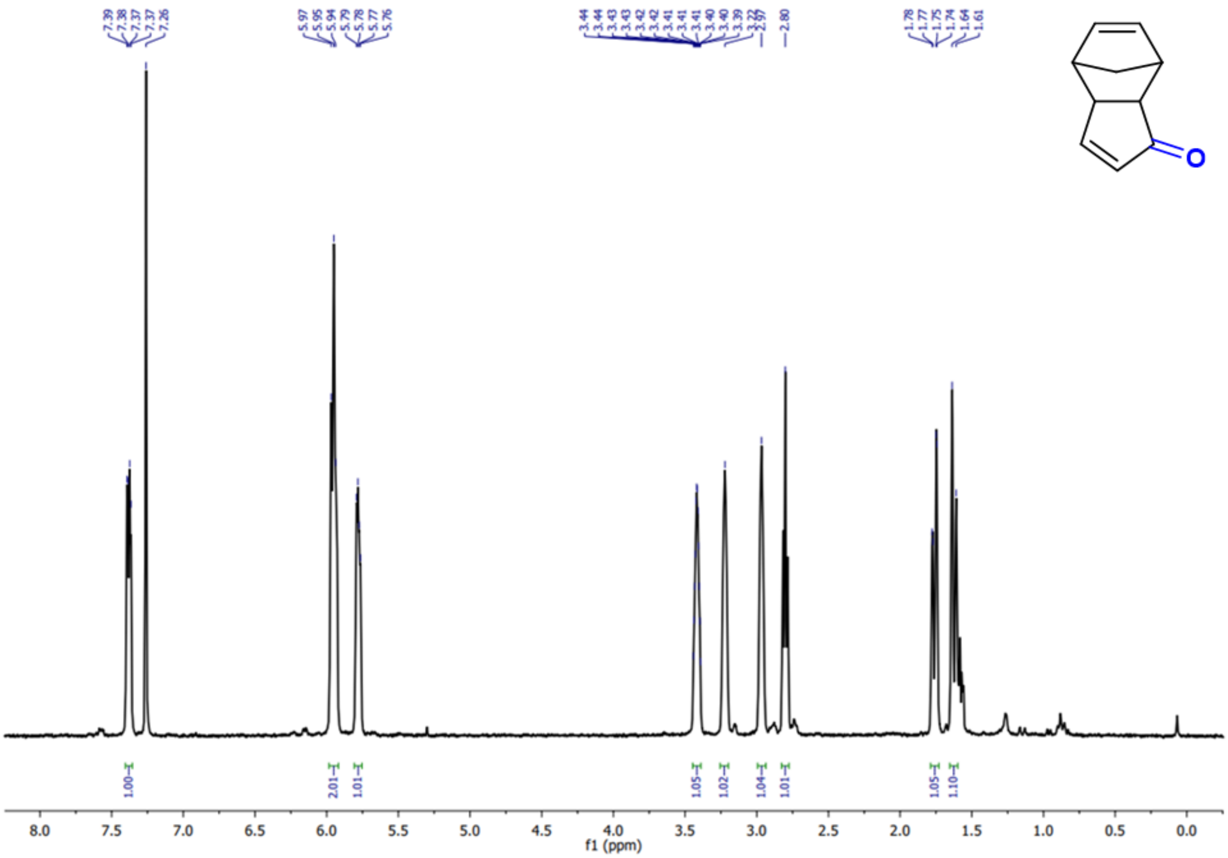


Figure S1. ^{1}H NMR spectrum for *endo*-dicyclopentadienone at 300.27 MHz in CDCl3.

Contains trace exo-dicyclopentadienone.

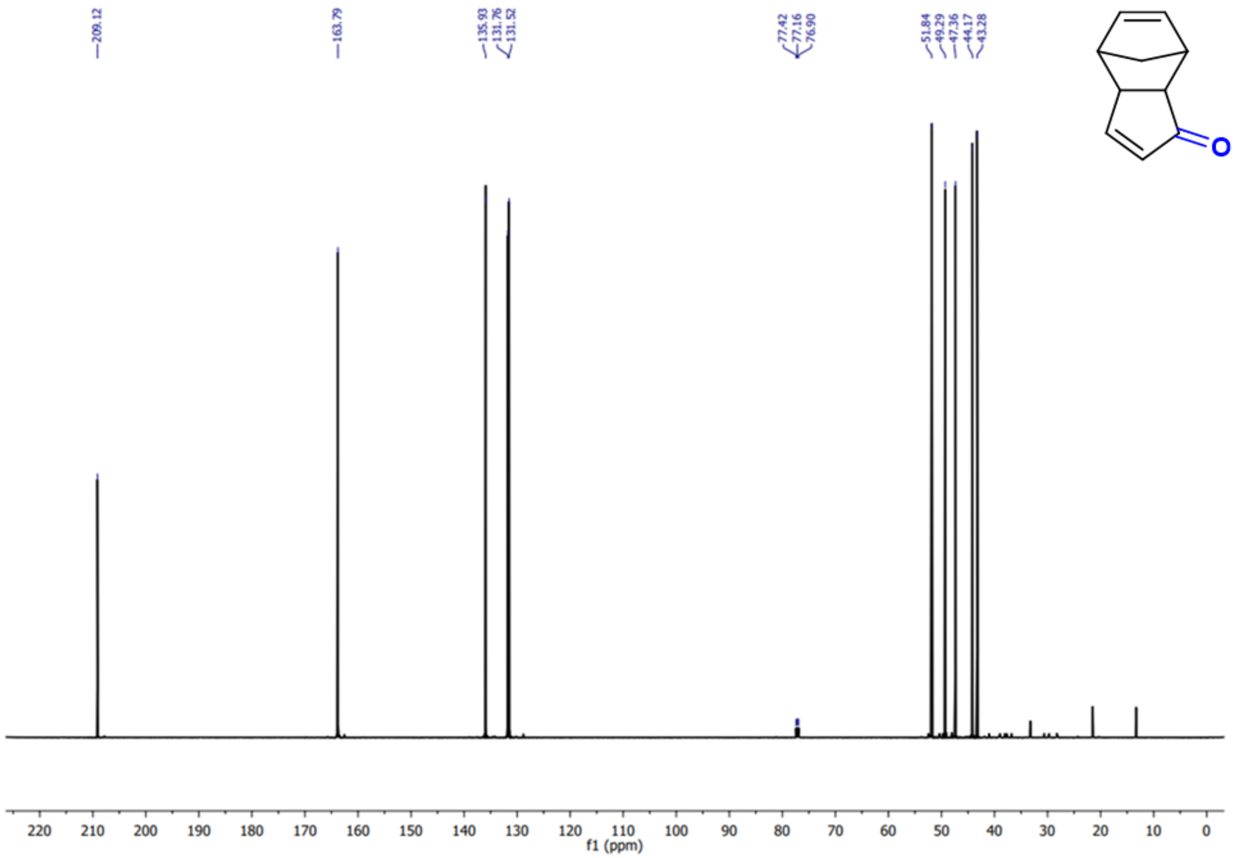


Figure S2. **^{13}C NMR spectrum for *endo*-dicyclopentadienone at 125.81 MHz in CDCl3.**

Infrared Spectra

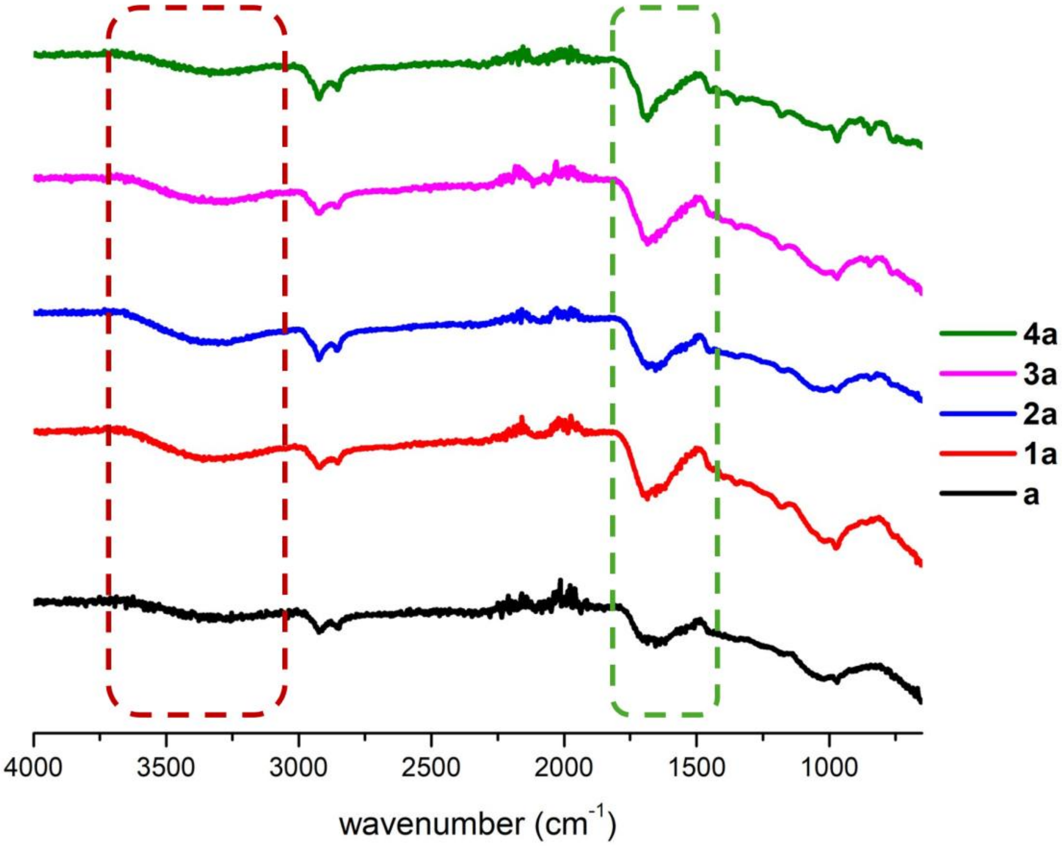


Figure S3. AT-IR spectrum of a-type polymer and copolymers after exposure to air for greater then 24 hours.

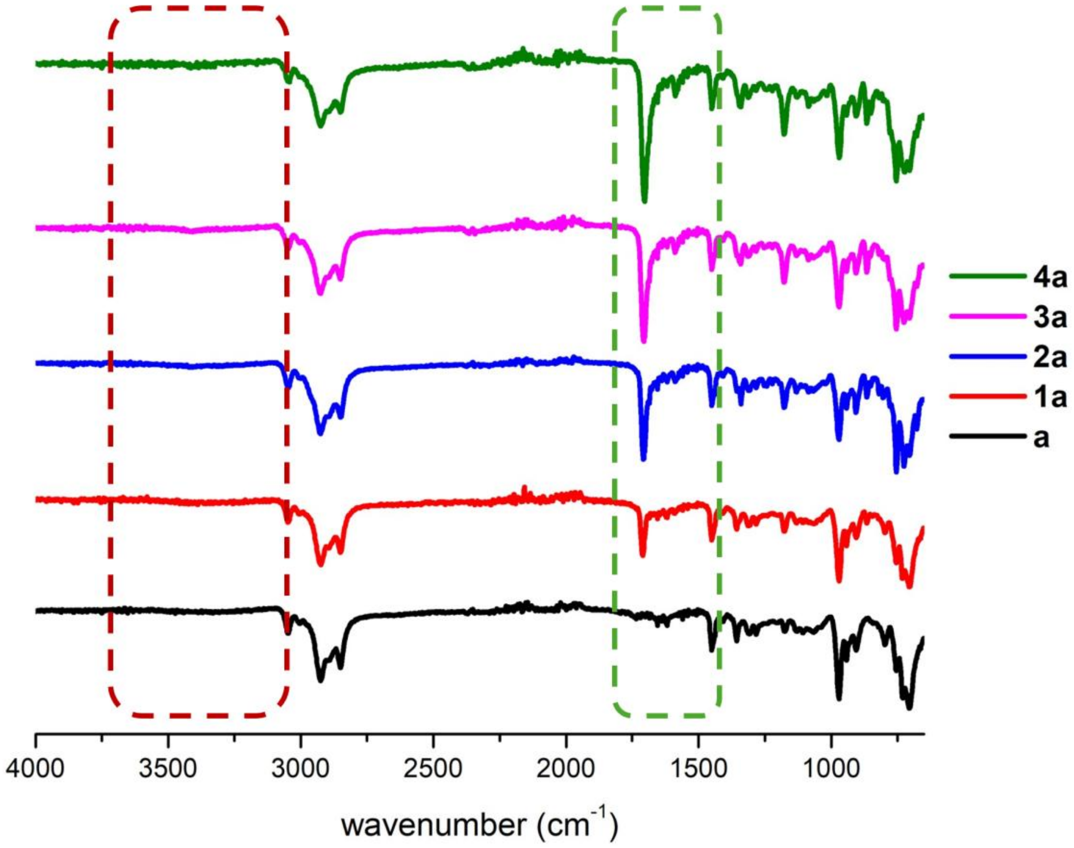


Figure S4. AT-IR spectrum of freshly exposed surface of a-type polymer and copolymers.

