

**Reprocessable, Creep-Resistant Covalent Adaptable Networks
Synthesized Using Conventional Free-Radical Polymerization Conditions with
Piperidine-Based and Non-Piperidine-Based Dynamic Dialkylamino Disulfide Chemistry**

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Supporting Information

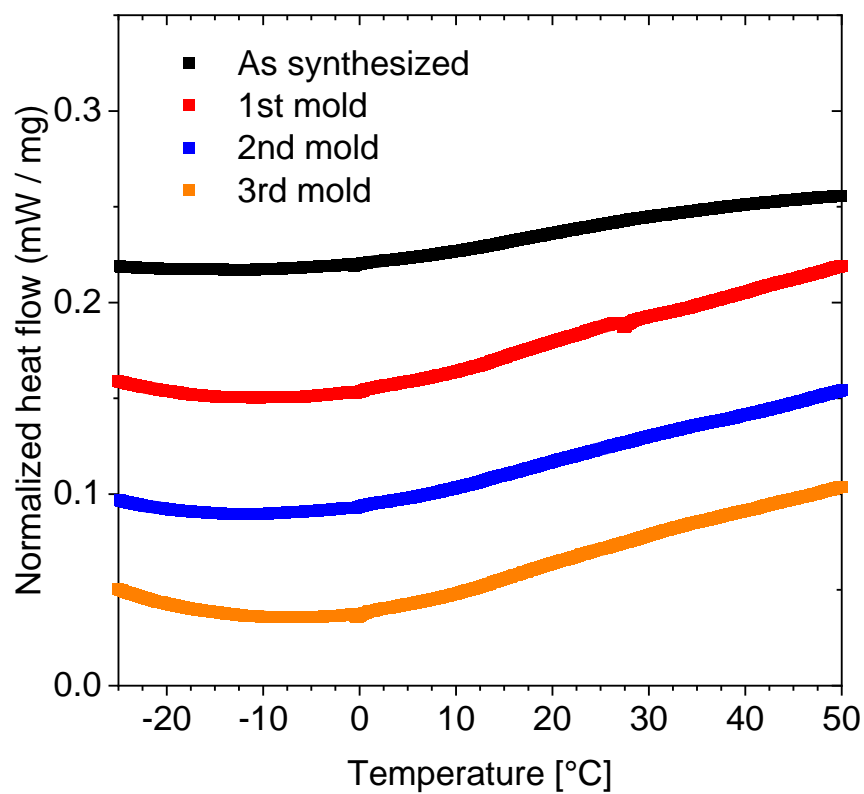


Figure S1. DSC curves of as-synthesized and (re)processed PHMA network samples with 5 mol% BiTEMPS methacrylate and 1 mol% AIBN.

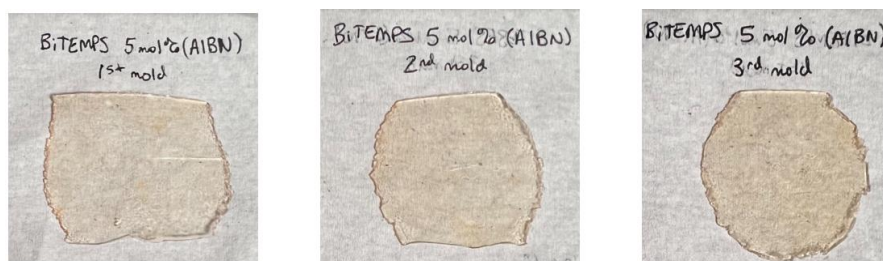


Figure S2. Images of molded PHMA networks synthesized with 5 mol% BiTEMPS methacrylate and 1 mol% AIBN.

