

Hypervalent Iodine-Based Dynamic and Self-Healing Network Polymers

Avichal Vaish and Nicolay V. Tsarevsky*

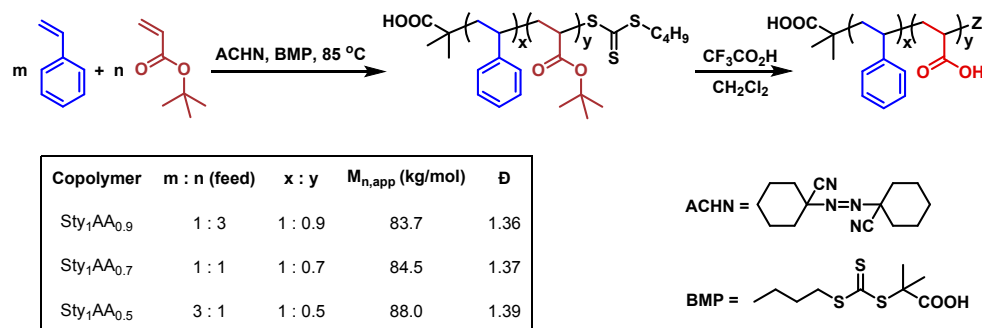
Department of Chemistry, Southern Methodist University, Dallas, TX, USA 75275

SUPPORTING INFORMATION

Table of Contents

1. Polymerization kinetics	2
2. Conversion of poly(Sty- <i>co</i> -tBA) to poly(Sty- <i>co</i> -AA).....	3
3. Effect of nucleophiles and reducing agents.....	3
4. Conversion of dynamic to permanent gels.....	4
4.1. Thermal curing	4

1. Polymerization kinetics



Scheme S1. Synthesis of carboxylate group-containing copolymers by copolymerization of Sty and tBA under RAFT polymerization conditions, followed by deprotection of the tert-butyl ester groups in the presence of $\text{CF}_3\text{CO}_2\text{H}$.

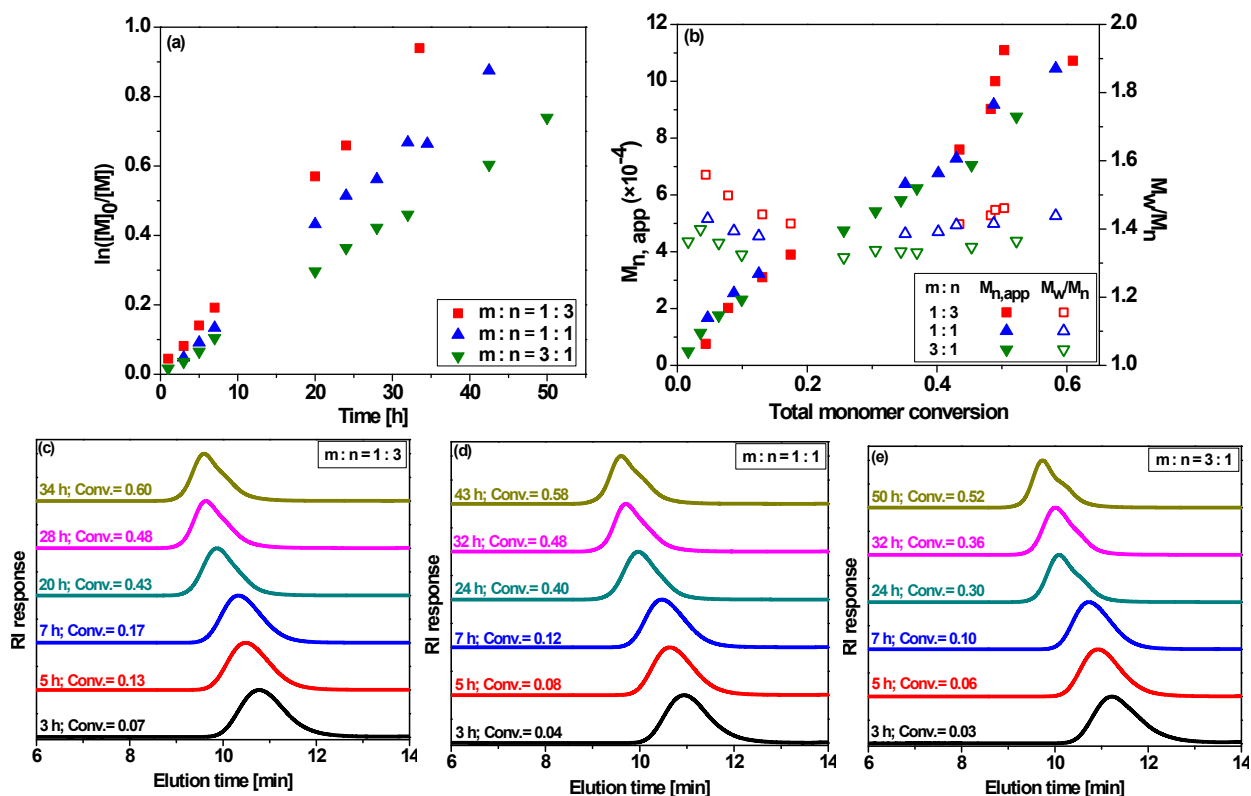


Figure S1. Kinetics of RAFT copolymerization of Sty and tBA (a); evolution of $M_{n,app}$ and M_w/M_n with monomer conversion (b) and evolution of SEC traces of the polymers obtained using feed molar ratios of Sty and tBA equal to 1:3 (c), 1:1 (d), and 3:1 (e). The reaction times and monomer conversions are shown at each curve.

