Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Grafting-Through ROMP for Gels with Tailorable Moduli and Crosslink Densities

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1. Materials and Instrumentation.

1.1 Reagents:

All materials were purchased from Sigma-Aldrich and used as received unless otherwise stated. 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride was purchased from Alfa Aesar. *Iso*-5-norbornene-2-methanol (Nb-OH) was purchased from TCI Chemicals. Dichloromethane was purchased from Acrōs Organics. The monomer *tert*-butyl acrylate (*t*BA) was purified by passing it through a basic alumina column immediately prior to use. Ultra-high purity grade nitrogen (Airgas, USA) was used to deoxygenate polymerizations.

1.2 Instruments:

NMR: Nuclear magnetic resonance (NMR) was used for the structural characterization of BDATC and linear polymers, as well as for monomer conversion calculations. ^{1}H and ^{13}C NMR spectra were acquired using a Varian Unity Inova 500 MHz NMR spectrometer and a 300 MHz NMR spectrometer, respectively. Samples were prepared in chloroform-d and transferred to 5 mm NMR tubes prior to room temperature spectra collection. ^{1}H NMR spectra were recorded using 128 scans and a 2 second relaxation delay. ^{13}C NMR spectra were recorded using 1,024 scans and a 2 second relaxation delay. To calculate monomer conversion, initial and final areas of monomer double bonds were compared to peak areas of a 1,3,5-trioxane internal standard.

THF-SEC: Size exclusion chromatography (SEC) was used to determine the number-average molecular weight (M_n), weight-average molecular weight (M_w), and dispersity ($Đ$) of all linear polymers. The SEC setup consisted of two in-series, Agilent PLgel MIXED B columns using HPLC grade tetrahydrofuran (THF) mobile phase at a flow rate of 1.0 mL/min at 35°C. Columns were calibrated using ten poly(methyl methacrylate) calibration standards with M_n values ranging from 800 to 2,570,000 g/mol. A Shimadzu RID-20A 120V refractive index detector equipped with a Shimadzu LD-20AD HPLC pump was used. LabSolutions Version 5.81 SP 1 software was used for data collection and analysis.

Rheometer: Rheology data was collected using a TA Instruments (New Castle, DE, USA) ARES DHR-3 rheometer. Gel samples were cut to 8 mm diameters using a razor blade, carefully loaded onto the rheometer using a spatula, and inspected for any damage prior to testing. A stainless steel parallel plate geometry with an 8 mm plate diameter was used. The top parallel plate was lowered to apply a slight positive force on each sample (~0.08 Newtons), marking the testing height. The gel thickness was also measured at this testing height. Tests were run at 23°C. TRIOS software was used for instrument control and data collection, while OriginLab's Origin software was used for data analysis. An initial set of amplitude sweeps were performed from 0.1 – 10% at 0.1, 1, and 10 rad/s to obtain the ranges of strain %'s that were in the linear viscoelastic regime for these gels. For each gel, the first test run was an angular frequency sweep (ω = 100 – 0.1 rad/s) at constant oscillation strain (0.1-0.5 %), shown in Fig. S7A-B and S8A-B. Average storage modulus (G′) values, reported in Fig. 2B-C, were calculated from moduli data points collected during angular frequency sweeps between 100 – 0.1 rad/s. The second test run was an oscillation amplitude sweep (0.10-100% oscillation strain) at a constant angular frequency ($\omega = 1.0$ rad/s) as shown in Fig. S7C-D and S8C-D. The constant oscillation strain used in each frequency sweep resided in the linear viscoelastic region of the amplitude sweep. The loss modulus measured for chemically-crosslinked networks is directly related to the amount of axial force applied during testing. For reference, the average axial forces applied during frequency sweeps are reported below.

RAFT Gel Series	
Gel Designation (DP_{RAFT}-DP_{ROMP})	Axial Force (N)
23-50	0.17
29-50	0.04
37-50	0.05
52-50	0.02
72-50	0.03

ROMP Gel Series	
Gel Designation (DP_{RAFT}-DP_{ROMP})	Axial Force (N)
23-7	-0.02
23-16	0.05
23-30	0.01
23-33	0.07
23-50	0.17
23-96	0.75
23-141	0.07

Raman: Raman spectra were taken of HOOC-poly(*t*BA)-COOH, Nb-poly(*t*BA)-Nb, and dried MaGNet gels to determine percent norbornene conversion from macrocrosslinker to gel. The setup included a Renishaw inVia^{TM} confocal spectrometer with a 488 nm laser excitation source set to 5% laser power. Laser alignment and calibration was done using a Silicon wafer before solid samples were loaded onto a glass slide. Spectra were acquired using a 90 second accumulation time. Data was collected using Renishaw's WiRE software and analyzed using Origin Lab's Origin software.