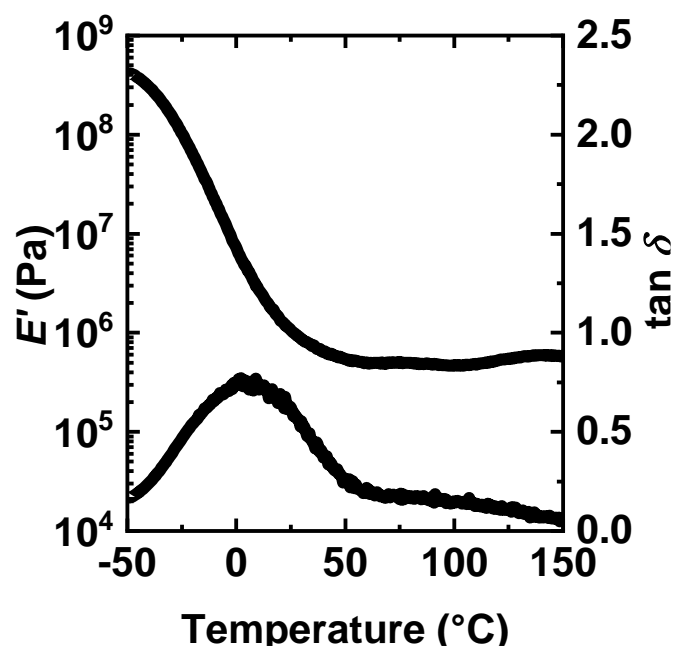


Figure S3. E' and $\tan \delta$ of 1st mold PHMA network synthesized with 5 mol% BiTEMPS methacrylate and 1 mol% BPO.

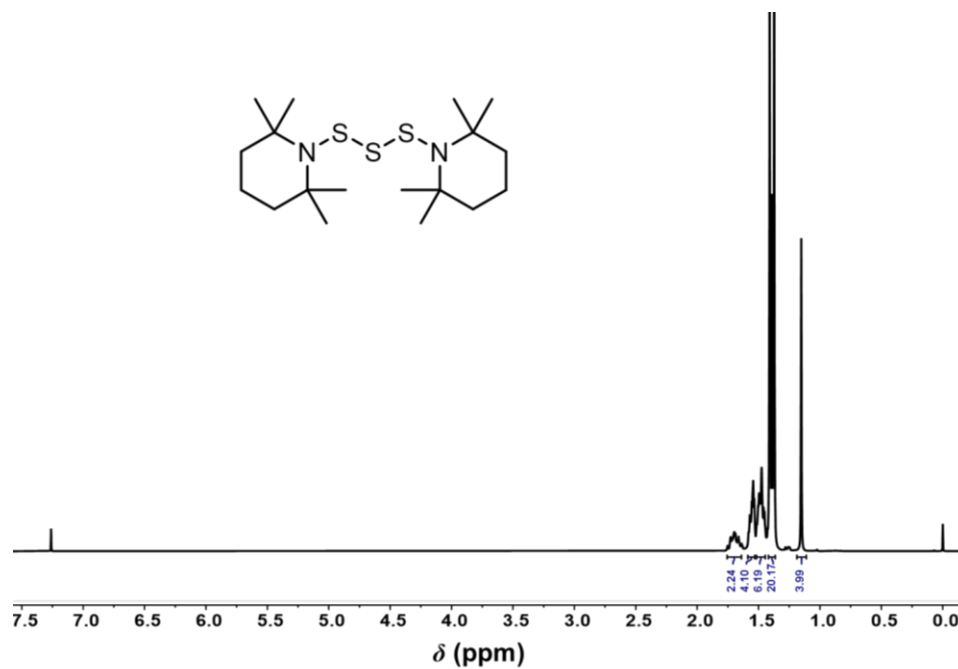


Figure S4. ^1H NMR spectrum of BiTEMPS-SM (500 MHz, CDCl_3).

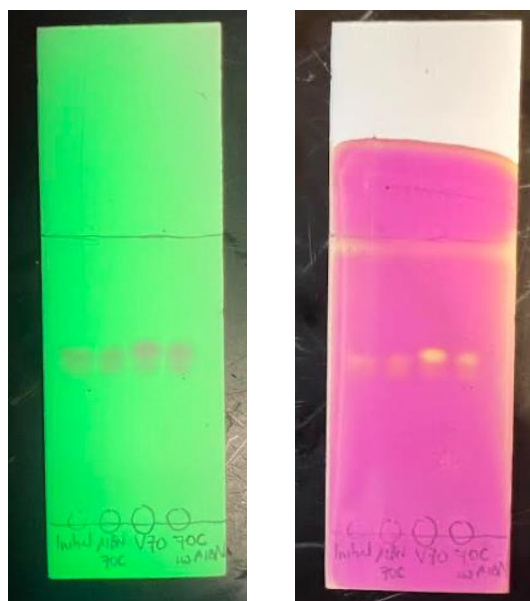


Figure S5. Thin-layer chromatography (TLC) plates (left: UV light exposed; right: KMnO_4 stained) of (spots left to right) BiTEMPS-SM, BiTEMPS-SM with AIBN at 70 °C after 4 h, BiTEMPS-SM with V-70 at 25 °C after 4 h, and BiTEMPS-SM without initiator at 70 °C after 4 h.

