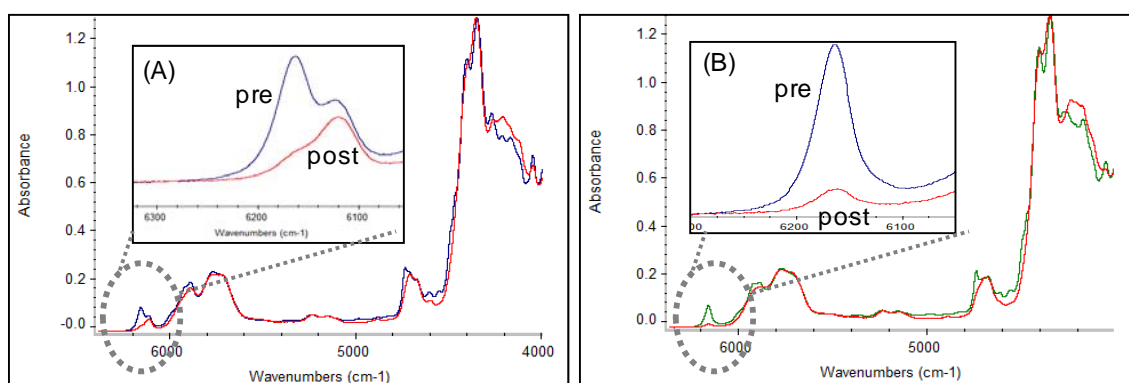


Supporting Information

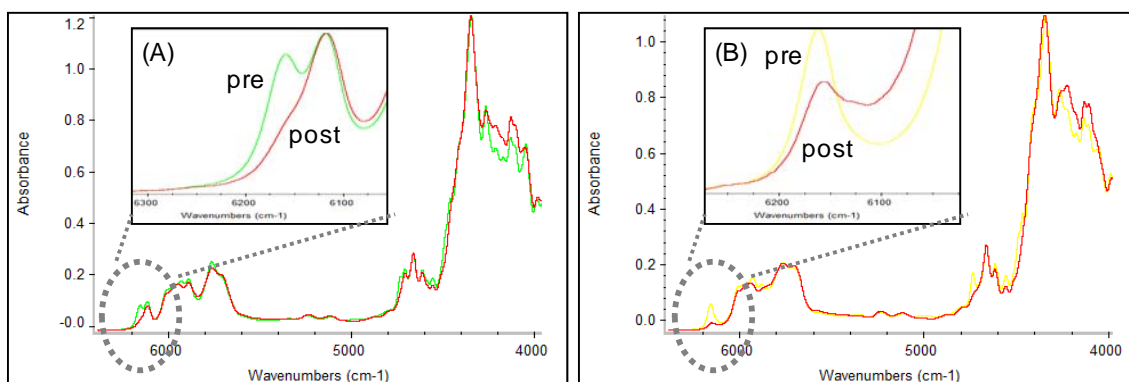
Stress relaxation via addition-fragmentation chain transfer in high T_g , high conversion methacrylate-based systems

Hee Young Park, Christopher J. Kloxin, Ahmed S. Abuelyaman, Joe D. Oxman, and Christopher N. Bowman*