2. Experimental Details.

2.1 Synthesis of BDATC

The synthesis of chain transfer agent S,S′-bis(α,α'-dimethyl-α''-acetic acid)trithiocarbonate (BDATC) was based on literature.[1] Typically, the following reagents were added to a room-temperature flask equipped with vigorous mechanical stirring: carbon disulfide (6.850 g, 0.0900 mol), chloroform (26.875 g, 0.225 mol), acetone (13.075 g, 0.225 mol), tetrabutylammonium bromide (0.572 g, 1.775 mmol) and 30.0 mL of mineral spirits. Once cooled to 0 °C with an ice bath, the flask was purged with nitrogen and an aqueous solution of sodium hydroxide in deionized water (50% NaOH by weight) (50.5 g total weight, 0.630 mol NaOH) was added dropwise over 30 minutes. The ice bath was then removed and the reaction was allowed to proceed at 25 °C for 12 hours. After 12 hours, 225 mL of deionized water was added to dissolve the solids which had formed overnight. Then, 30.0 mL of hydrochloric acid (37%) was added to acidify the aqueous layer. After vigorous stirring for an additional 30 min, the earth-colored insoluble solids were vacuum filtrated and washed with copious amounts of deionized water. The crude product was collected after drying *in vacuo* at 40 °C overnight. The crude product was slowly recrystallized at room temperature, thrice from 4:1 (by volume) toluene: acetone mixture yielding a bright yellow crystalline solid (~65% yield). ^{1}H NMR peak assignments: 1.71 ppm (s). ^{13}C NMR peak assignments: 217.24 ppm (s), 179.97 ppm (s), 55.82 ppm (s), and 25.16 ppm (s).

2.2 RAFT polymerization of HOOC-poly(*t*BA)-COOH

An example procedure is described here. A ratio of [*t*BA]: [BDATC]: [AIBN] ≈ 25:1:0.025 was targeted along with a monomer weight percent of *ca.* 33%. The following components of the RAFT polymerization were added to a 10-mL Schlenk flask: inhibitor-free *t*BA (3.00 g, 23.4 mmol); chain-transfer agent, BDATC (0.264 g, .936 mmol); radical initiator, azobisisobutyronitrile (0.00380 g, 0.0234 mmol); internal standard, 1,3,5-trioxane (0.175 g, 1.95 mmol); and solvent, dimethyl sulfide (5.99 g, 76.7 mmol). A small sample of the crude reaction mixture was saved for ^{1}H NMR analysis serving as time zero of the polymerization. A magnetic stir bar was added. The flask was sealed using rubber septa secured with electrical tape. The solution was deoxygenated by bubbling with ultra-high purity N_2 for 30 minutes, lowered into an oil bath equilibrated to 70°C while still bubbling, and then disconnected from the Schlenk line. After 3 hours, the flask was removed from the oil bath, opened to air, and quickly placed in a refrigerator. A sample of the crude reaction mixture was immediately collected and analyzed by SEC (to determine molecular weight and dispersity) and ^{1}H NMR (to determine percent monomer conversion). The crude polymer was purified *via* precipitation thrice from a 3:1 methanol: deionized water (by weight) solution. The purified polymer was oven-dried for 1 day in a vacuum oven at 40°C. The molecular weight and dispersity of pure HOOC-poly(*t*BA)-COOH was determined by SEC. The structure of HOOC-poly(*t*BA)-COOH was verified by ^{1}H NMR. Similar procedures were followed for the series of RAFT polymers of different molecular weights (Table S1). Formulations and characterization results for each polymer are summarized in Table S1.

2.3 Synthesis of Nb-poly(*t*BA)-Nb

All macrocrosslinkers reported in this work were synthesized using carbodiimide-mediated esterification in methylene chloride. An example procedure is described here. Nb-poly(*t*BA)-Nb was synthesized by esterification of the hydroxyl group of *iso*-5-norbornene-2-methanol (0.2704 g, 0.0021 mol) with the carboxy-terminated chain ends of HOOC-poly(*t*BA)-COOH (1.436 g, 0.00053 mol; $M_{\mathrm{n,theo}}$ = 2,708 g/mol), using 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDAC) (1.043 g, 0.00544 mol) as a condensation reagent and 4-dimethyaminopyridine (DMAP) (0.665 g, 0.00544 mol) as a catalyst. A ratio of [Nb-OH]:[HOOC-poly(*t*BA)-COOH]:[EDAC]:[DMAP] ≈ 4:1:10:10 was targeted. The crude product was purified *via* precipitation thrice from a 3:1 methanol:deionized water (w/w) solution. The purified polymer was oven-dried for 1 day in a vacuum oven at 40°C. The molecular weight and dispersity of pure Nb-poly(*t*BA)-Nb was determined by SEC. The structure and molecular weight of Nb-poly(*t*BA)-Nb were verified by ^{1}H NMR. Key ^{1}H NMR peaks (see Figure 1) correspond to the norbornene double bond protons (**a**, 6.15-5.94 ppm, integration of 3.83), methylene protons (b, 4.10-3.64 ppm, integration of 3.98), and ultimate methine protons (**c**, 4.59 ppm, integration of 2.00). Similar procedures were followed to synthesize all macrocrosslinkers described in Table S1 (see Table S3 for ^{1}H NMR integration details).

2.4 Gel synthesis by grafting-through ROMP

An example procedure for gel synthesis is described here (Table S2, Entry 1). Chloroform was deoxygenated by sparing with nitrogen for 30 minutes and then brought into a glovebox. In a glovebox, two solutions were prepared: (1) a solution of Grubbs' 3rd generation catalyst (G3) (0.0040 g, 4.52×10^{-6} mol) in chloroform (0.400 mL) and (2) a solution of a Nb-poly(*t*BA)-Nb (0.045 g, 1.54×10^{-5} mol of Nb-poly(*t*BA)-Nb, 3.08×10^{-5} mol of norbornene end groups) in chloroform (0.260 mL). Once the two solutions were prepared, 0.055 mL of G3 solution was quickly added by Hamilton syringe to a round poly(tetrafluoroethylene) jar containing the macrocrosslinker solution. The solutions were quickly stirred by shaking the jar by hand. The jar was then tightly capped to prevent chloroform evaporation and set aside inside the glovebox for 1 hour to allow gel formation. Each gel formed as a flat disk with the same diameter as the jar. After 1 hour, the gels were removed from the glovebox, removed from the jars, and transferred to a glass container filled with *N*-methyl-2-pyrrolidone (NMP). Gel samples underwent solvent exchange by submersion in NMP for two weeks prior to rheological testing. For the first series of gels, each gel was made from a Nb-poly(*t*BA)-Nb of a different degree of polymerization (DP). For each gel of this first study, the weight percent of Nb-poly(tBA)-Nb was kept constant and the [norbornene]:[G3] ratio was kept constant during ROMP at 50. For the second series of gels, the RAFT degree of polymerization was kept constant. For each gel of this second study, the weight-percent of Nb-poly(*t*BA)-Nb was kept constant and the G3 concentration was adjusted depending on the targeted norbornene: G3 molar ratio. After solvent exchange, the gels were cut into 8 mm diameter discs in preparation for rheological testing.