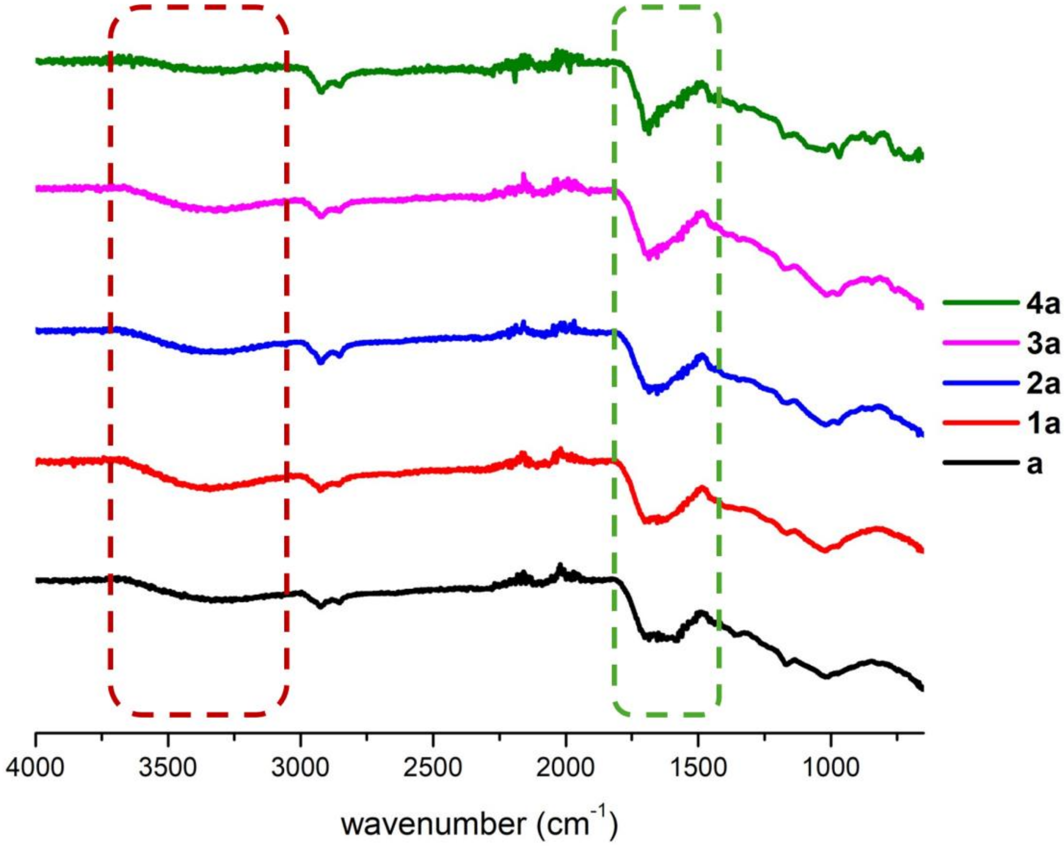


Figure S5. AT-IR spectrum of a-type polymer and copolymers after heating during DMTA.

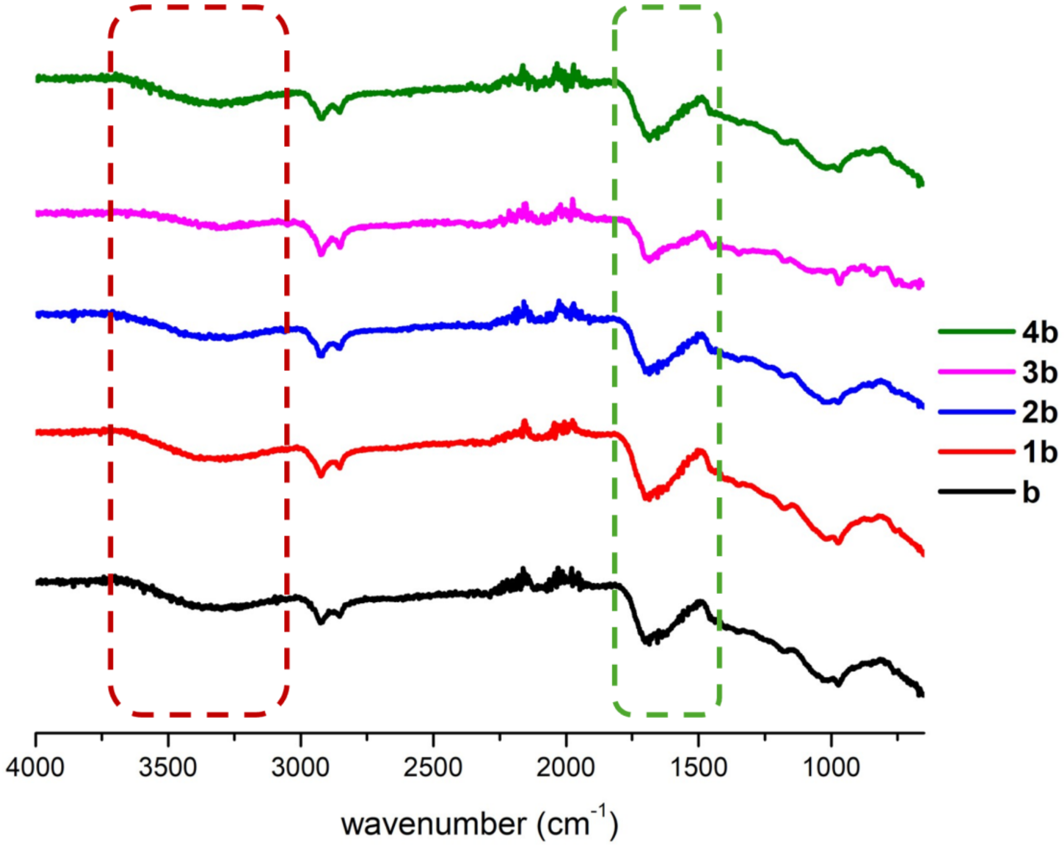


Figure S6. AT-IR spectrum of b-type copolymers after exposure to air for greater then 24 hours.

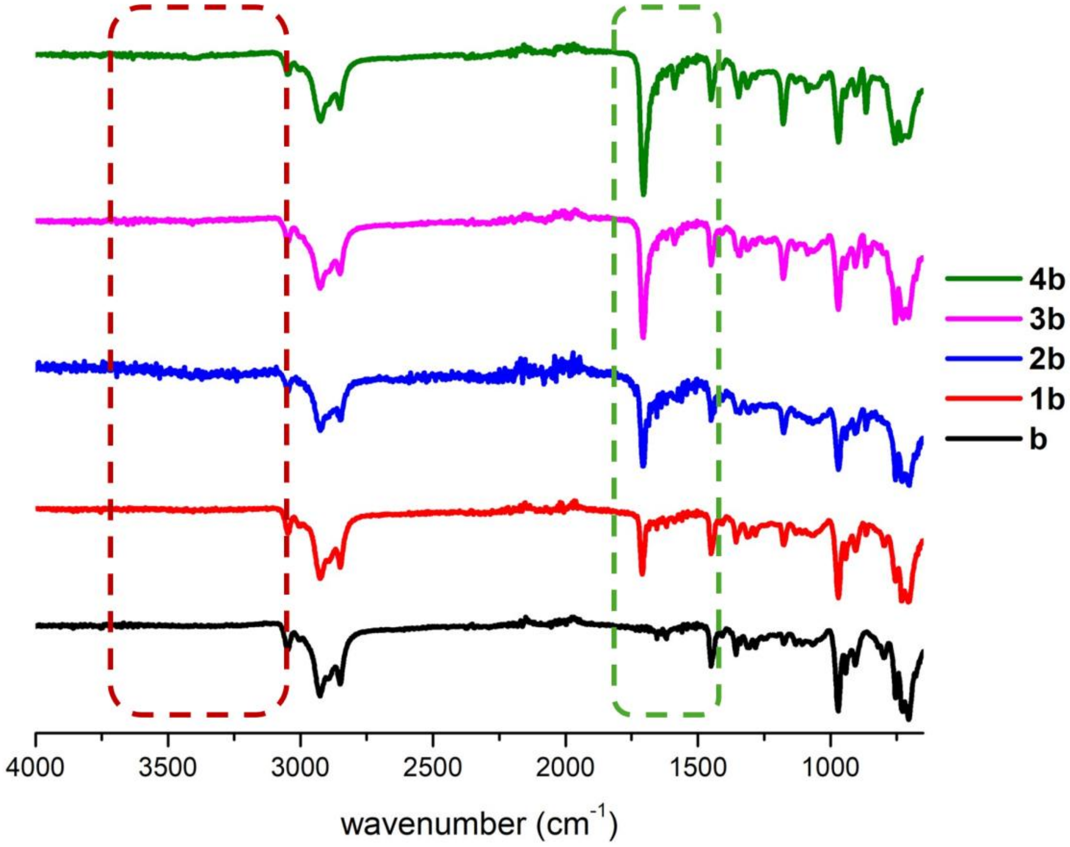


Figure S7. AT-IR spectrum of freshly exposed surface of b-type copolymers.

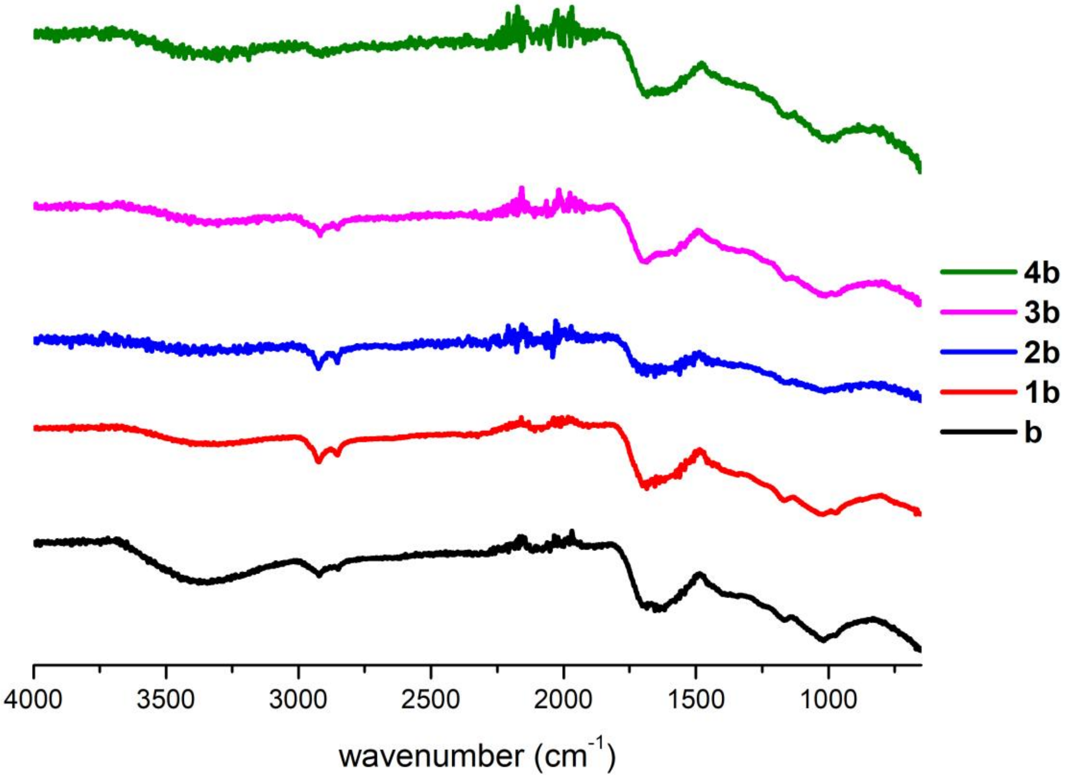


Figure S8. AT-IR spectrum of b-type copolymers after heating during DMTA.

Supplementary Figures

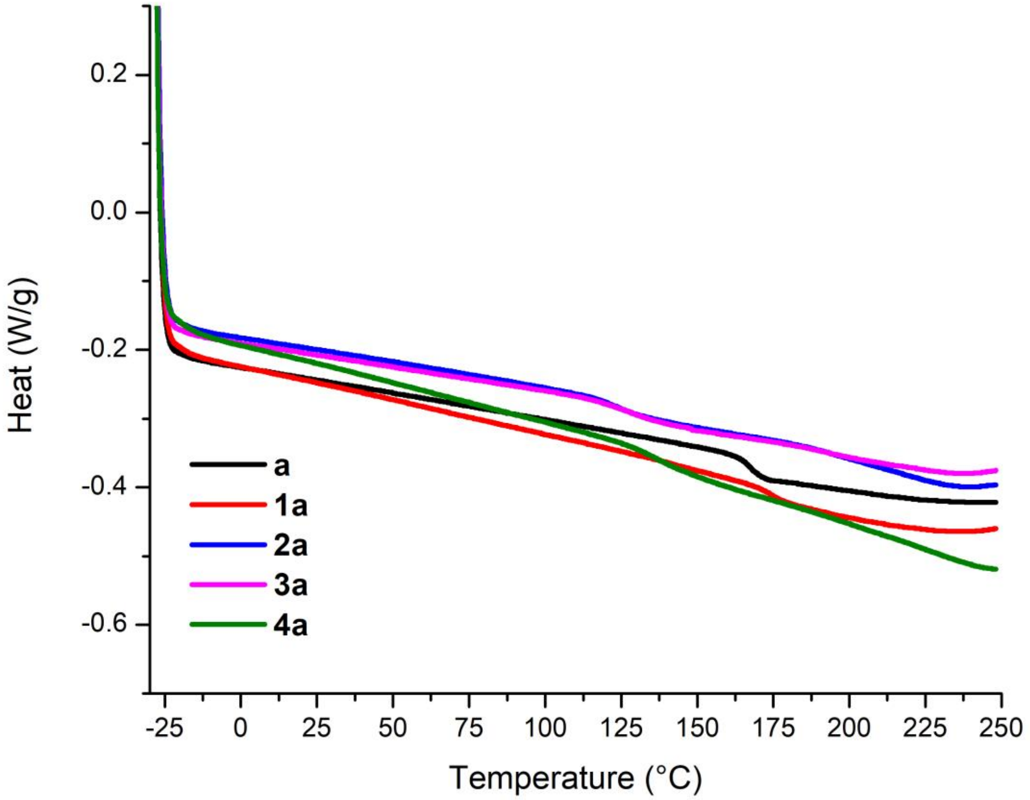


Figure S9. Differential scanning calorimetry heating traces of a-type polymer and copolymers from which glass transition temperatures were extracted.