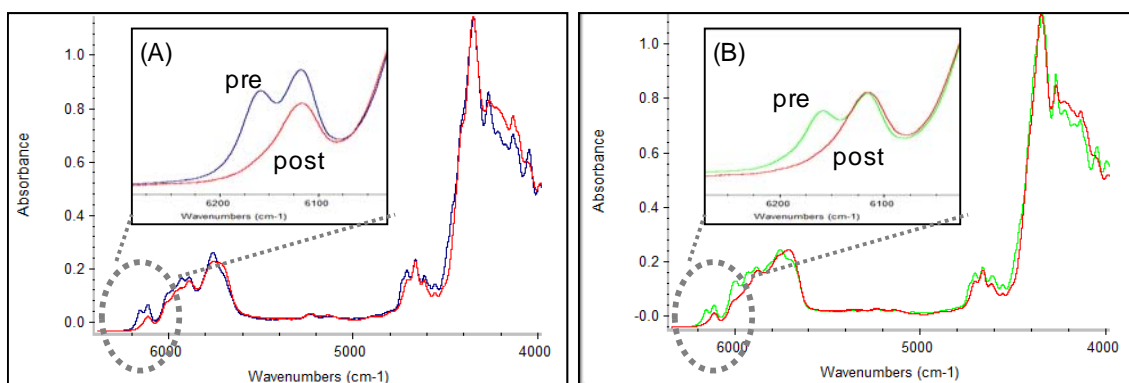
Infrared Spectra and the conversion measurement



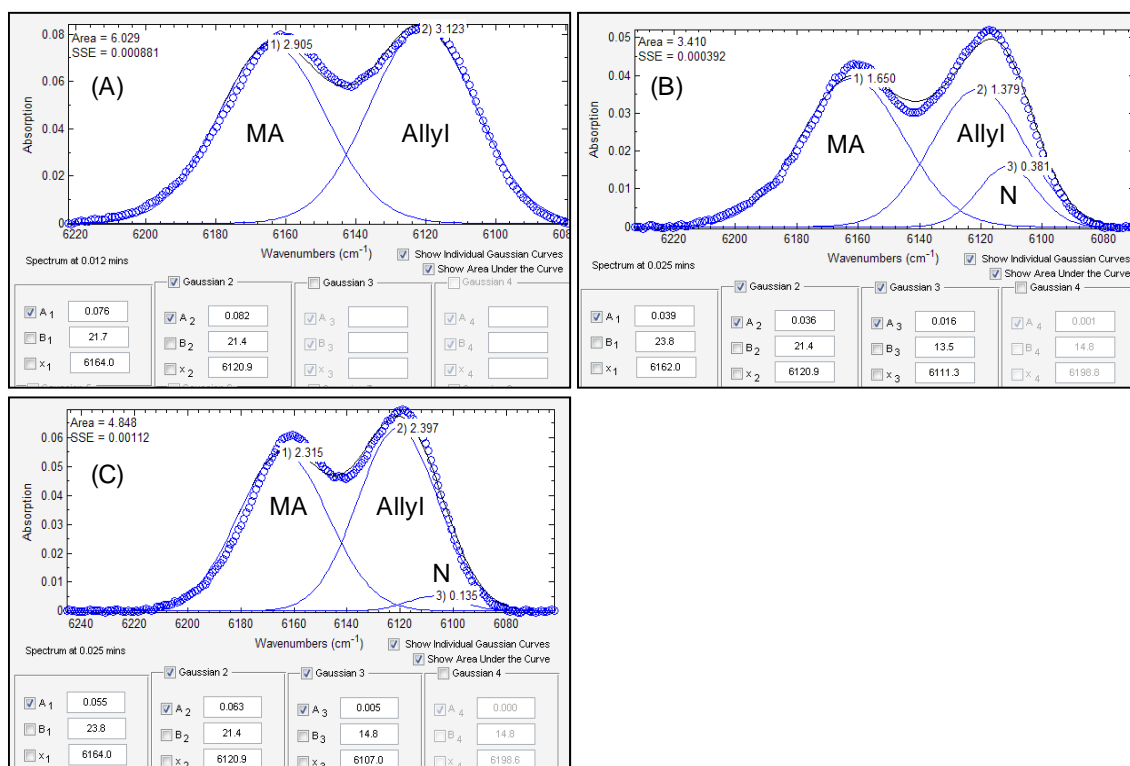
Supplemental Figure 1. Infrared spectra pre- and post-polymerization of SAS (A) and SPS (B) used in these studies. The disappearance of the peaks centered at 6164 and 6121 cm⁻¹ indicates the consumption of methacrylate (C=C-H stretch, overtone) and allyl sulfide (C=C-H stretch, overtone), respectively. As the methacrylate peak is overlapped with the allyl sulfide peaks in the spectrum of SAS, Gaussian fitting was used to deconvolute these peak areas as a function of time to determine the conversion.