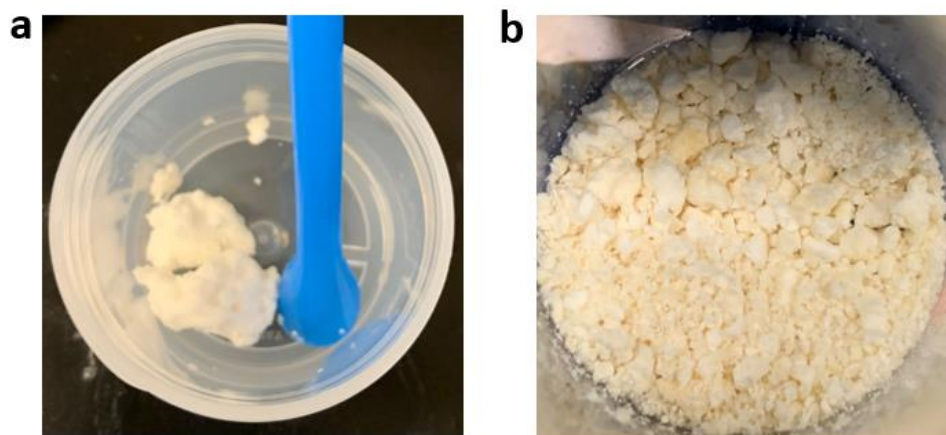


Figure S6. Pictures of cross-linker, BiTEBES methacrylate, (a) before and (b) after drying.

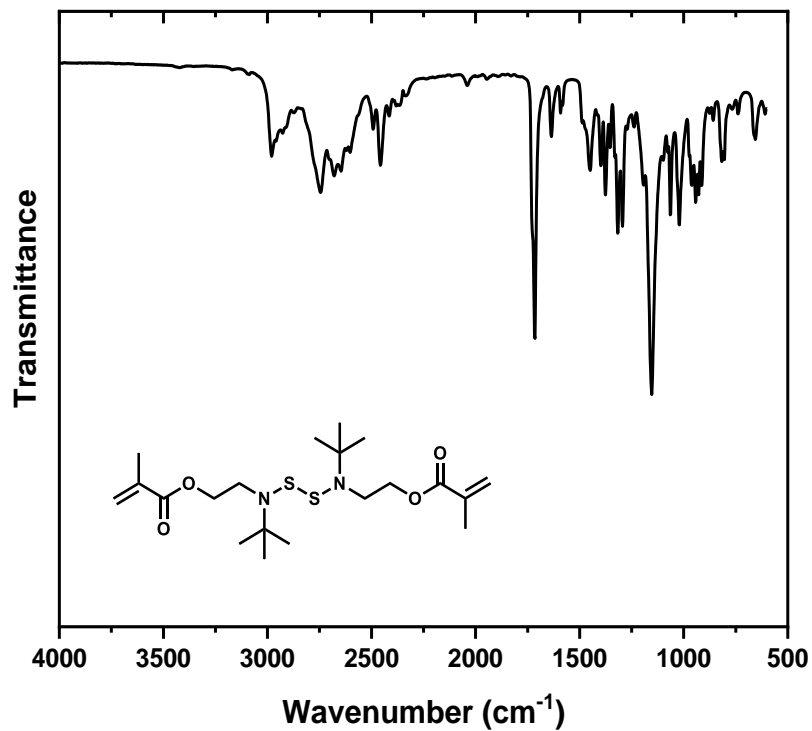


Figure S7. FTIR spectrum of BiTEBES methacrylate.