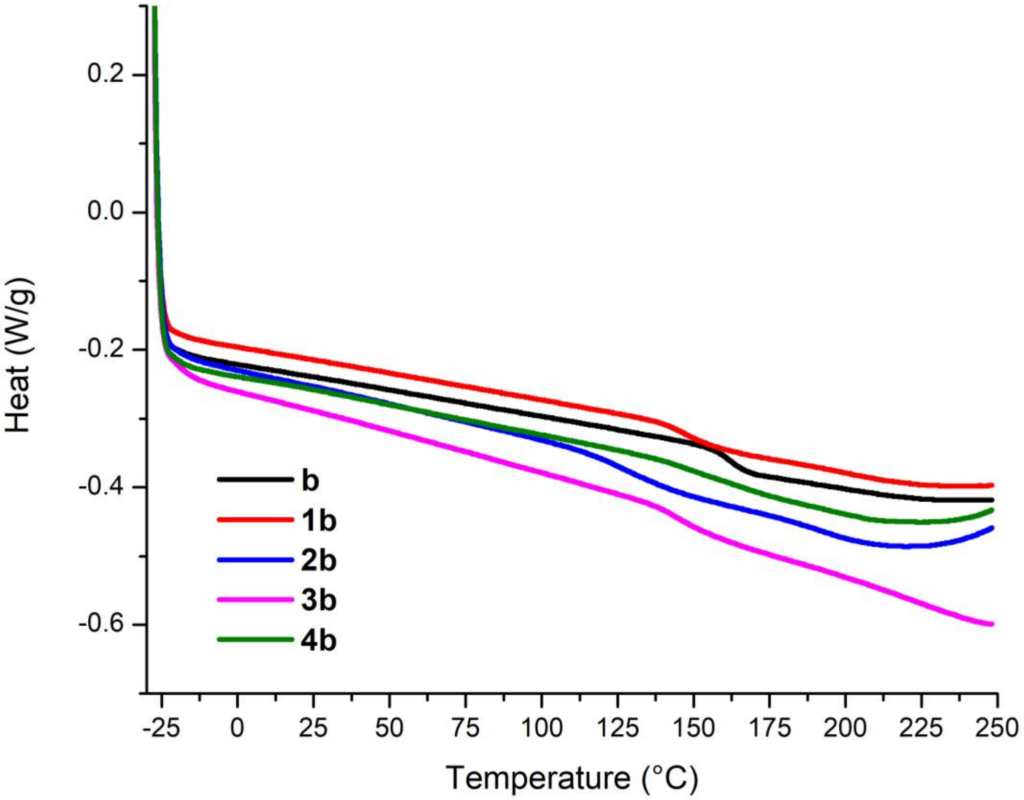


Figure S10. Differential scanning calorimetry heating traces of b-type copolymers from which glass transition temperatures were extracted.

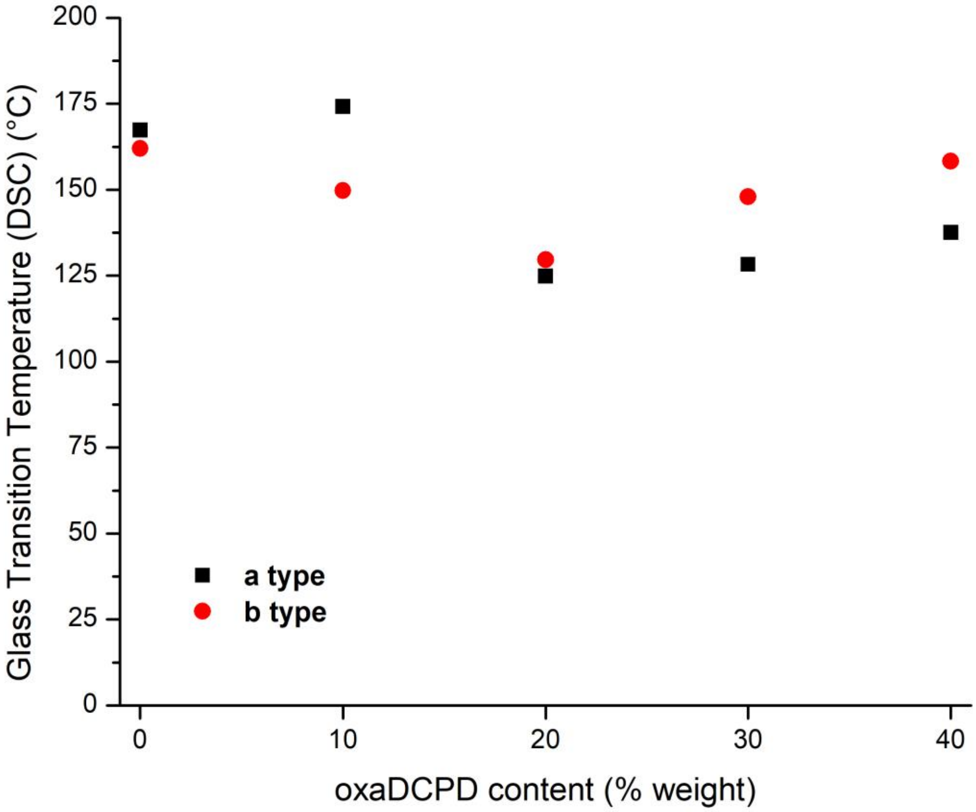


Figure S11. Glass transition temperatures as determined by differential scanning calorimetry of homopolymers and copolymers.

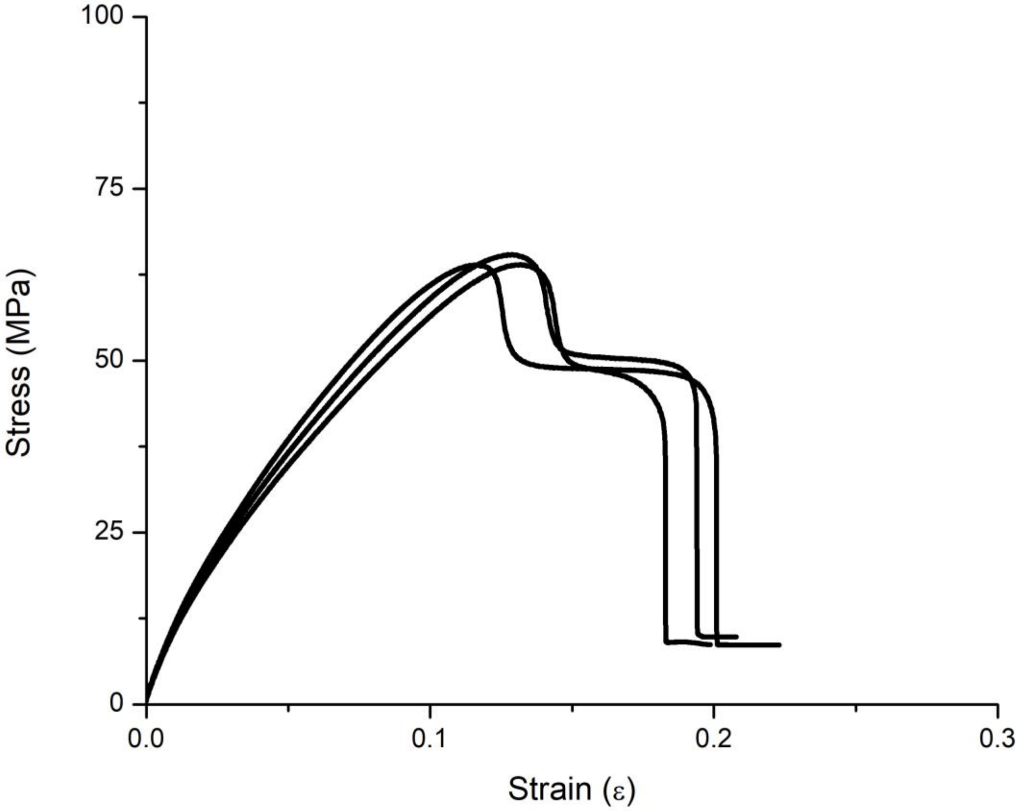


Figure S12. Stress-strain curves of a-type polymer.

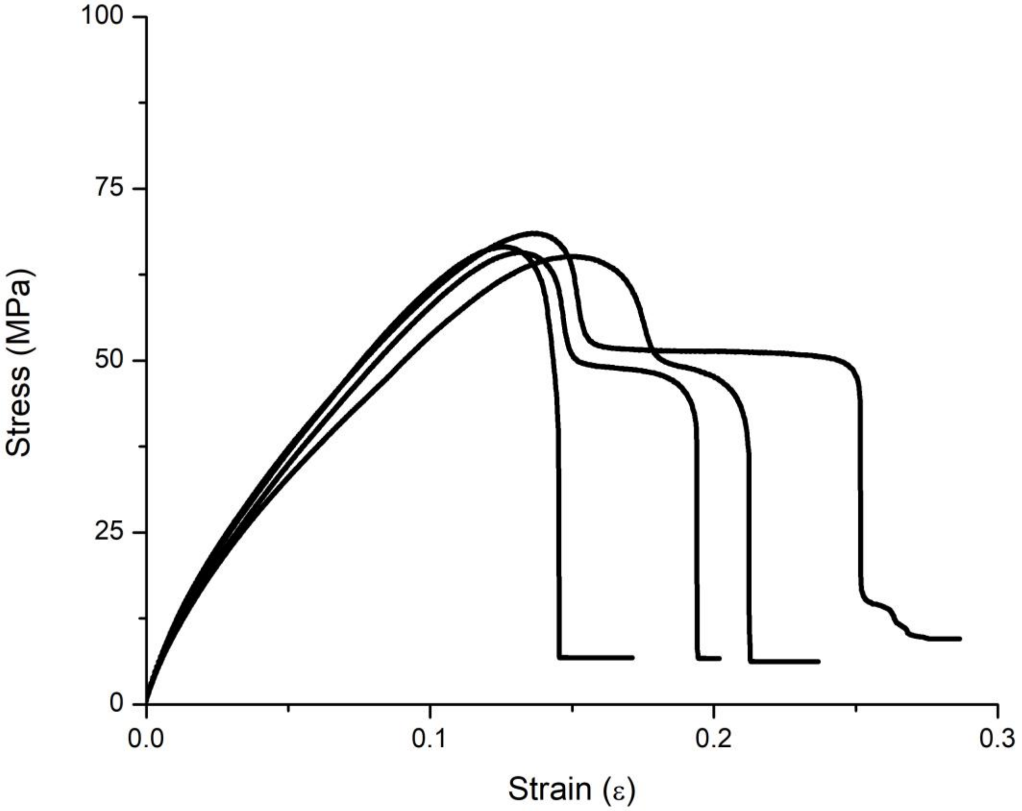


Figure S13. Stress-strain curves of 1a-type copolymer.

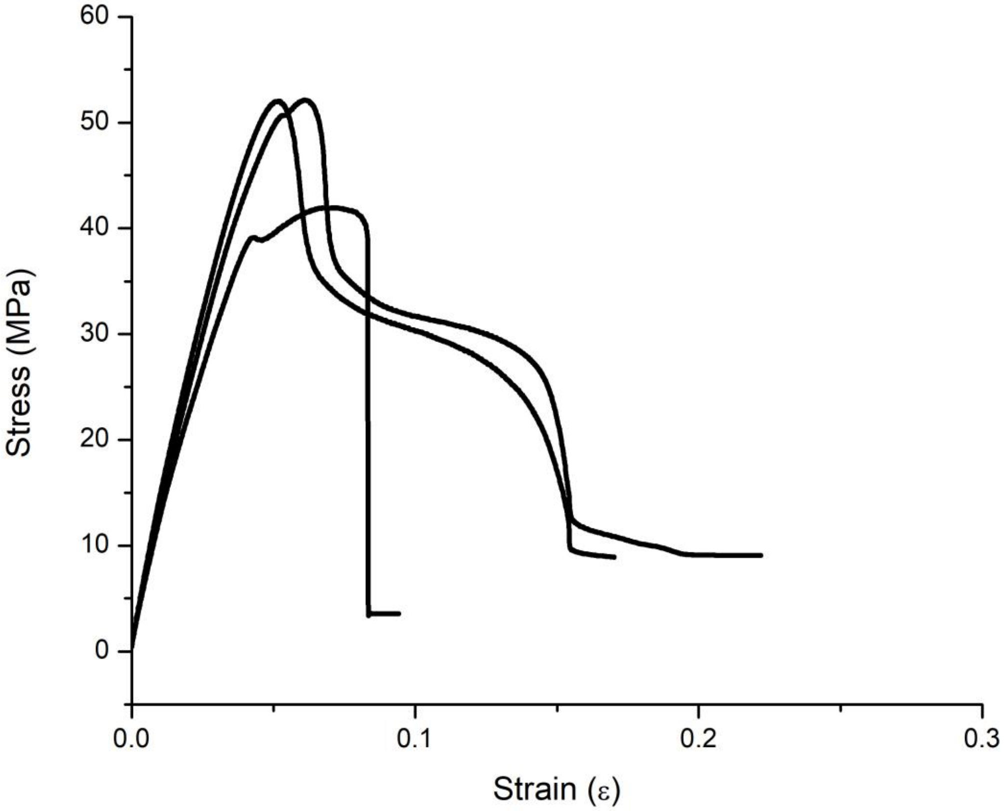


Figure S14. Stress-strain curves of 2a-type copolymer.