2. Conversion of poly(Sty-*co*-tBA) to poly(Sty-*co*-AA)

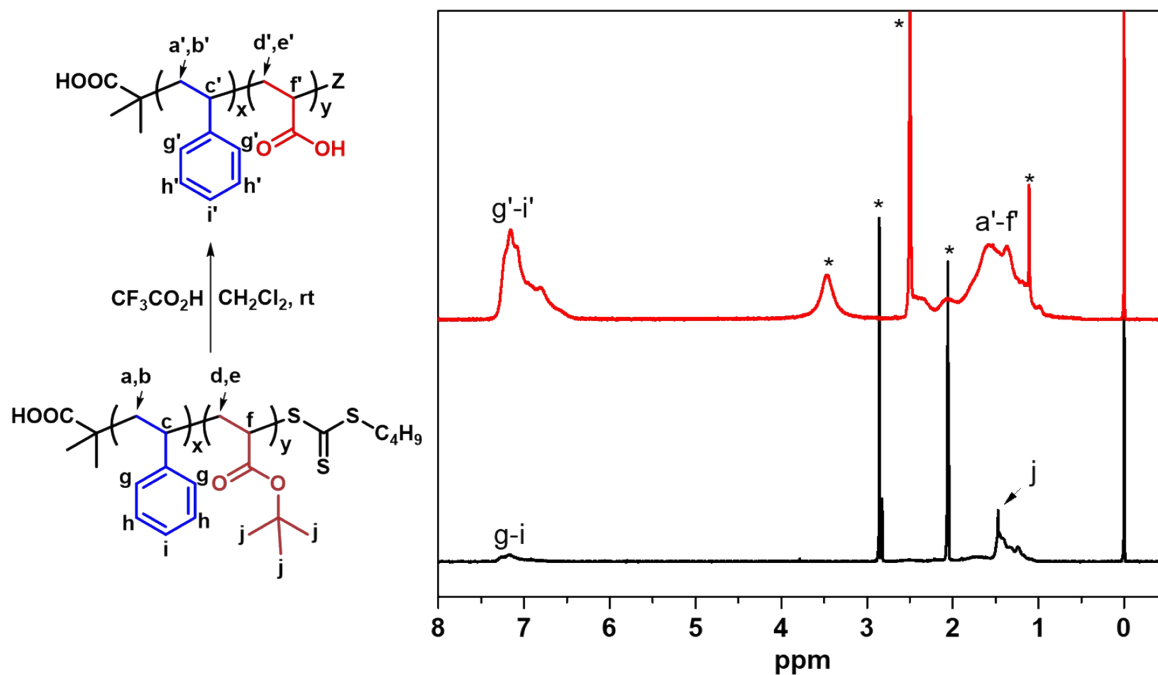


Figure S2. ¹H NMR spectra of poly(Sty-*co*-tBA) (bottom) and poly(Sty-*co*-AA) (top) in acetone-*d*₆ and DMSO-*d*₆, respectively. The peaks marked with asterisks belong to residual solvents.

3. Effect of nucleophiles and reducing agents

To demonstrate the ability of nucleophiles to cause polymer degradation via ligand-exchange, a gel was prepared by mixing PhI(O₂CCH₃)₂ (0.15 M) and Sty₁AA_{0.9} (0.73 M with respect to carboxylate groups) solutions in DMAc along with a trace amount of indigo carmine. Subsequently, 200 μL of saturated NaN₃ solution in DMAc was added to the gel. The gel degraded within 6 h, as shown in Figure S3a-b.

In a separate experiment, 200 μL of Bu₃P (nucleophile and reducing agent) was added to a gel with the same composition as above. The network degraded completely within 45 min (Figure S3c-d).