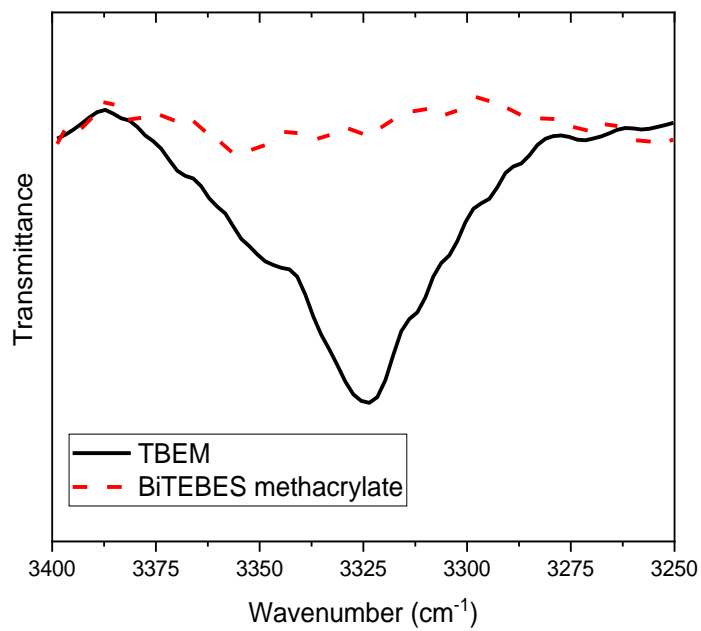


Figure S8. FTIR spectrum of TBEM and BiTEBES methacrylate from 3400 to 3250 cm⁻¹.

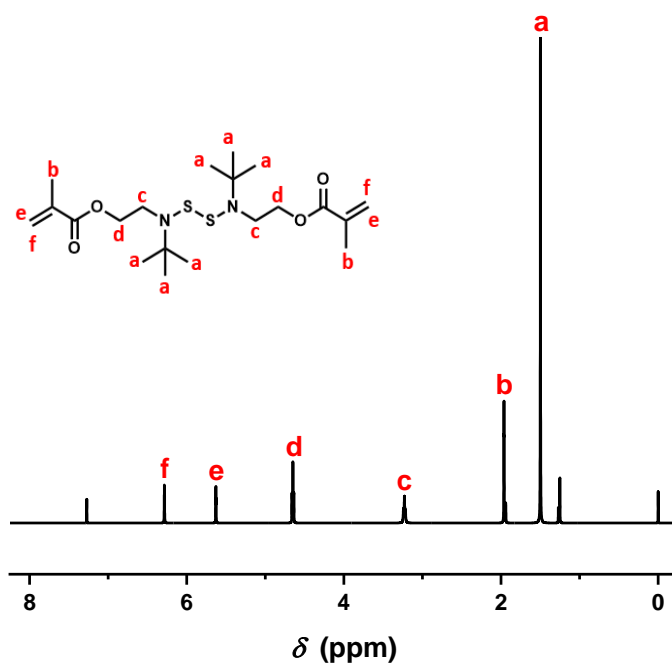


Figure S9. ^1H NMR spectrum of BiTEBES methacrylate (500 MHz, CDCl_3).

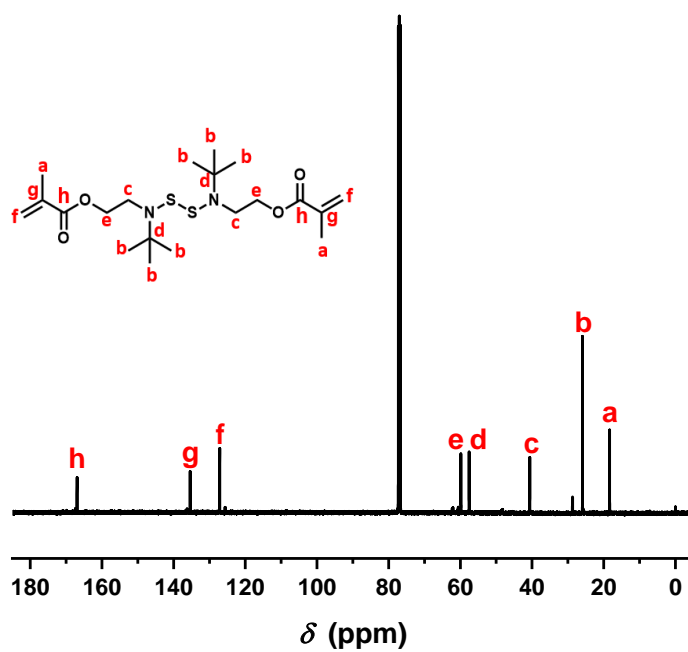


Figure S10. ^{13}C NMR spectrum of BiTEBES methacrylate (126 MHz, CDCl_3).