Supplemental Figure 2. Infrared spectra pre- and post-polymerization of PAS (A) and PES (B) used in these studies. The disappearance of the peaks centered at 6164 and 6121 cm⁻¹ indicates the consumption of methacrylate (C=C-H stretch, overtone) and allyl sulfide (C=C-H stretch, overtone), respectively. As the methacrylate peak is overlapped with the allyl sulfide peaks in the spectrum of PAS, Gaussian fitting was used to deconvolute these peak areas.



Supplemental Figure 3. Infrared spectra pre- and post-polymerization of NAS-PETMP-PAS (A) and NPS-PETMP-PAS (B) used in these studies. The disappearance of the peaks centered at 6164, 6121, 6111 cm⁻¹ indicate the consumption of methacrylate (C=C-H stretch, overtone), allyl sulfide (C=C-H stretch, overtone), and norbornene (C=C-H stretch, overtone), respectively. As the methacrylate peak is overlapped with the norbornene and allyl sulfide peaks in the spectrum of NAS-PETMP-PAS and NPS-PETMP-PAS, Gaussian fitting was used to deconvolute these peak areas.

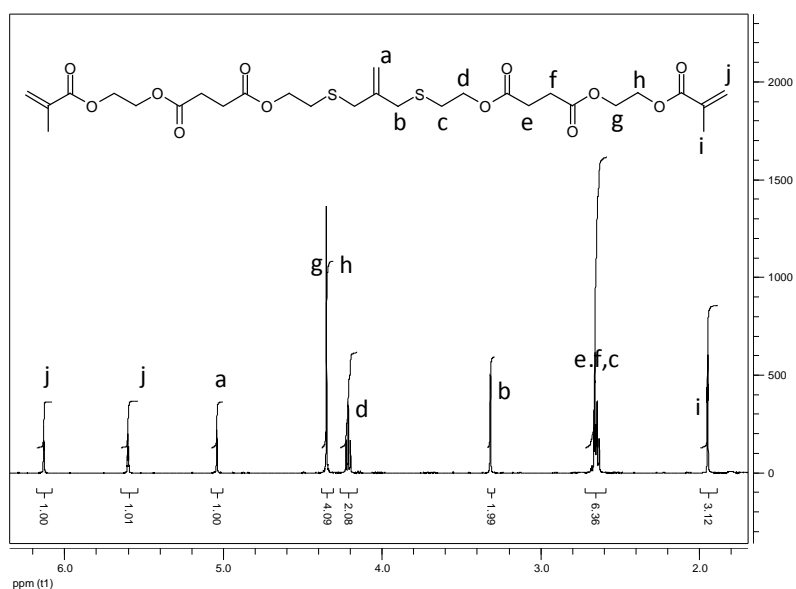


Supplemental Figure 4. (A) Deconvoluted methacrylate and allyl peak areas of PAS using Gaussian fitting. Deconvoluted methacrylate, allyl, and norbornene peak areas of NPS-PETMP-PAS (B) and NAS-PETMP-PAS (C) using Gaussian fitting.