3. Supporting Figures.

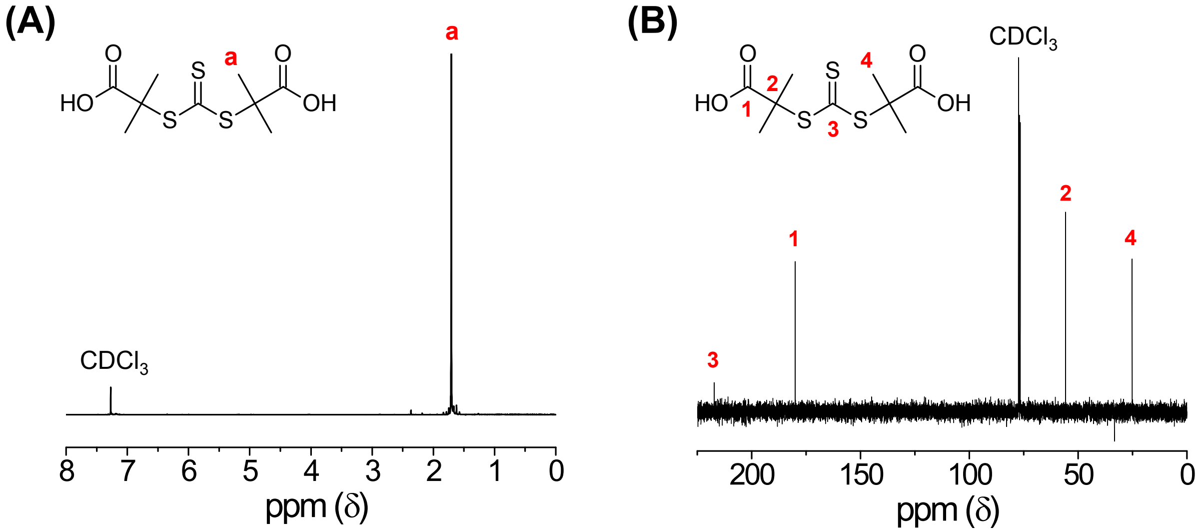

Figure S1: (A) ^{1}H NMR and (B) ^{13}C NMR spectrum with peak assignments of chain transfer agent (BDATC) in CDCl$_3$. Peaks were assigned based on literature.[1,2]

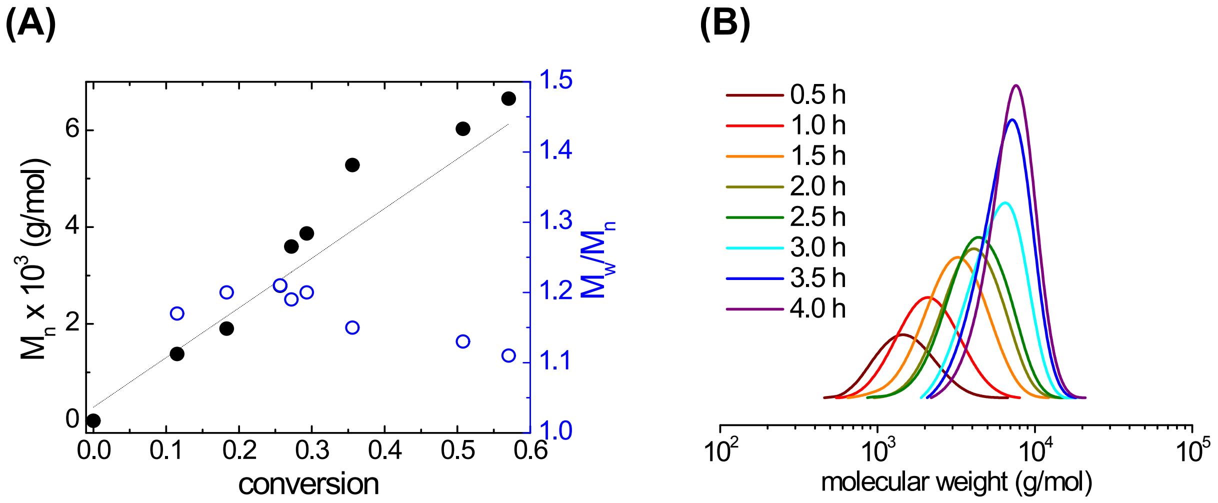

Figure S2: RAFT polymerization kinetics with BDATC. (A) Number-averaged molecular weight (M_n) and dispersity (Đ) as a function of monomer conversion during RAFT of *t*BA in DMSO. RAFT was conducted using a [*t*BA] of ~31 wt. % at 80 °C with molar ratios of [*t*BA]:[BDATC]:[AIBN] = 80:1:0.03. The dashed lined represents the theoretical molecular weight ($M_{n,theo}$), defined as $M_{n,theo}$ = conv. × MW_{tBA} × ([*t*BA]/[BDATC]) + MW_{BDATC}. (B) SEC traces illustrating the evolution of molecular weight with time during RAFT.