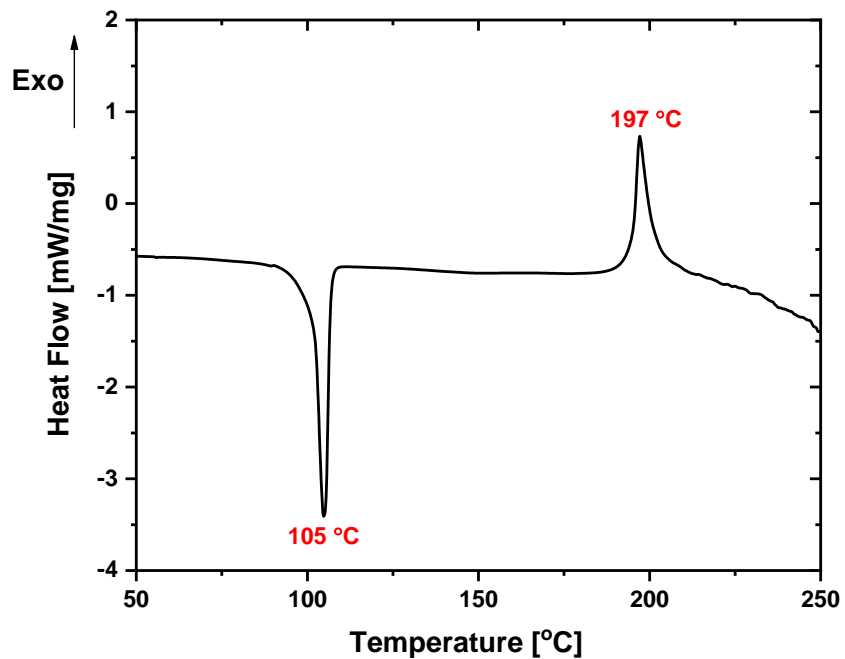


Figure S11. DSC thermogram of BiTEBES methacrylate.

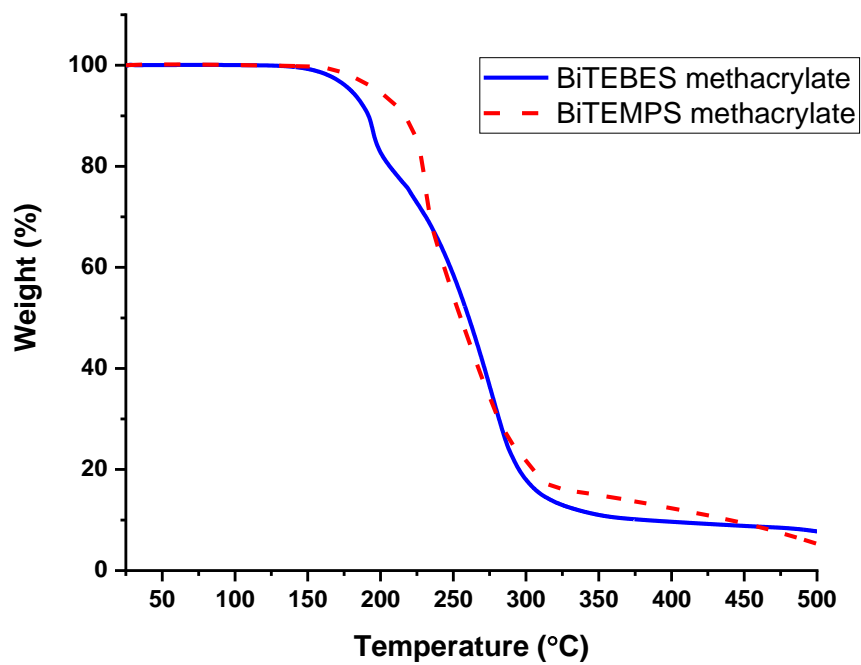


Figure S12. TGA curve of BiTEBES methacrylate.