NMR spectroscopic characterization of the monomers synthesized herein

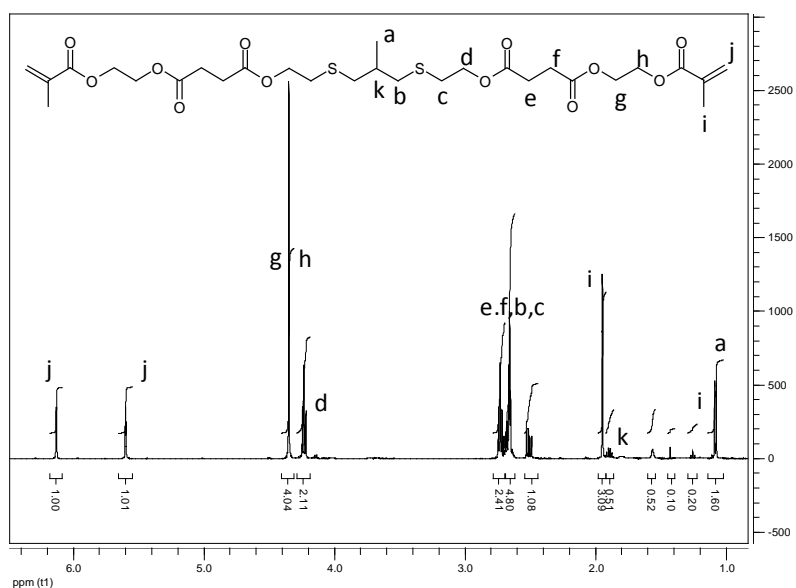
1,9-bis[2-(methacryloyloxyethyl) succinyloxy]-3,7-dithia-5-methylene-nonane (SAS, Succinate Allyl Sulfide)

^1H NMR (500 MHz, CDCl_3 , δ): 6.17(s,2H), 5.60(s,2H), 5.02(s,2H), 4.37(s,8H), 4.2(t,4H), 3.31(s,4H), 2.7-2.6(m,12H), 1.98(s,6H)



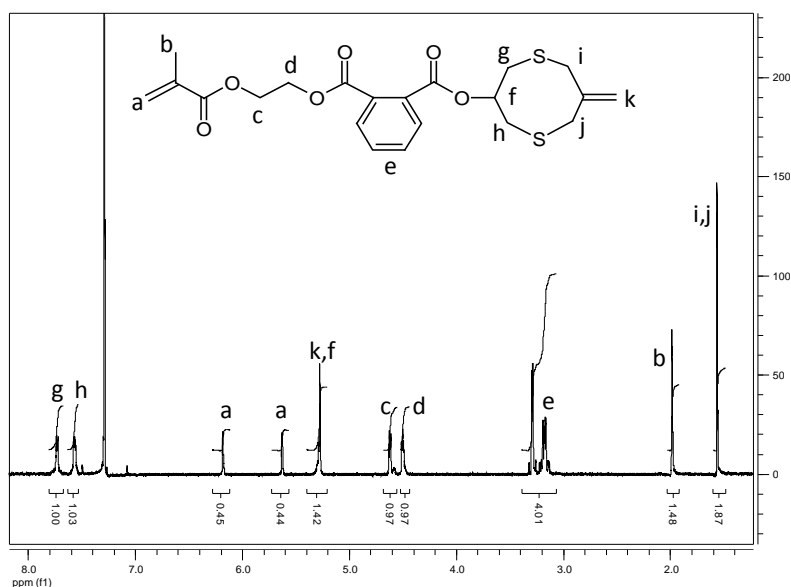
1,9-bis[2-(methacryloyloxyethyl) succinyloxy]-3,7-dithia-5-methyl-nonane (SPS, Succinate Propyl Sulfide)

^1H NMR (500 MHz, CDCl_3 , δ): 6.17(s,2H), 5.60(s,2H), 4.37(s,8H), 4.2(t,4H), 2.75(m,6H), 2.7-2.6(m,8H), 2.5(m,2H), 1.98(s,6H), 1.90(m,1H), 1.10(d,3H)