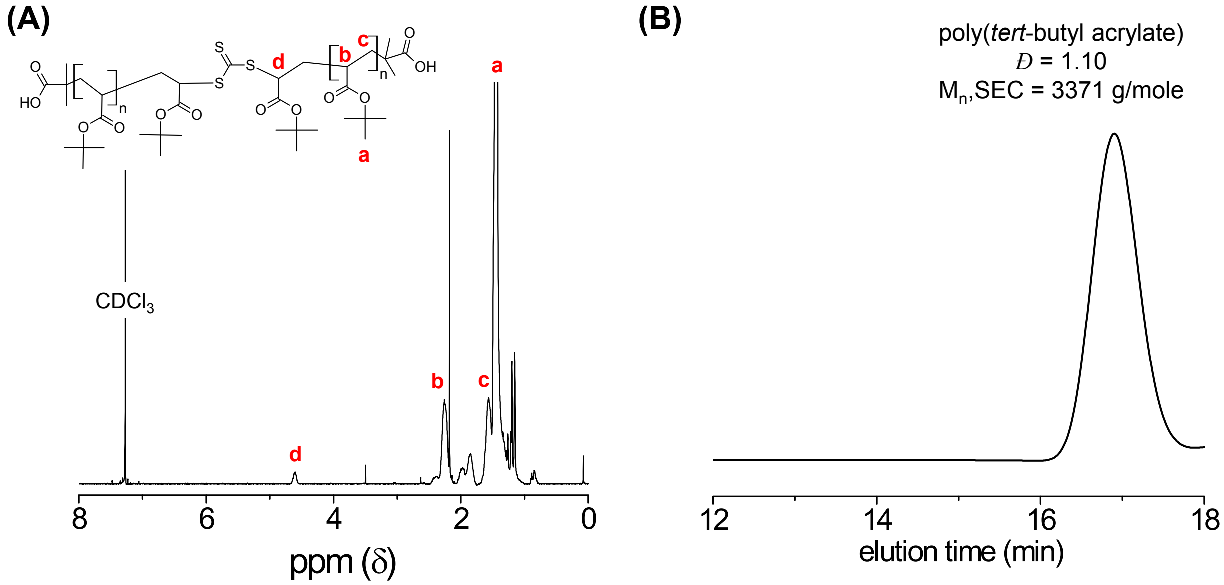

Figure S3: (A) ^{1}H NMR of HOOC-poly(*t*BA)-COOH in CDCl$_3$. Peaks were assigned based on literature and Marvin Sketch predictive software.[3,4,9] (B) THF-SEC trace of HOOC-poly(*t*BA)-COOH.

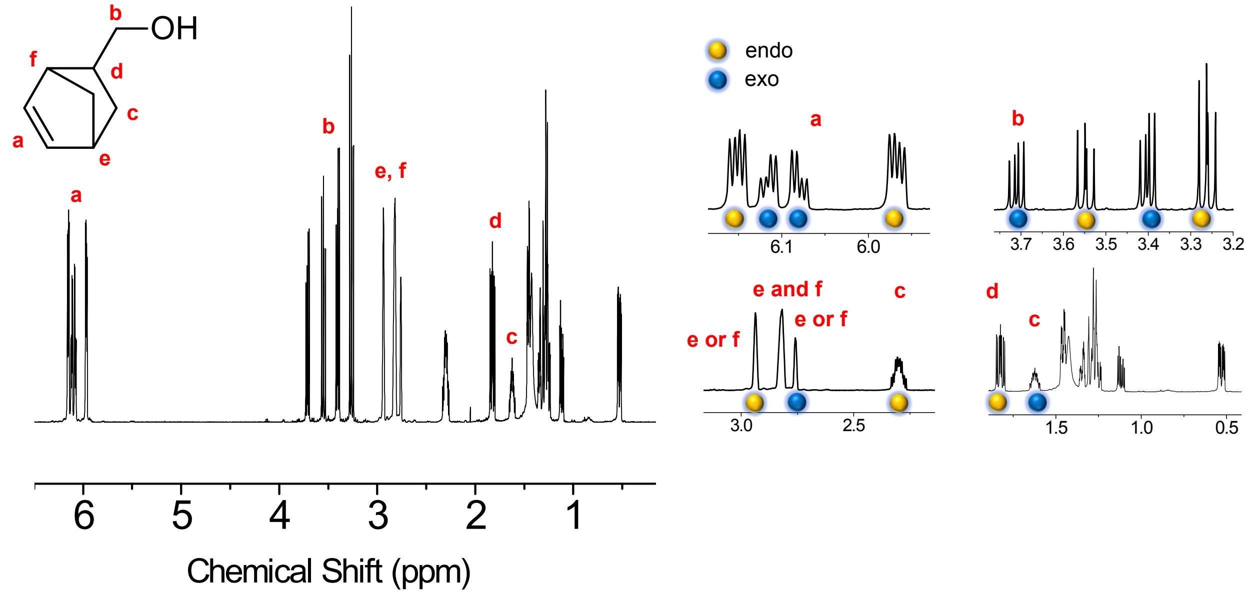

Figure S4: ^{1}H NMR and relevant peak assignments of *iso*-5-norbornene-2-methanol in CDCl$_3$. Peaks were assigned based on literature[6,8] and Marvin Sketch predictive software.[9]