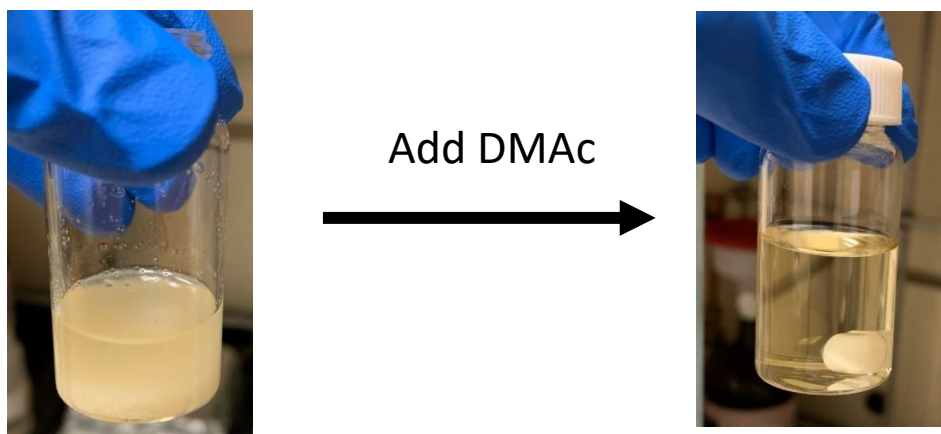


Figure S13. Solubility of BiTEBES methacrylate in HMA (a) before and (b) after adding DMAc.

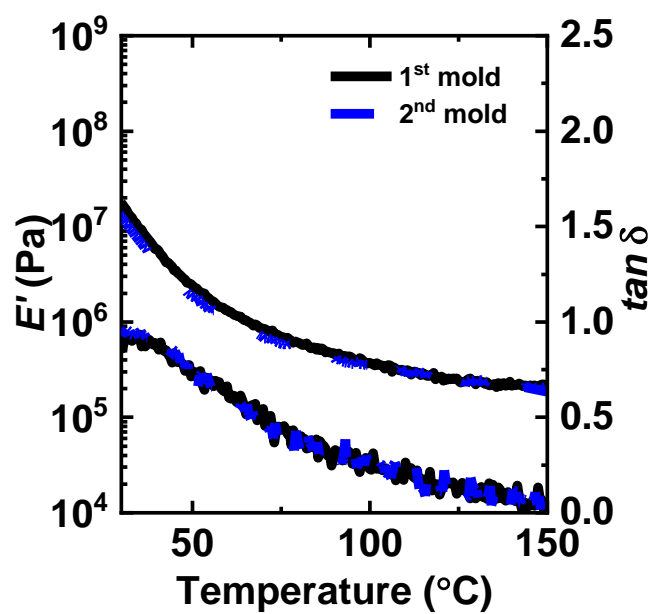


Figure S14. E' and $\tan \delta$ of PHMA network synthesized with 5 mol% BiTEBES methacrylate and 1 mol% V-70 initiator after one reprocessing step.

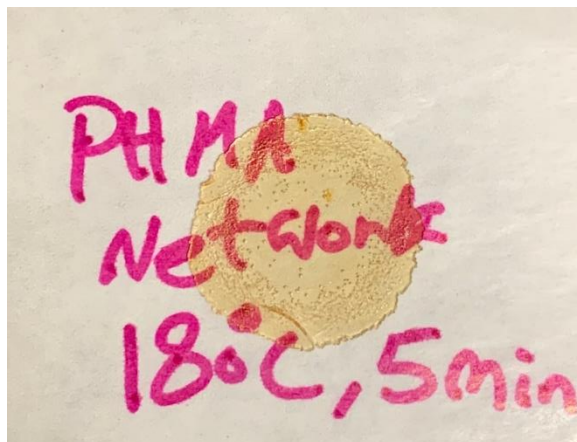


Figure S15. Pictures of 1st mold PHMA-5 network sample molded at 180 °C for 5 min.