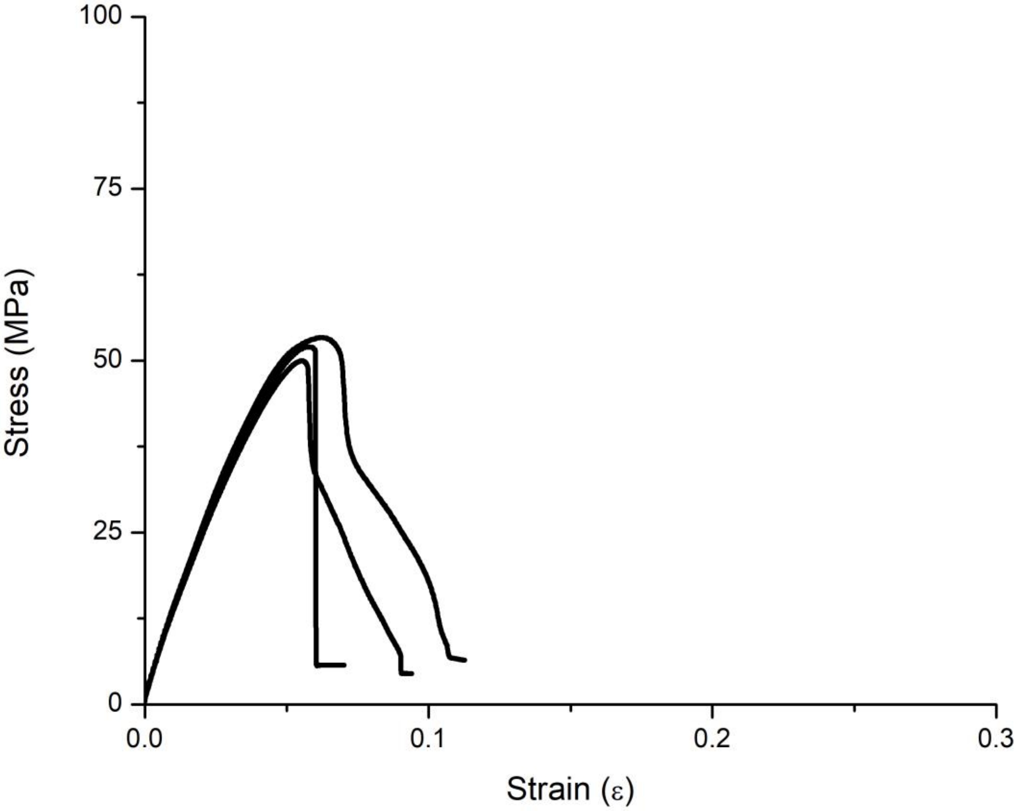


Figure S15. Stress-strain curves of 3a-type copolymer.

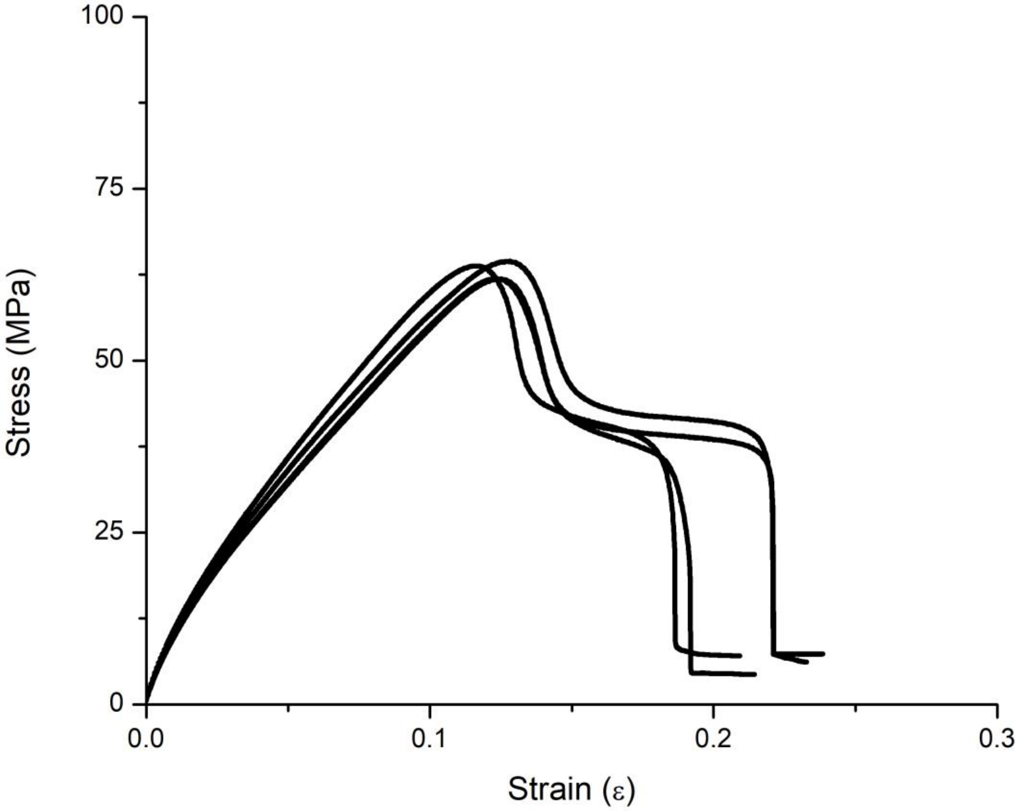


Figure S16. Stress-strain curves of 4a-type copolymer.

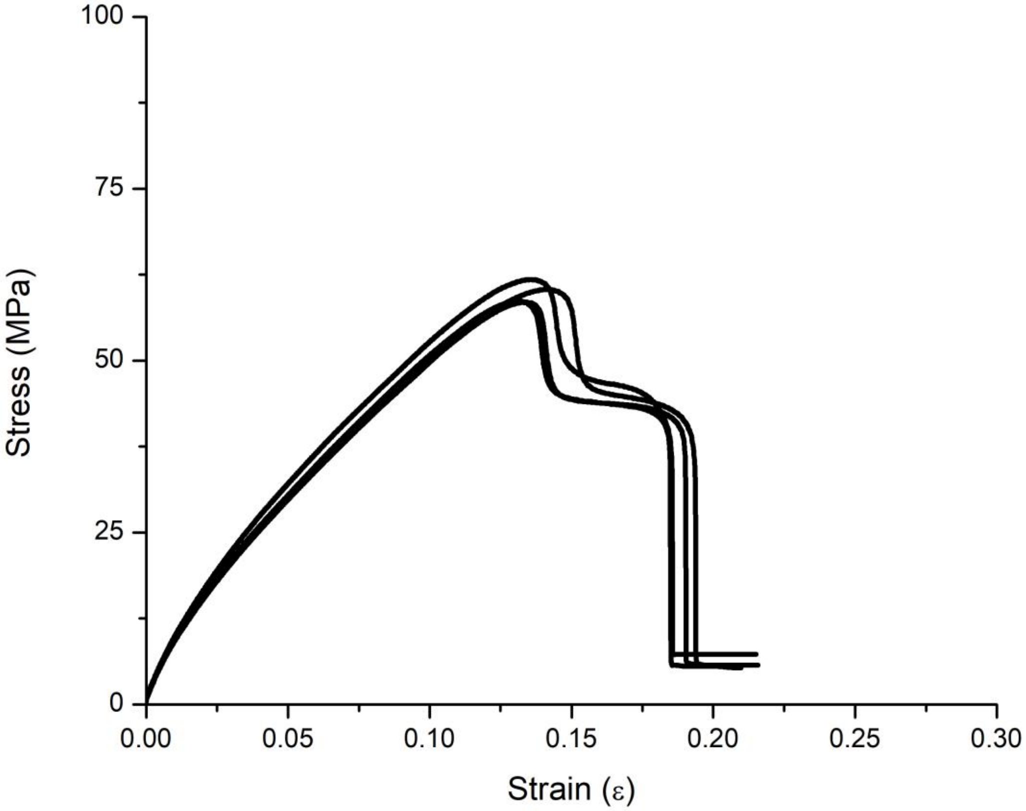


Figure S17. Stress-strain curves of b-type copolymer.

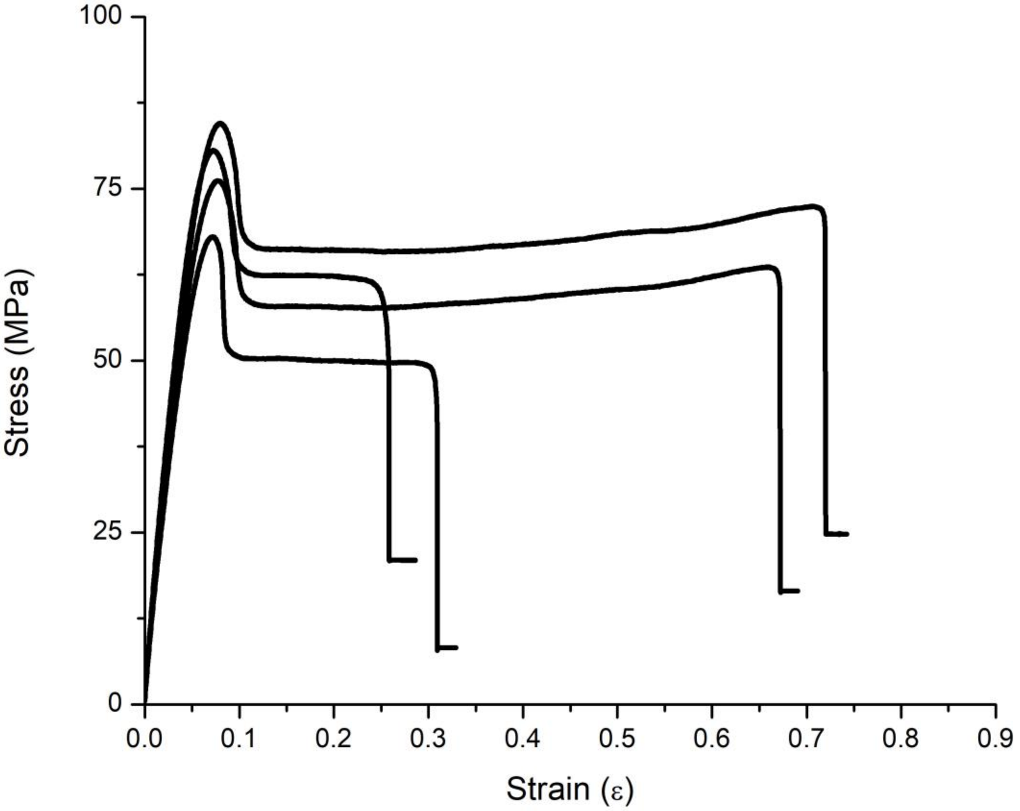


Figure S18. Stress-strain curves of 1b-type copolymer.

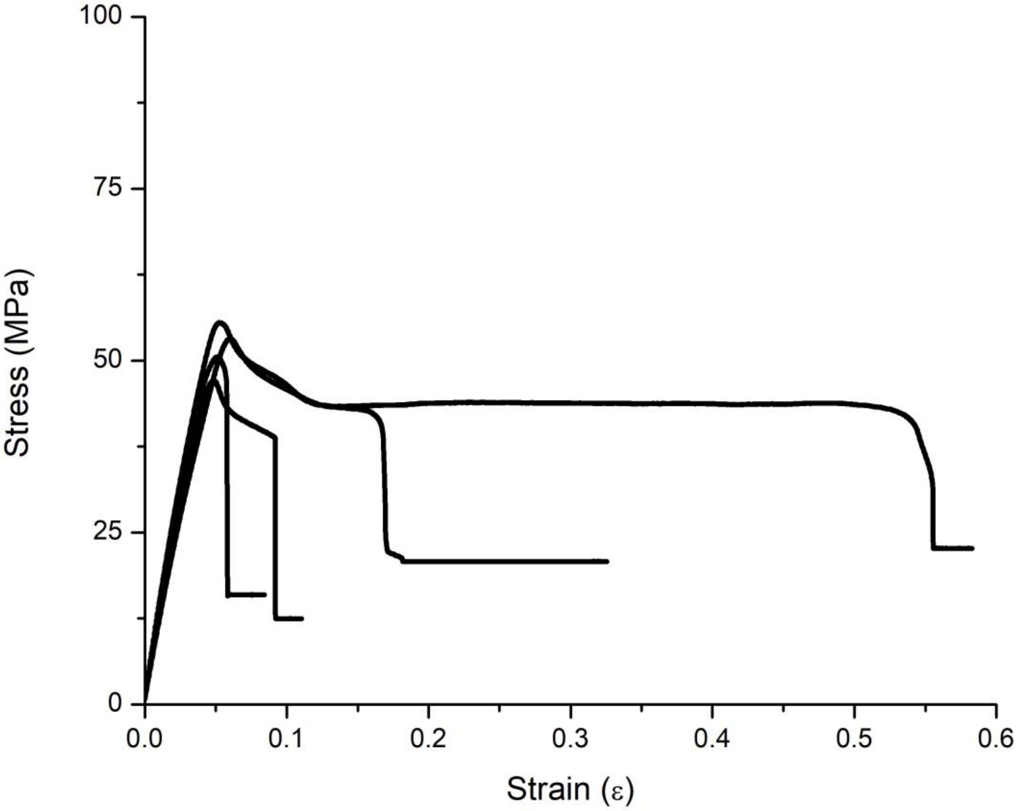


Figure S19. Stress-strain curves of 2b-type copolymer.