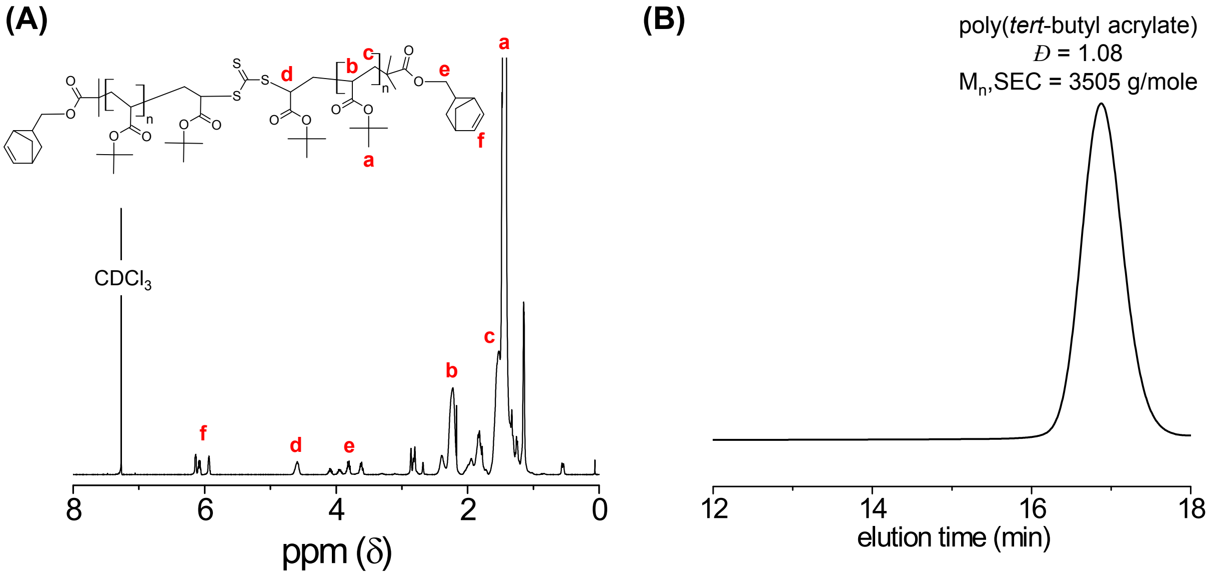

Figure S5: (A) ^{1}H NMR of Nb-poly(*t*BA)-Nb in $CDCl_3$. Peaks were assigned based on literature and Marvin Sketch predictive software.[5,6,7,8,9] (B) THF-SEC trace of Nb-poly(*t*BA)-Nb.