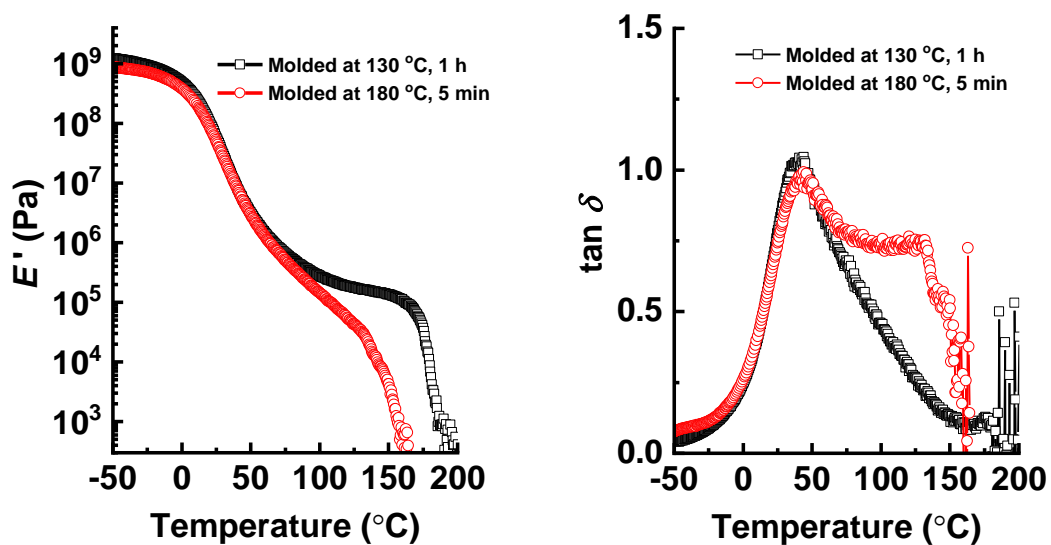


Figure S16. High-temperature DMA response of 1st mold PHMA-5 network samples.



Figure S17. Images of molded PHMA networks synthesized with 5 mol% BiTEBES methacrylate and 1 mol% AIBN.

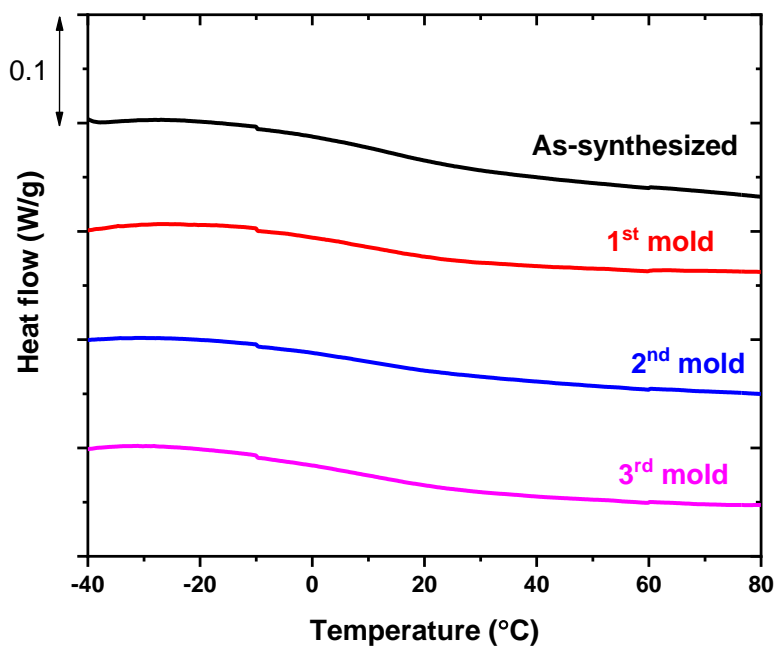


Figure S18. Heat flow curves of as-synthesized and molded network samples.