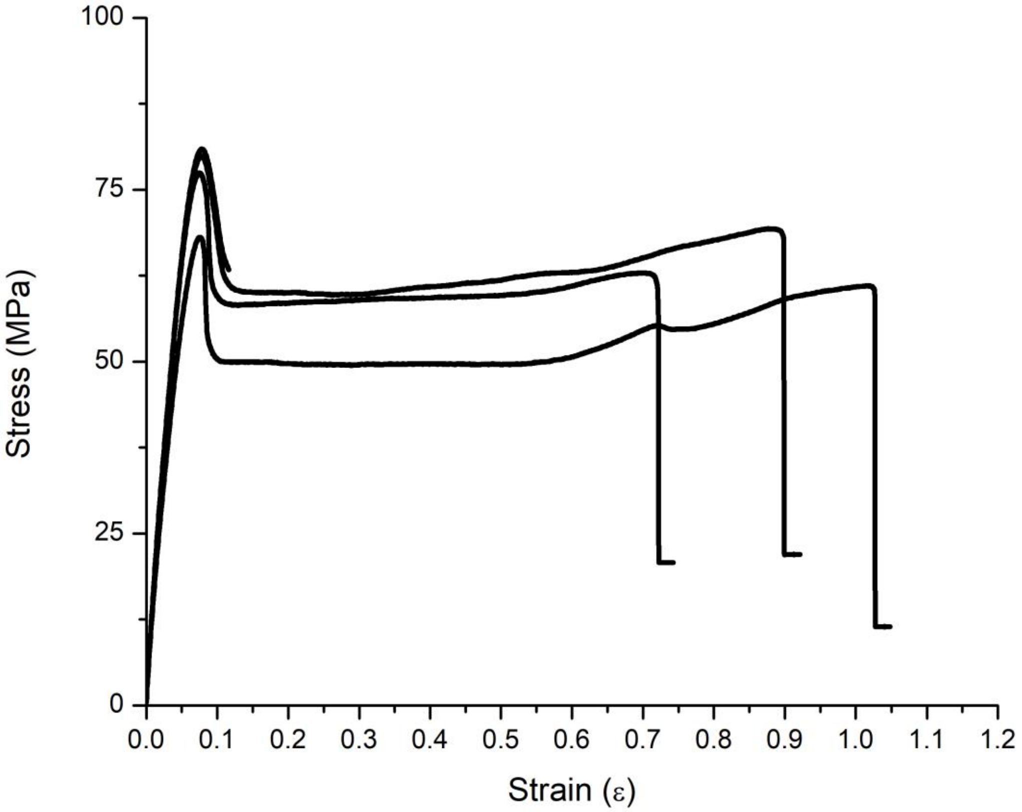


Figure S20. Stress-strain curves of 3b-type copolymer.

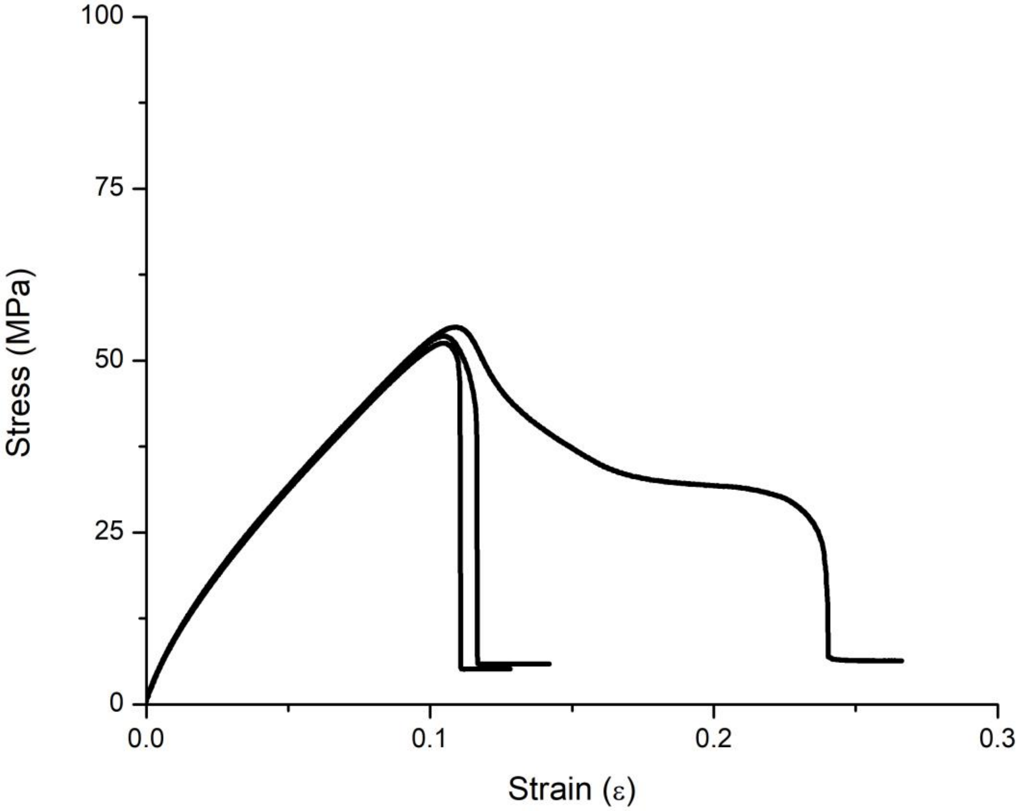


Figure S21. Stress-strain curves of 4b-type copolymer.

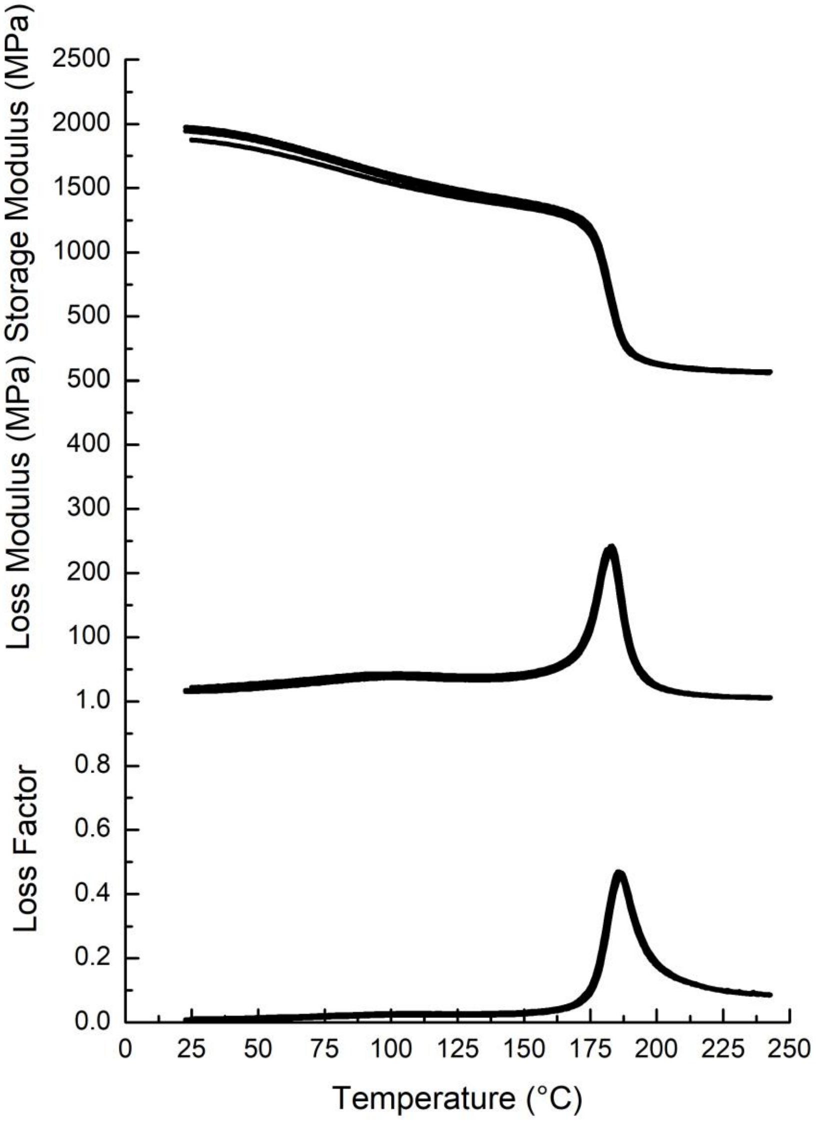


Figure S22. DMTA traces of reaction injection molded a-type polymer.

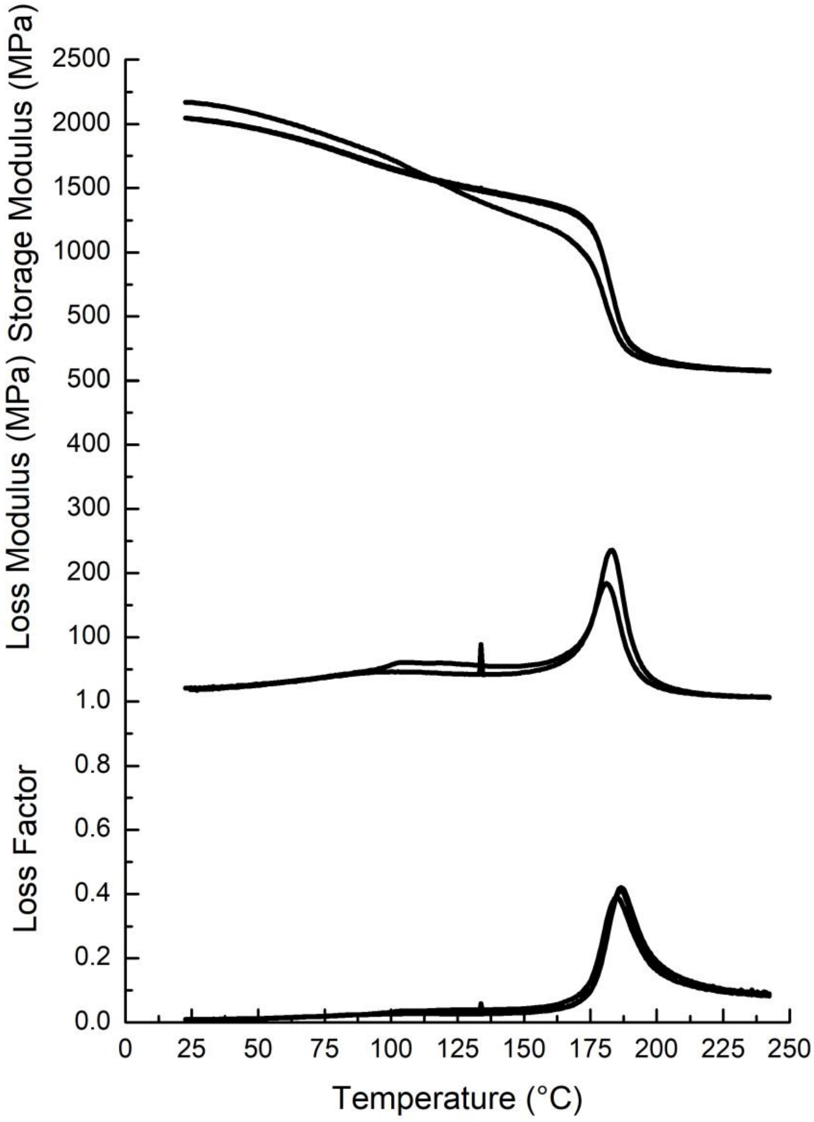


Figure S23. DMTA traces of reaction injection molded 1a-type copolymer.