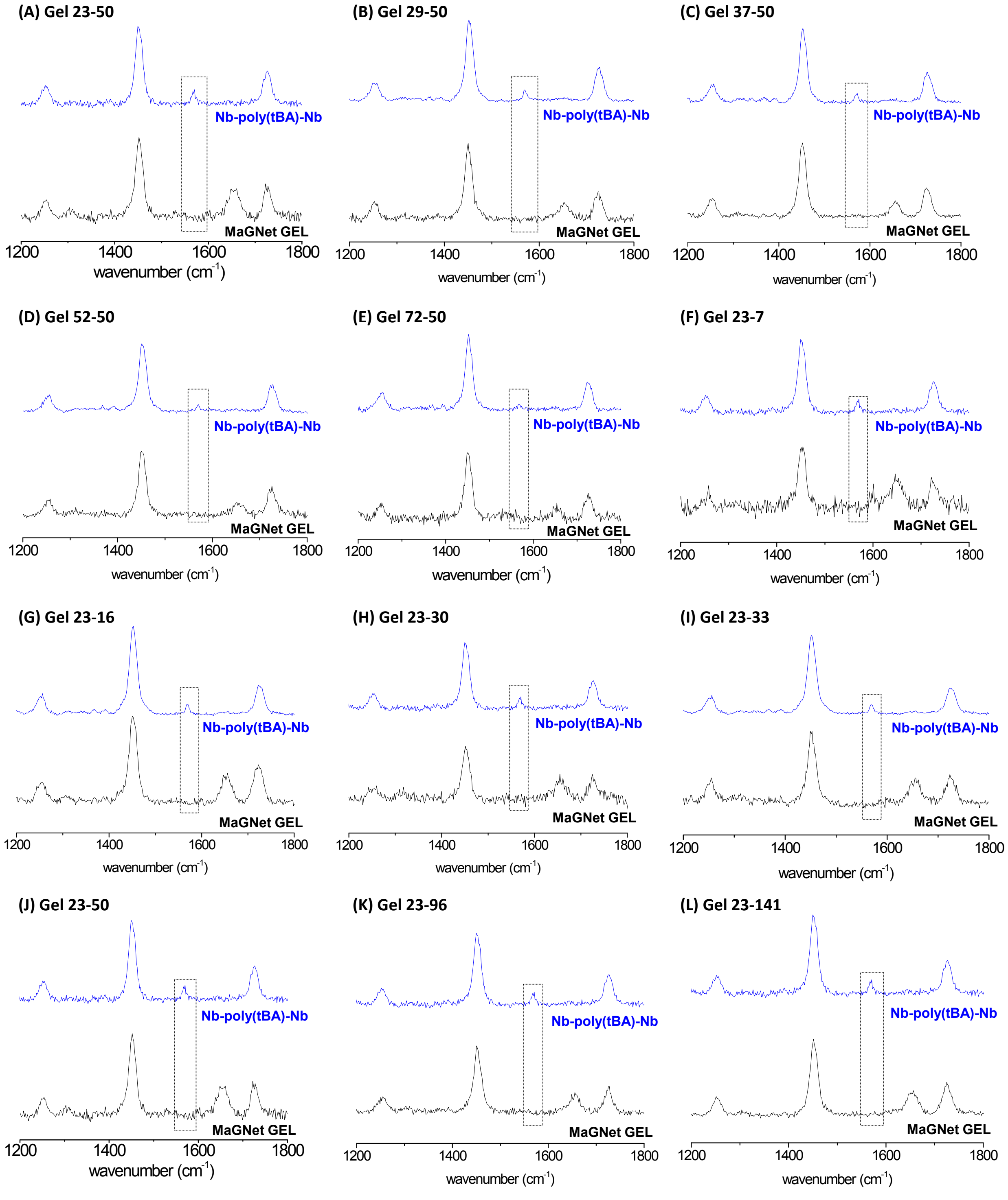

Figure S6: Raman spectra before and after *gt*-ROMP corresponding to each gel reported in Table S2.

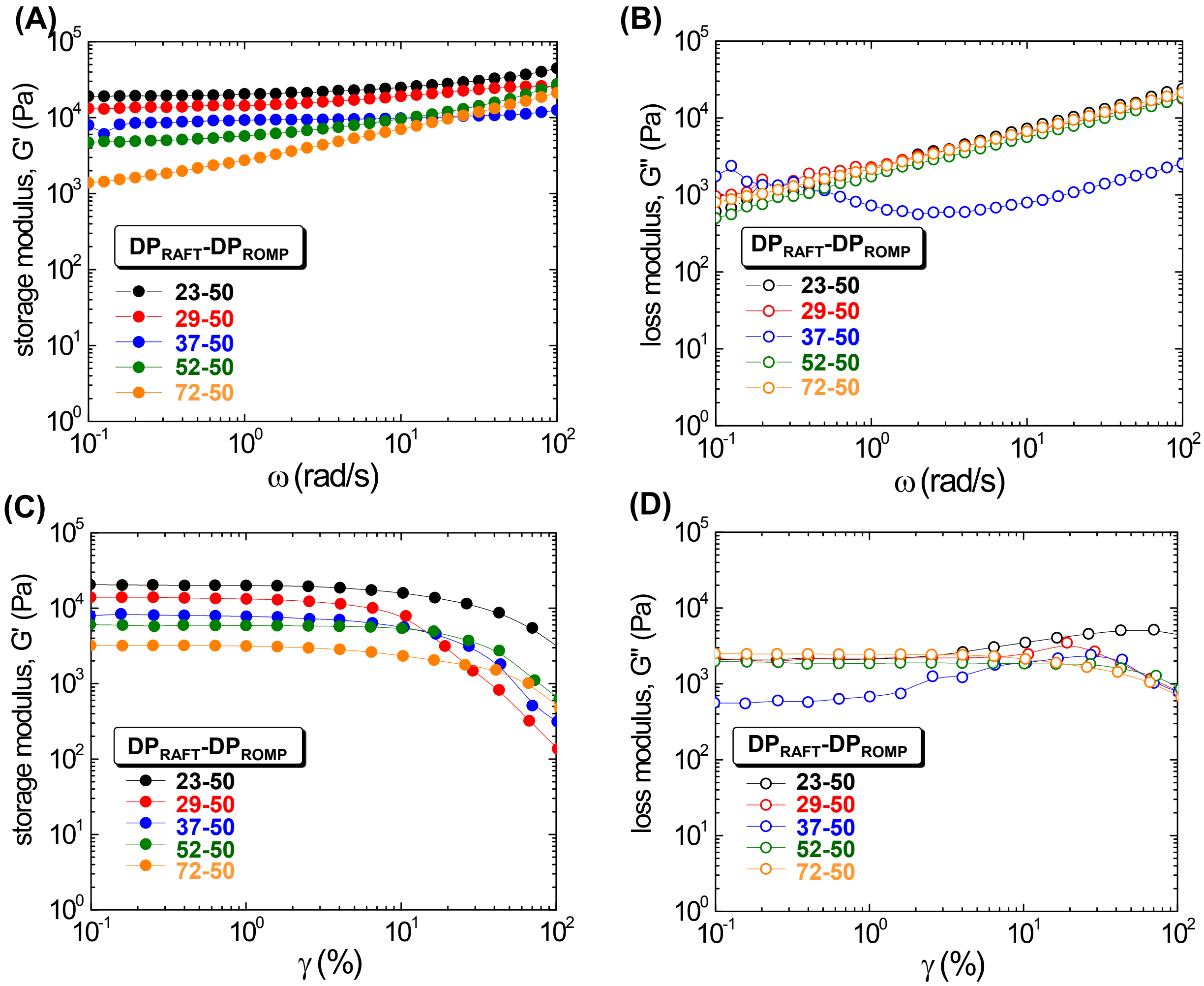

Figure S7. Rheological characterization of the RAFT series of gels. (A-B) Dependence of moduli (storage, G′ = solid symbol, loss, G″ = open symbol) on frequency (ω). (C-D) Dependence of moduli (storage, G′ = solid symbol, loss, G″ = open symbol) on strain (γ).