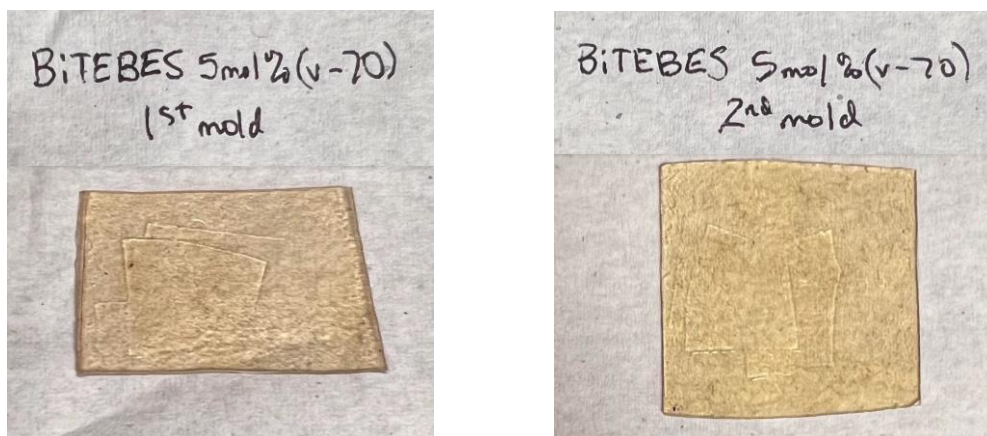


Figure S19. Images of molded PHMA networks synthesized with 5 mol% BiTEBES methacrylate and 1 mol% V-70.

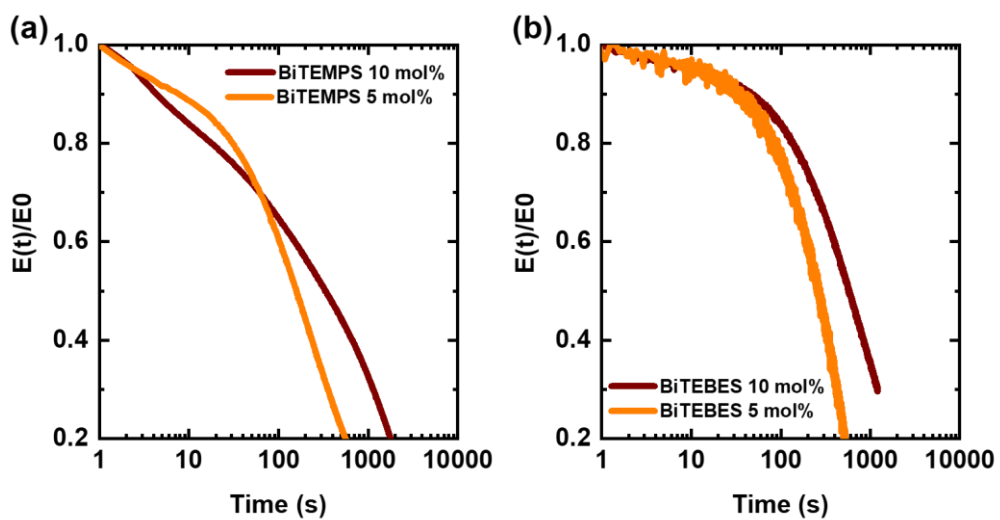


Figure S20. Normalized stress relaxation curves of (a) PHMA networks with 5 mol% and 10 mol% BiTEMPS methacrylate with AIBN as initiators, and (b) BiTEBES-based PHMA networks, i.e., PHMA-5 and PHMA-10 at 130 °C.

Table S1. Comparison of stress relaxation data at 130 °C for various samples of PHMA networks with different cross-linker identity, loading, and initiators.

Sample	τ^*	β	$\langle\tau\rangle$	R^2
5 mol% BiTEMPS w/ AIBN	415	0.67	835	0.999
5 mol% BiTEMPS w/ v-70	650	0.75	773	0.999
10 mol% BiTEMPS w/ AIBN	1080	0.46	4520	0.989
5 mol% BiTEBES w/ AIBN	355	1.00	--	0.989
5 mol% BiTEBES w/ v-70	563	1.00	--	0.940
10 mol% BiTEBES w/ AIBN	948	0.77	1110	0.999

Table S2. Gel contents of AIBN-initiated PHMA networks synthesized with 10 mol% BiTEMPS methacrylate.

Mold	Gel Content (%)
1 st Mold	98 ± 1
2 nd Mold	97 ± 1