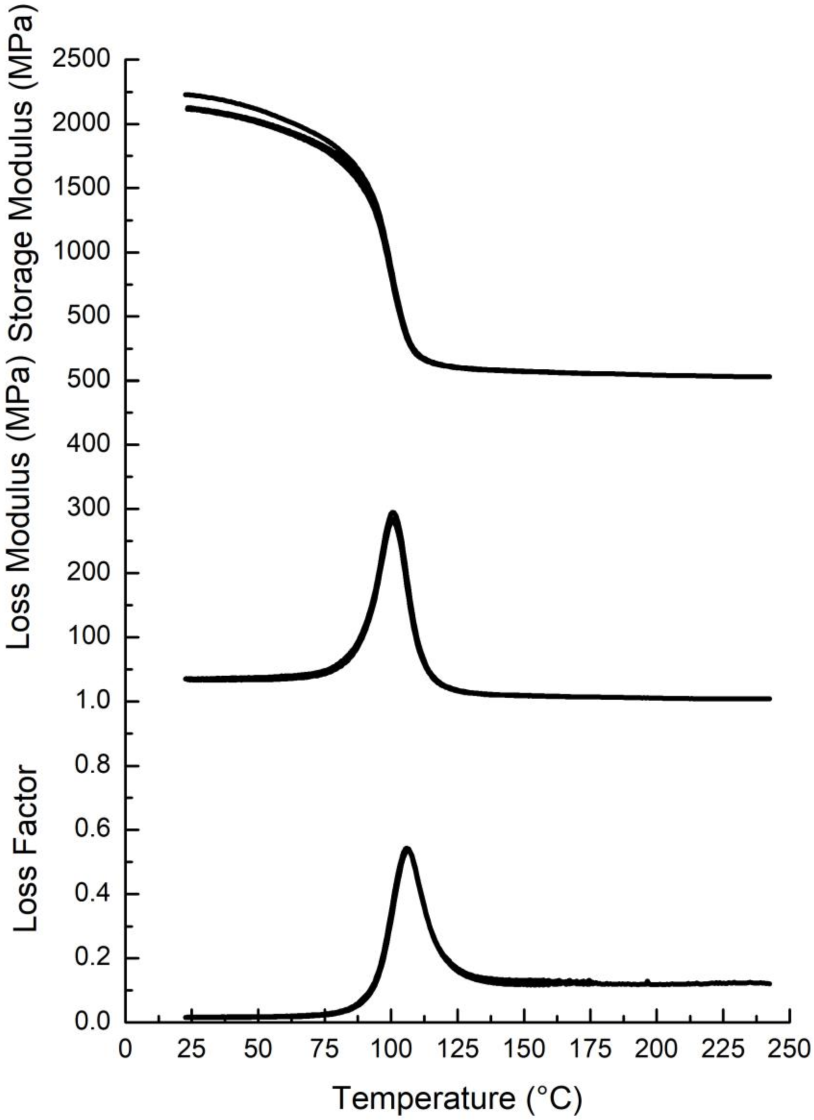


Figure S24. DMTA traces of reaction injection molded 2a-type copolymer.

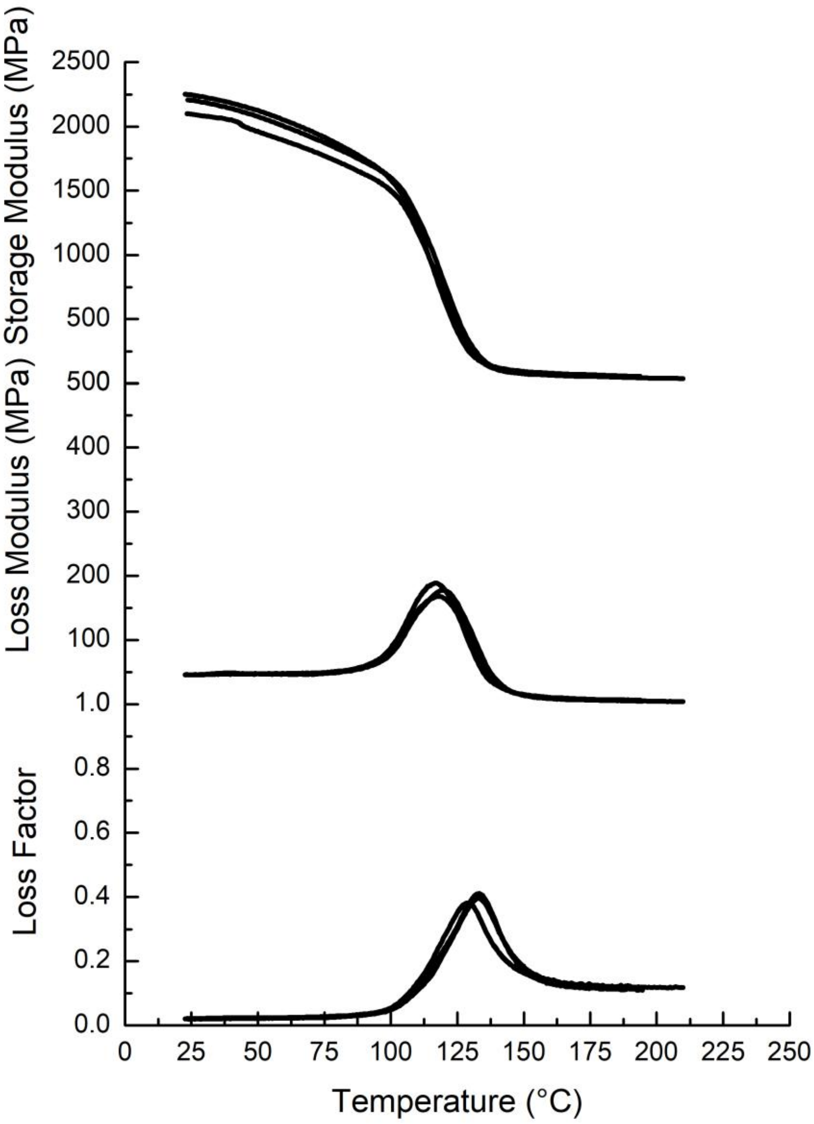


Figure S25. DMTA traces of reaction injection molded 3a-type copolymer.

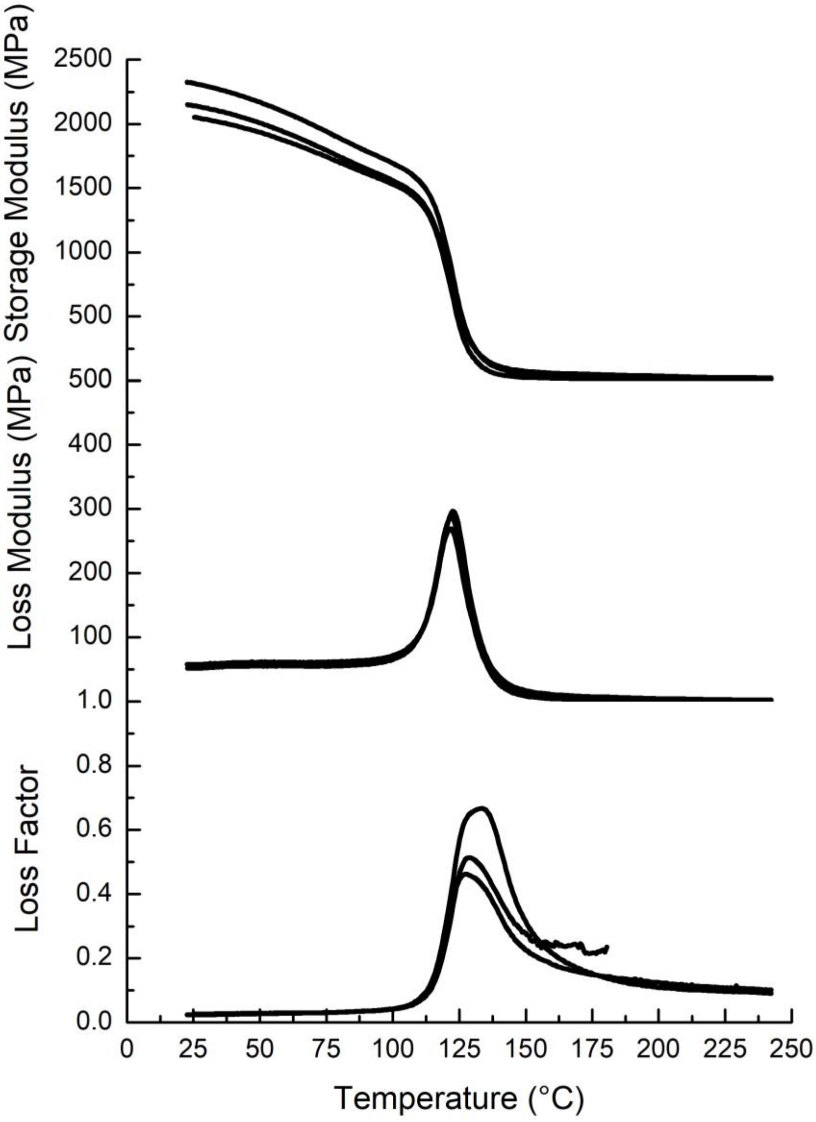


Figure S26. DMTA traces of reaction injection molded 4a-type copolymer.

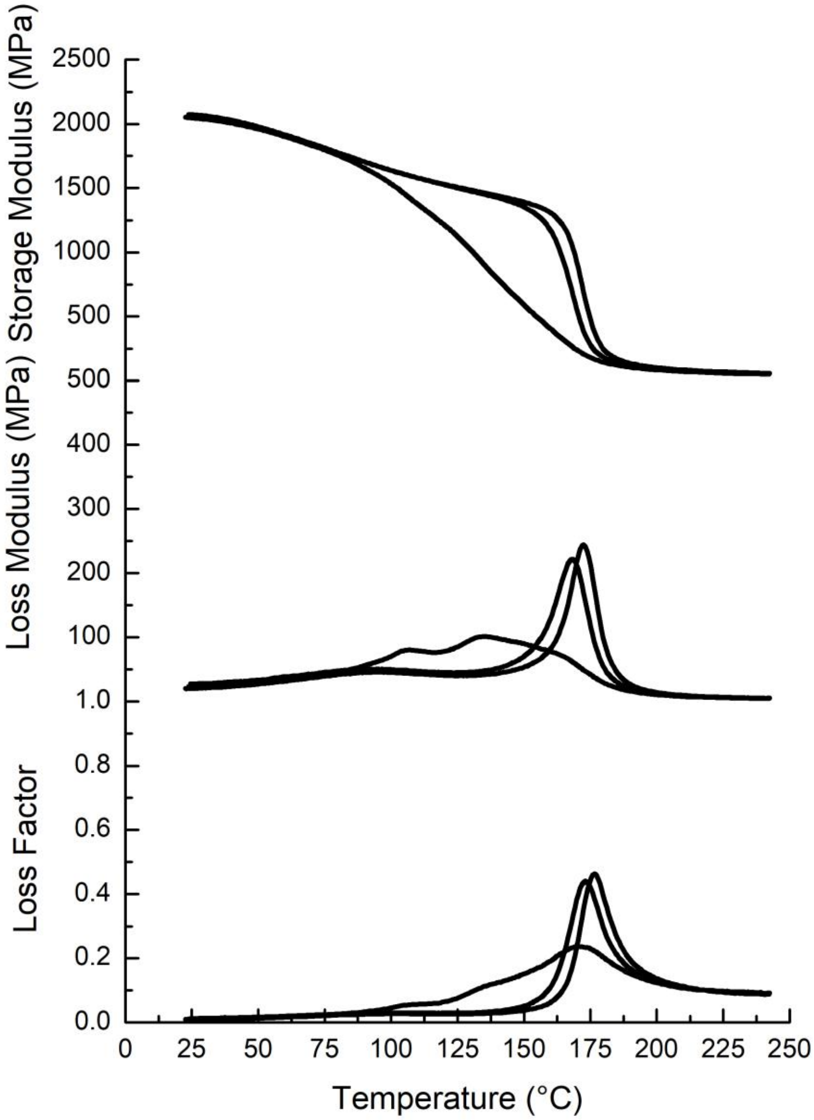


Figure S27. DMTA traces of reaction injection molded b-type copolymer.

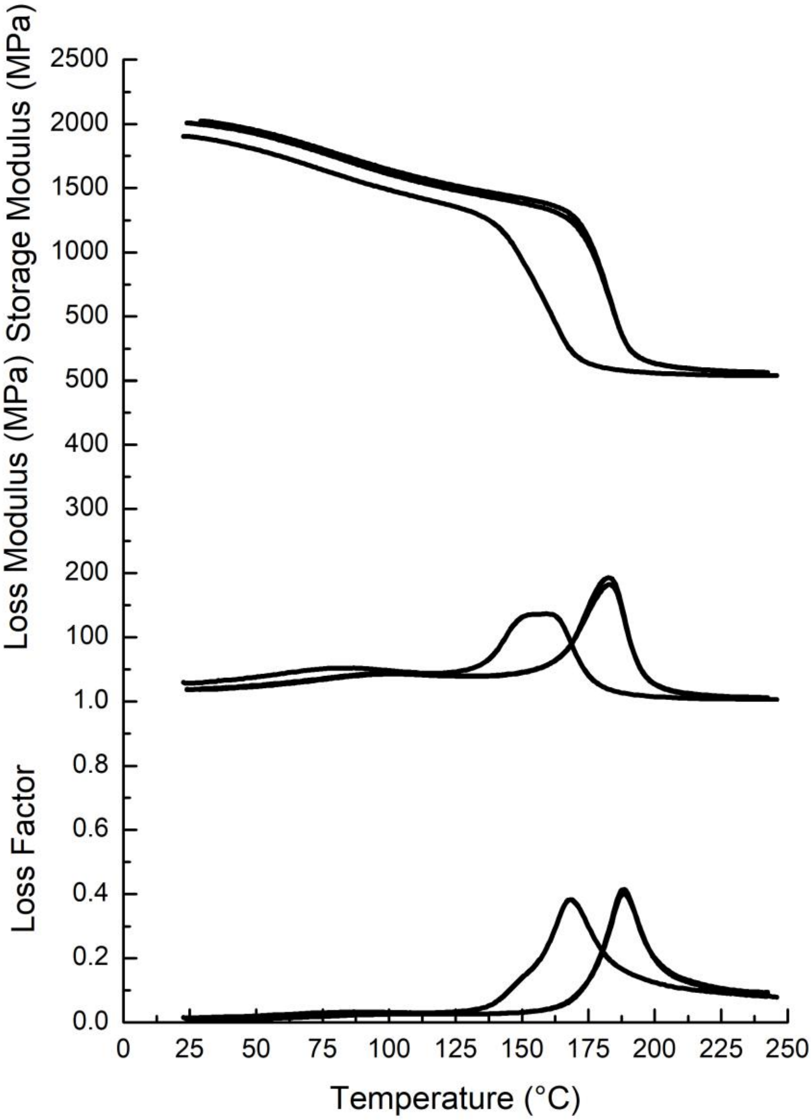


Figure S28. DMTA traces of reaction injection molded 1b-type copolymer.