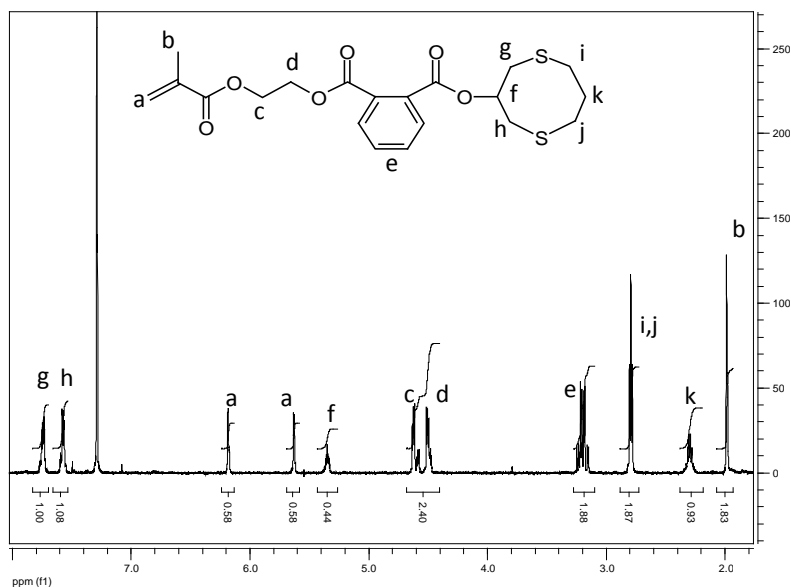
2-(methacryloyloxyethyl) 7-methylene-1,5-dithiocan-3-yl phthalate (PAS, Phthalate Allyl Sulfide)

^1H NMR (500 MHz, CDCl_3 , δ): 7.78(d,2H), 7.6(d,2H), 6.2(s,1H), 5.61(s,1H), 5.32(m,1H), 5.28(s,2H), 4.6(t,2H), 4.45(t,2H), 3.3-3.1(m,8H), 1.98(s,3H), 1.58(s,4H)

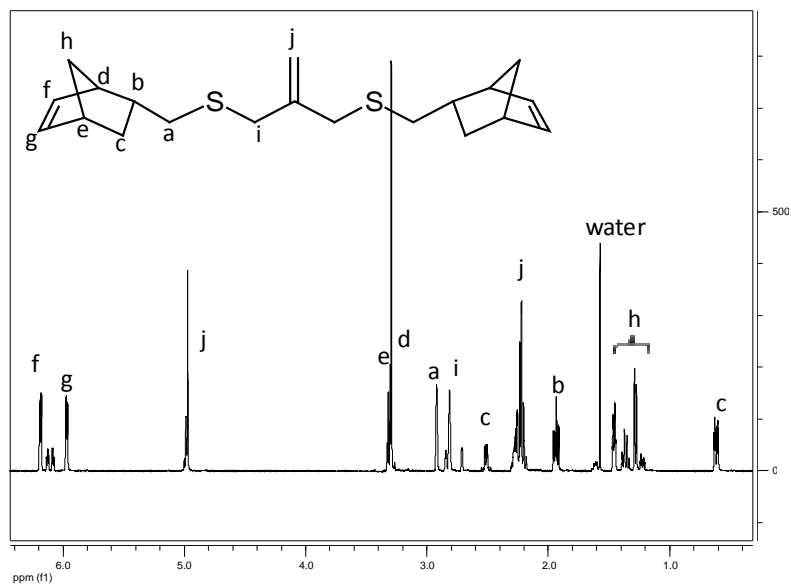


2-(methacryloyloxyethyl) 7-methyl-1,5-dithiocan-3-yl phthalate (PES, Phthalate Ethyl Sulfide)

^1H NMR (500 MHz, CDCl_3 , δ): 7.78(d,2H), 7.6(d,2H), 6.2(s,1H), 5.61(s,1H), 5.32(m,1H), 4.6-4.45(m,4H), 3.3-3.1(m,4H), 2.8(t,4H), 2.3(m,2H), 1.98(s,3H)



2-Methylene-propane-1,3-di(norbornene sulfide) (NAS)



2-Methyl-propane-1,3-di(norbornene sulfide) (NPS)