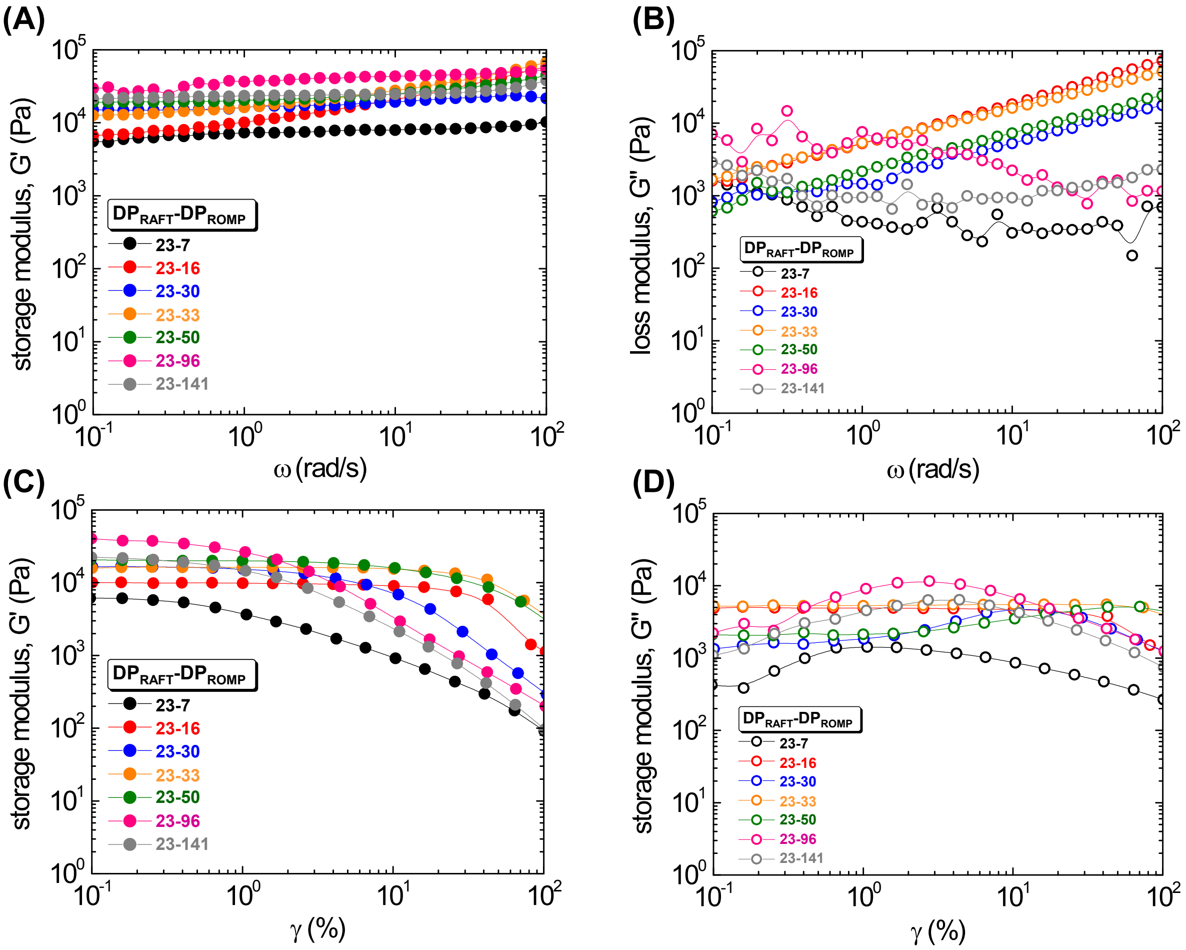

Figure S8. Rheological characterization of the ROMP series of gels. (A-B) Dependence of moduli (storage, G′ = solid symbol, loss, G″ = open symbol) on frequency (ω). (C-D) Dependence of moduli (storage, G′ = solid symbol, loss, G″ = open symbol) on strain (γ).

4. Supporting Tables.

Table S1: Experimental and structural details for RAFT precursors and macrocrosslinkers.

	HOOC-poly(*t* BA)-COOH								Nb-poly(*t* BA)-Nb							
Entry[a]	[*t* BA]/[BDATC]/[AIBN]			time (h)	conversion (%)	$M_{n,\,theo}$[b] (g/mol)	$M_{n,\,SEC}$ (g/mol)	*Đ*	f_{Nb}[c] (%)	$M_{n,\,theo}$[d] (g/mol)	$M_{n,\,NMR}$[e] (g/mol)	$M_{n,\,SEC}$ (g/mol)	*Đ*	$M_{n,\,avg}$ (g/mole)	DP[f]
1	25	1	0.025	3.0	76	2,708	3,371	1.10	96	2,920	3,769	3,505	1.08	3,398	23
2	30	1	0.025	4.0	54	3,031	3,193	1.08	95	3,243	3,763	3,147	1.08	3,384	23
3	40	1	0.025	5.0	77	4,210	3,963	1.09	100	4,422	4,485	3,896	1.10	4,268	29
4	50	1	0.025	8.0	63	4,320	5,152	1.10	93	4,532	5,850	5,292	1.10	5,225	37
5	55	1	0.025	8.0	86	6,366	7,484	1.08	93	6,578	7,571	7,451	1.08	7,200	52
6	80	1	0.030	8.3	81	8,563	8,869	1.10	97	8,776	10,894	9,393	1.08	9,688	72

a - All polymerizations were performed at 70 °C (except for Entry 6, conducted at 80 °C) in DMSO at [*t* BA] of *ca.* 34 wt. %.