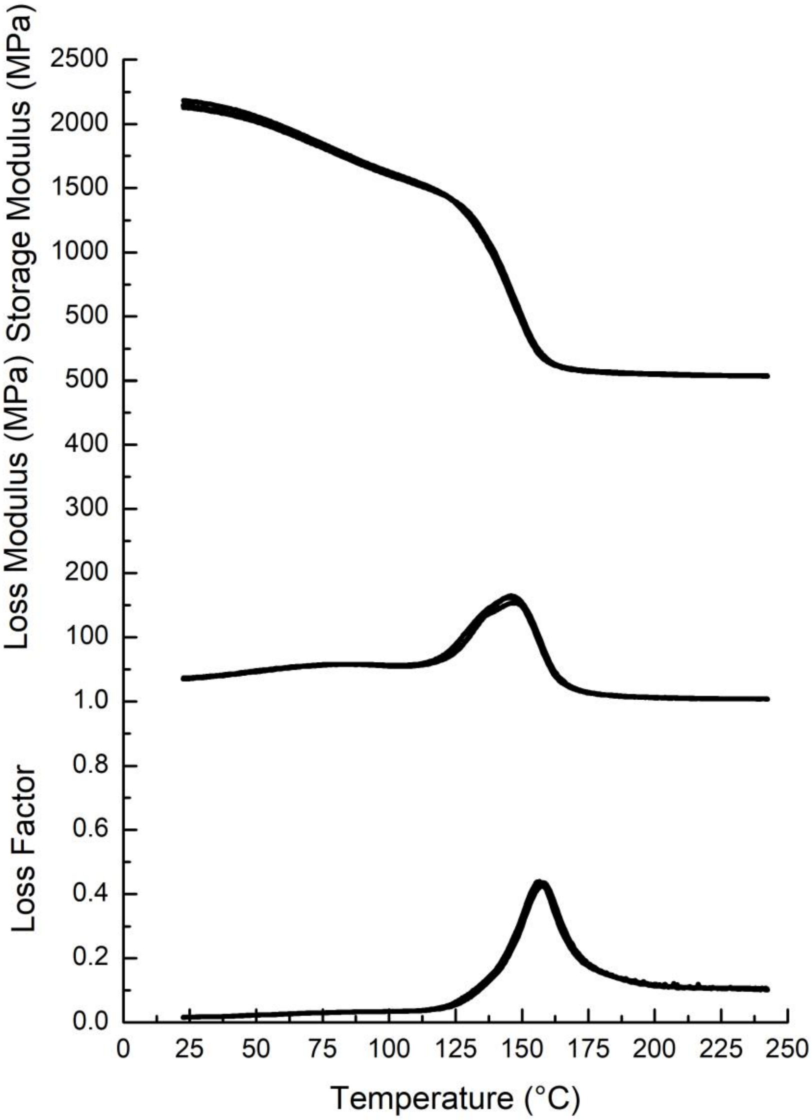


Figure S29. DMTA traces of reaction injection molded 2b-type copolymer.

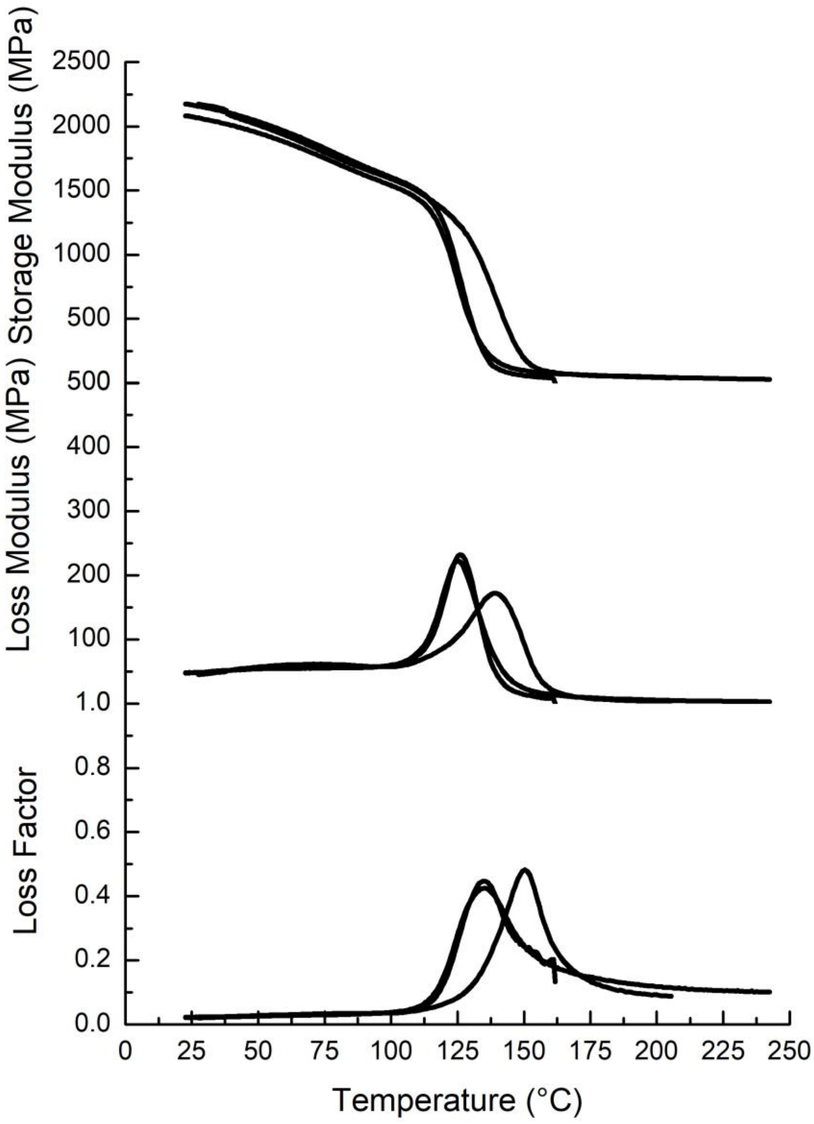


Figure S30. DMTA traces of reaction injection molded 3b-type copolymer.

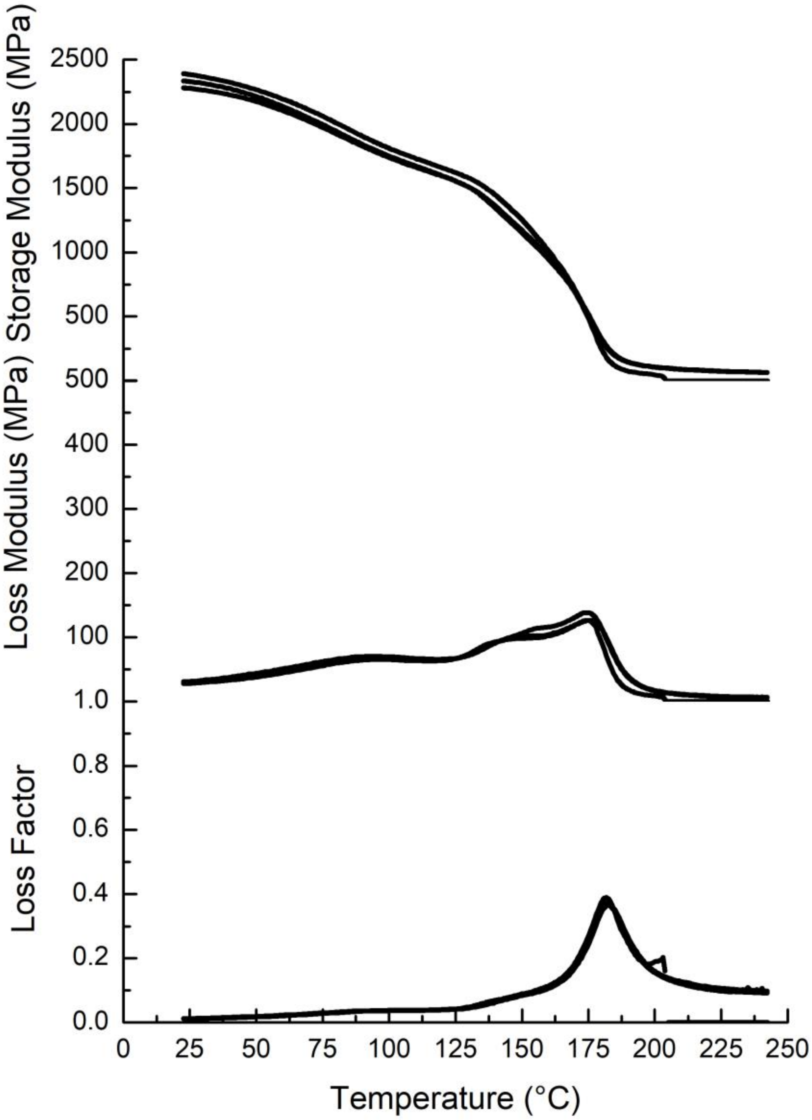


Figure S31. DMTA traces of reaction injection molded 4b-type copolymer.

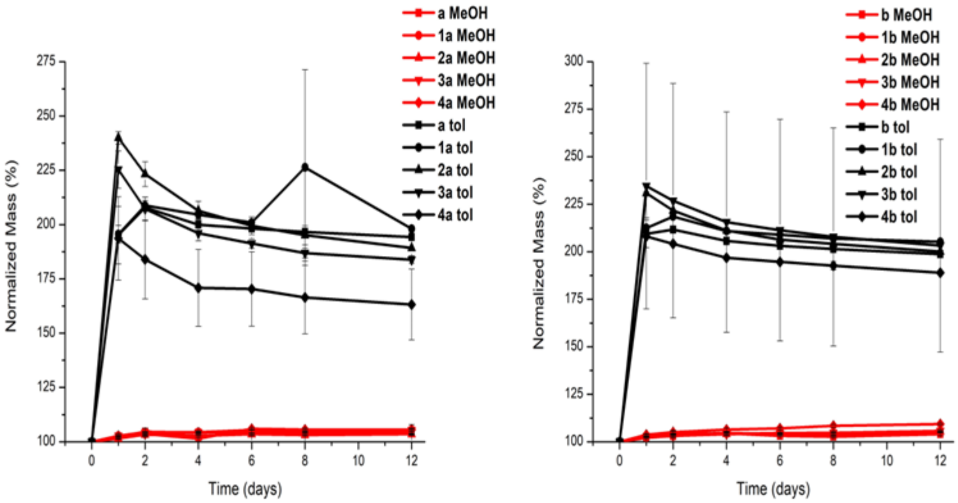


Figure S32. Swelling of a and b type polymers and copolymers in polar (methanol, black) and nonpolar (toluene, red) solvents.

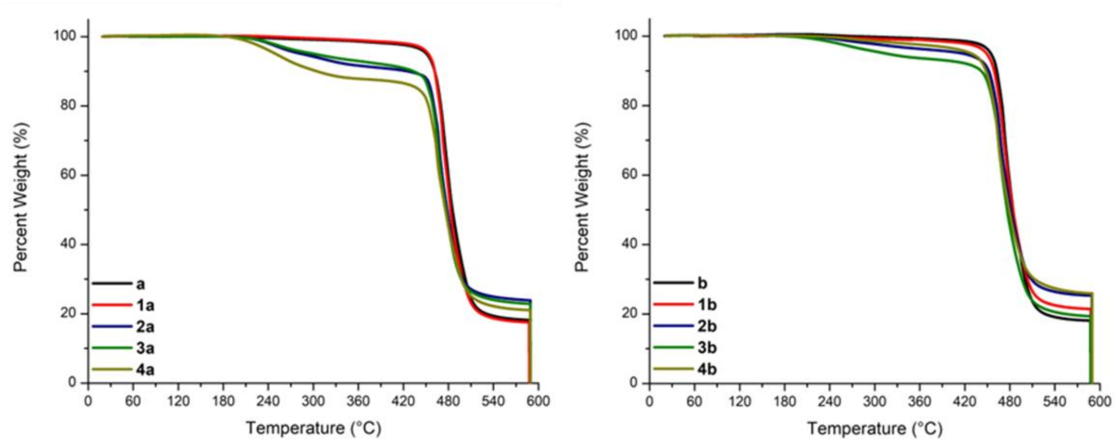


Figure S33. Thermogravimetric analysis of copolymers. Complete mass loss starts at approximately 450 °C.