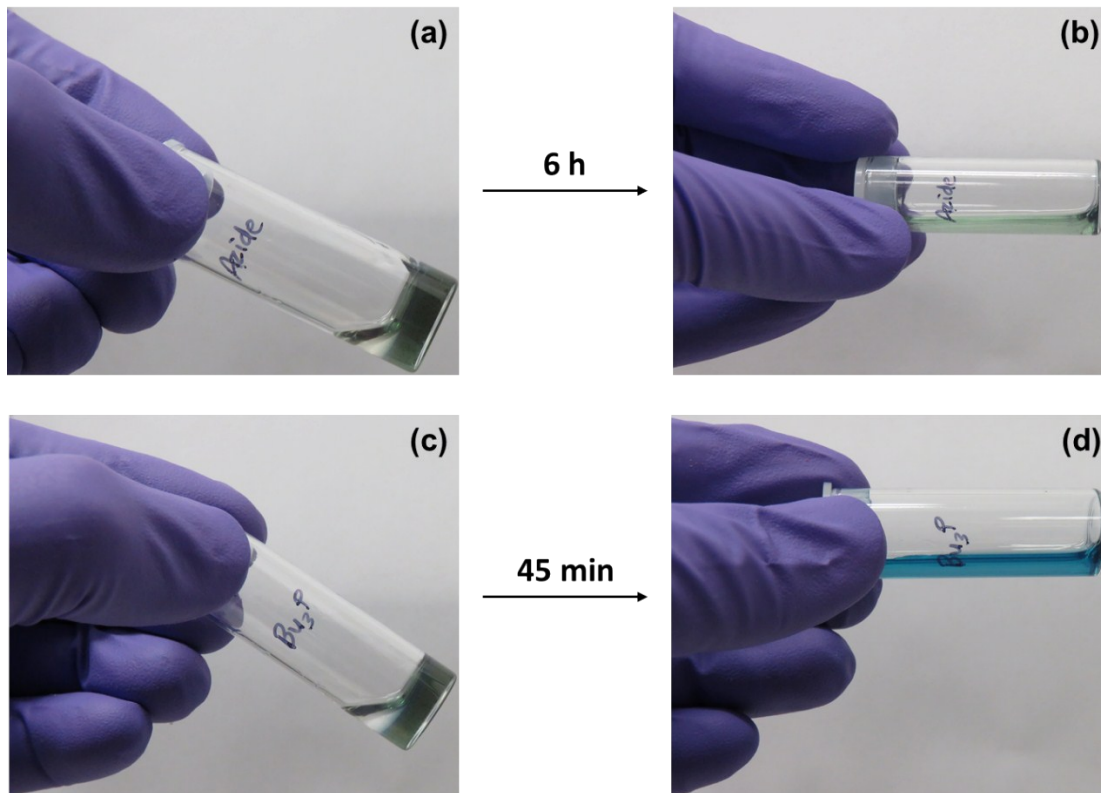


Figure S3. Gels with (diacyloxyiodo)benzene-type groups at the crosslinks treated with NaN_3 solution (a, b) or Bu_3P (c, d). The first picture in each case shows the gel right after the addition of the reagent, and the second picture shows the degraded gel after the specified time.

4. Conversion of dynamic to permanent gels

4.1. Thermal curing

Gels were prepared by mixing 300 μL of $\text{Sty}_1\text{AA}_{0.9}$ solution (0.21 M with respect to carboxylate groups) with 200 μL of $\text{PhI}(\text{O}_2\text{CCH}_3)_2$ solution (0.10 M) in 1,4-dioxane in a microwave tube, which was then kept in a microwave reactor at 200 $^\circ\text{C}$ for 2 min. The power set to 300 W and the timer was started when the temperature reached at 200 $^\circ\text{C}$. The total reaction time (including heating and cooling) was 40 min. After the reaction, the gel was washed 1,4-dioxane ($2 \times 500 \mu\text{L}$), which was discarded and then 100 μL of $\text{CH}_3\text{CO}_2\text{H}$ along with 500 μL of

1,4-dioxane were added to the tube (Figure S4a). The gel remained intact even after 72 h (Figure S4b), which proved the formation of permanent crosslinks during the thermal treatment.

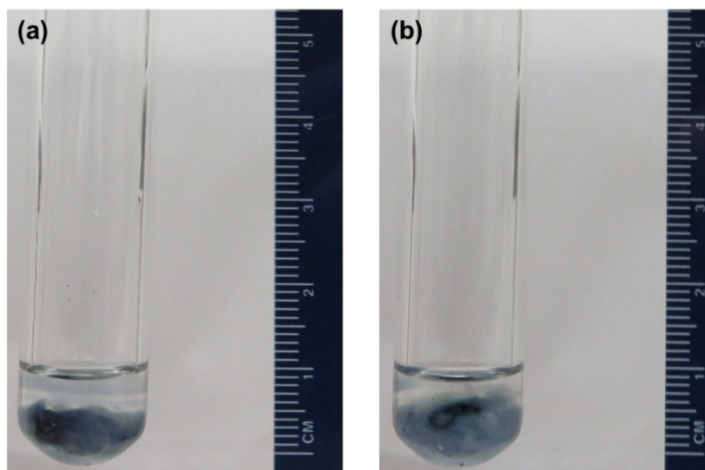


Figure S4. Set gel prepared by microwave heating of dynamic gel just after the addition of $\text{CH}_3\text{CO}_2\text{H}$ (a) and 72 h later (b).