b - M_n,theo = conv.· MW_{tBA} · ([*t* BA]/[BDATC]) + MW_{BDATC}

c - Percent Nb functionalization (f_{Nb}) was determined using integration (I) values from ^{1}H NMR. $f_{Nb} = (I_{6.14\text{-}5.93\ ppm}/4)/(I_{4.59\ ppm}/2)\cdot 100$

d - M_n,theo = conv.· MW_{tBA} · ([*t* BA]/[BDATC]) + $MW_{BDATC} + 2 \cdot (MW_{Nb\text{-}OH} - MW_{H2O})$

e - M_n from NMR (M_n, NMR) was determined using M_n, NMR = $MW_{tBA} \cdot (I_{2.49\text{-}2.11\ ppm}/1)/(I_{4.59\ ppm}/2) + 2 \cdot MW_{chain\text{-}end} + MW_{TTC+ultimate}$

f - DP = $(M_{n,avg} - MW_{TTC} - 2 \cdot MW_{chain\text{-}end})/MW_{tBA}$

Table S2: Summary of experimental details and characterization results for MaGNet gels.

Entry[a]	Gel designation (DP_{RAFT}-DP_{ROMP})	Precursor (Table S1, entry #)	RAFT DP	ROMP DP[b]	Total mass (g)	[Nb-poly(*t* BA)-Nb] (wt. %)	[Nb]/[G3]	Nb conv.[b] (%)	% *f*	G'[c] (Pa)
1	23-50	1	23	48	0.516	8.72	50	100	96	19,432
2	29-50	3	29	50	0.516	8.72	50	100	100	13,312
3	37-50	4	37	47	0.516	8.72	50	100	93	8,460
4	52-50	5	52	47	0.516	8.72	50	100	93	5,127
5	72-50	6	72	49	0.516	8.73	50	100	97	1,941
6	23-7	1	23	7	0.519	8.66	7	100	96	6,410
7	23-16	2	23	16	0.517	8.70	17	100	95	8,076
8	23-30	1	23	30	0.516	8.71	31	100	96	15,127
9	23-33	2	23	33	0.516	8.72	35	100	95	14,089
10	23-96	1	23	96	0.516	8.72	100	100	96	30,811
11	23-141	1	23	141	0.517	8.71	147	100	96	22,376

a - All gels were synthesized using a total reaction mass of approx. 0.516 g (0.32 mL) at room temperature in chloroform for 45 minutes.

b - ROMP DP was calculated as [Nb]/[G3] · Nb conv. · *f*. For each gel, conversion of Nb was approx. quantitative as determined by Raman spectroscopy.

c - G' is reported as an average modulus value taken from frequency sweeps between 0.1 to 100 rad/s at an oscillation strain of 0.1-0.5 %

Table S3: Summary of ^{1}H NMR integration values for macrocrosslinkers.

	Integration Values for Nb-poly(*t* BA)-Nb			
Entry	f_{Nb}[a] (%)	$I_{(6.14\text{-}5.93\ ppm)}$[b]	$I_{(4.10\text{-}3.64\ ppm)}$[c]	$I_{(4.59\ ppm)}$[d]
1	96	3.83	3.98	2.00
2	95	3.82	3.81	2.00
3	100	4.10	3.99	2.00
4	93	3.72	3.85	2.00
5	93	3.74	3.45	2.00
6	97	3.88	3.95	2.00

a - Percent Nb functionalization (f_{Nb}) was determined using integration (I) values from ^{1}H NMR. $f_{Nb} = (I_{6.14\text{-}5.93\ ppm}/4)/(I_{4.59\ ppm}/2)\cdot 100$

b - Integration values for double bond protons of the macrocrosslinker.

c - Integration values for methylene protons of the macrocrosslinker.

d - Integration values for ultimate methine protons of the macrocrosslinker.

5. Supporting References:

(1) Lai, J.; Filla, D.; Shea, R., Functional polymers from novel carboxyl-terminated trithiocarbonates as highly efficient RAFT agents. *Macromolecules* **2002,** *35* (18), 6754.

(2) Wei, K.; Wang, L.; Li, L.; Zheng, S., Synthesis and characterization of bead-like poly(N-isopropylacrylamide) copolymers with double decker silsesquioxane in the main chains. *Polymer Chemistry* **2015,** *6* (2), 256-269.

(3) Grieshaber, S. E.; Paik, B. A.; Bai, S.; Kiick, K. L.; Jia, X., *Soft Matter*, **2013**, 9, 1589.

(4) Suchoparek, M.; Spevacek, J., *Macromolecules*, **1993**, 26 (1), 102.

(5) Stone, D.; Welna, D.; Allcock, H., Synthesis and characterization of lithium-ion conductive membranes with low water permeation. *Chem. Mater.* **2007,** *19*, 2473-2482.

(6) Yan, J.; Ye, Q.; Han, X.; Zhou, F., Step-by-step build-up of ordered p-n heterojunctions at nanoscale for efficient light harvesting. *RSC Advances,* **2013,** *3*, 166**.**

(7) Silverstein, R.; Bassler, G.; Morrill, T., Spectrometric identification of organic compounds (Fifth edition). Wiley, New York, 1991.

(8) Blanco, J.; Fernandez, F.; Garcia-Mera, X.; Rodriguez-Borges, J., Divergent synthesis of two precursors of 3’-homo-2’-deoxy- and 2’-homo-3’-homo-deoxy carbocyclic nucleosides. *Tetrahedron* **2002,** *58,* 8843-8849.

(9) Chem Axon NMR Predictor – Version 16.1.18.0.