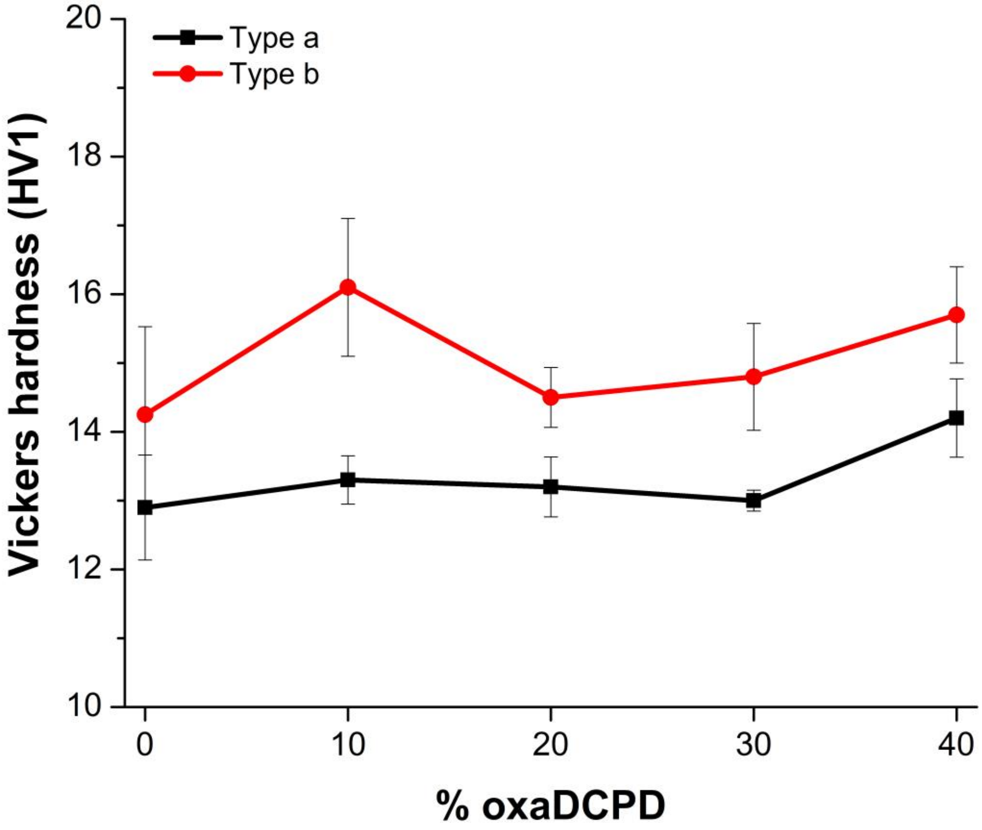


Figure S34. Vickers hardness data of a and b type polymers.

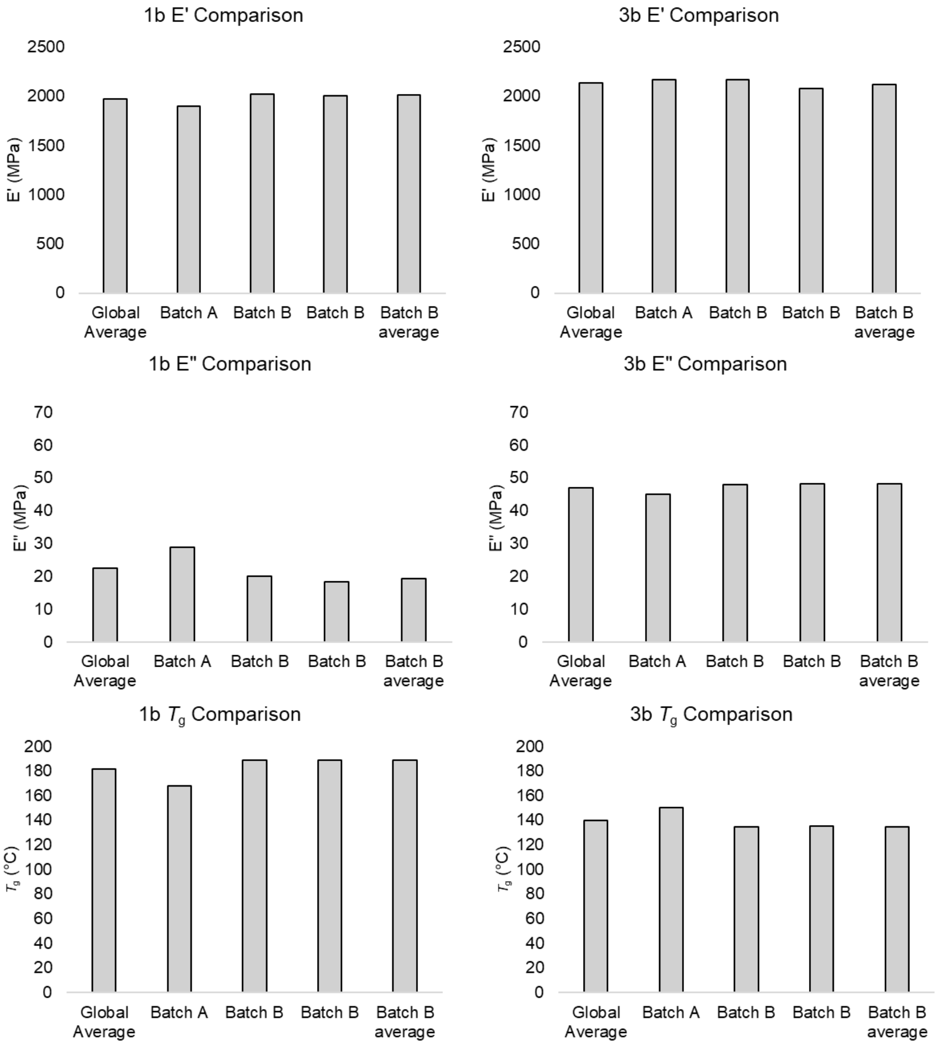


Figure S35. Batch-to-batch comparison of copolymers 1b and 3b. Batch A and Batch B were synthesized from different batches of resin.

Table S3. Vickers hardness values (HV1).

Sample	**Vickers hardness (HV1)**
a	12.9 ± 0.8
1a	13.3 ± 0.4
2a	13.2 ± 0.4
3a	13.0 ± 0.2
4a	14.2 ± 0.6
b	14.3 ± 1.3
1b	16.1 ± 1.0
2b	14.5 ± 0.4
3b	14.8 ± 0.8
4b	15.7 ± 0.7

Table S4. Swelling of type a and b polymers and copolymers in methanol.

Methanol							
Day	**0**	**1**	**2**	**4**	**6**	**8**	**12**
Sample	**Mass**						
a - x	0.1451	0.148	0.1536	0.151	0.1518	0.151	0.1526
a - y	0.144	0.1473	0.1482	0.1489	0.1487	0.1488	0.149
a - z	0.1191	0.1222	0.1252	0.1251	0.1258	0.1248	0.1248
1a - x	0.1323	0.136	0.1386	0.1379	0.1381	0.1382	0.1396
1a - y	0.1308	0.1349	0.1361	0.1366	0.1396	0.1383	0.1391
1a - z	0.1544	0.158	0.161	0.1614	0.1621	0.1619	0.1617
2a - x	0.1217	0.123	0.1271	0.1238	0.126	0.1257	0.1253
2a - y	0.1216	0.1237	0.1243	0.1255	0.1266	0.1255	0.1263
2a - z	0.127	0.1294	0.1312	0.131	0.1306	0.1305	0.1317
3a - x	0.1194	0.1221	0.125	0.1241	0.1252	0.1249	0.1263
3a - y	0.1574	0.1618	0.1631	0.1641	0.1634	0.1638	0.1648
3a - z	0.1545	0.1593	0.1605	0.1613	0.1628	0.1622	0.1631
4a - x	0.1195	0.1218	0.1237	0.1226	0.126	0.1256	0.1255
4a - y	0.0977	0.0996	0.1004	0.0977	0.1034	0.1027	0.1013
4a - z	0.119	0.1236	0.1244	0.121	0.1269	0.1267	0.1287
b - x	0.1329	0.1359	0.1374	0.1396	0.1375	0.1358	0.1392
b - y	0.1165	0.1198	0.1197	0.1224	0.1199	0.1197	0.1204
b - z	0.1304	0.1335	0.1342	0.1346	0.1344	0.1346	0.1357
1b - x	0.125	0.1284	0.1301	0.1308	0.1302	0.1303	0.1311
1b - y	0.142	0.1458	0.1473	0.1489	0.1468	0.1461	0.1487
1b - z	0.1331	0.1374	0.1381	0.1386	0.139	0.1384	0.1396
2b - x	0.1209	0.1238	0.1271	0.1247	0.1259	0.1263	0.1277
2b - y	0.111	0.1157	0.1175	0.116	0.1162	0.1161	0.1169
2b - z	0.1103	0.114	0.1146	0.1157	0.1156	0.1158	0.1161
3b - x	0.1003	0.1027	0.1042	0.105	0.1051	0.1058	0.1068
3b - y	0.1194	0.1211	0.1218	0.1235	0.124	0.1239	0.1254
3b - z	0.1483	0.152	0.1535	0.1542	0.1547	0.1555	0.1565
4b - x	0.1421	0.1469	0.15	0.151	0.1519	0.1537	0.1552
4b - y	0.1527	0.1582	0.1594	0.1612	0.1626	0.1647	0.1663
4b - z	0.1363	0.1418	0.1433	0.1462	0.1468	0.1488	0.1496

Table S5. Swelling of type a and b polymers and copolymers in toluene.

Toluene							
Day	**0**	**1**	**2**	**4**	**6**	**8**	**12**
Sample	**Mass**						
a - x	0.1393	0.2913	0.2897	0.2748	0.275	0.273	0.268
a - y	0.1238	0.2396	0.2567	0.2471	0.2451	0.2449	0.2412
a - z	0.1638	0.2994	0.3409	0.3325	0.3264	0.3209	0.3202
1a - x	0.1342	0.2612	0.2784	0.2713	0.2689	0.2685	0.267
1a - y	0.1226	0.2452	0.2543	0.2515	0.2435	0.3412	0.2423
1a - z	0.1608	0.3088	0.3401	0.332	0.3276	0.3226	0.3177
2a - x	0.132	0.3129	0.2885	0.2673	0.2598	0.2527	0.2458
2a - y	0.1631	0.396	0.3745	0.3444	0.3329	0.3261	0.3154
2a - z	0.1266	0.3038	0.2807	0.2599	0.2501	0.2455	0.2383
3a - x	0.112	0.2598	0.2281	0.2163	0.212	0.2071	0.2041
3a - y	0.151	0.3447	0.3223	0.302	0.2923	0.2858	0.2803
3a - z	0.1214	0.2618	0.2483	0.2367	0.2318	0.2264	0.223
4a - x	0.0979	0.2111	0.2001	0.1873	0.1859	0.1815	0.1779
4a - y	0.0843	0.1809	0.1731	0.1578	0.1595	0.1567	0.1532
4a - z	0.1024	0.2144	0.2026	0.1901	0.1879	0.1828	0.1799
b - x	0.1158	0.249	0.2434	0.2358	0.2337	0.2319	0.2277
b - y	0.1205	0.2555	0.2547	0.2481	0.2449	0.242	0.2407
b - z	0.1503	0.3026	0.3207	0.3122	0.3072	0.3056	0.3002
1b - x	0.1386	0.2935	0.3041	0.2945	0.2925	0.2865	0.2849
1b - y	0.1093	0.2385	0.2389	0.2297	0.2268	0.2253	0.2242
1b - z	0.1528	0.3171	0.3325	0.321	0.3184	0.3177	0.3133
2b - x	0.1549	0.3585	0.3427	0.3277	0.3177	0.3143	0.3104
2b - y	0.1398	0.322	0.31	0.2944	0.2888	0.286	0.2805
2b - z	0.1511	0.3487	0.3354	0.3197	0.3133	0.3095	0.3012
3b - x	0.1422	0.3141	0.3049	0.2883	0.2826	0.2785	0.2705
3b - y	0.1646	0.3641	0.3508	0.333	0.3282	0.3226	0.3158
3b - z	0.1225	0.2638	0.2557	0.2448	0.2379	0.2333	0.2296
4b - x	0.1297	0.2709	0.2661	0.2551	0.2523	0.2475	0.2457
4b - y	0.117	0.2438	0.238	0.229	0.2269	0.2247	0.22
4b - z	0.1257	0.2603	0.2562	0.2488	0.2457	0.2452	0.238

References

(1) Godwin, B.; Anvari, M. H.; Olfatbakhsh, T.; Mahbod, M.; Milani, A. S.; DiLabio, G. A.; Wulff, J. E. A Single-Atom Upgrade to Polydicyclopentadiene. *Macromolecules* **2023**, *56* (4), 1592–1600. https://doi.org/10.1021/acs.macromol.2c02260.