Storage moduli and porosity of soft PDMS polyMIPEs can be controlled independently using thiol-ene click chemistry

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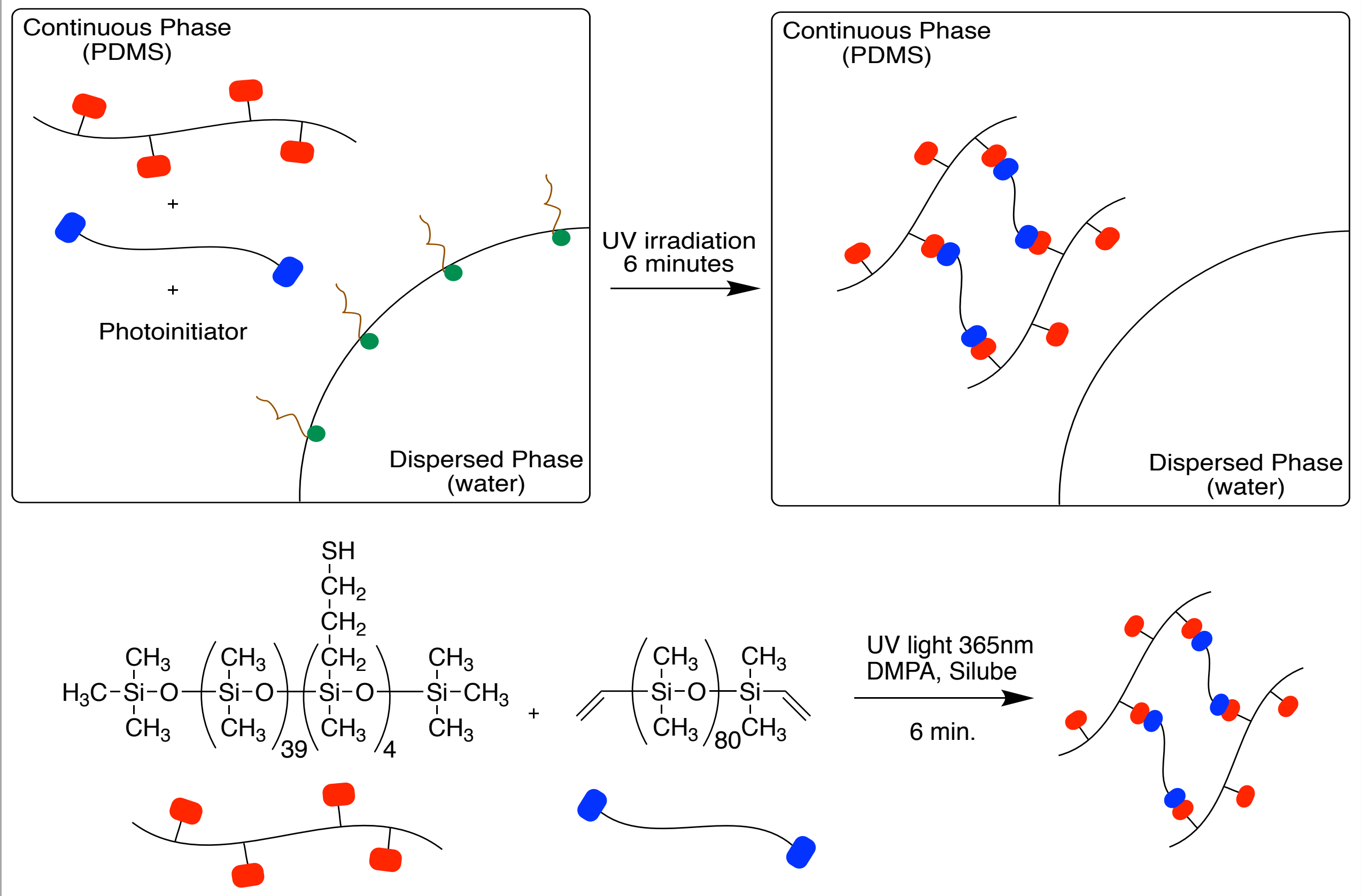
Porous polymers are increasingly used to make soft acoustic metamaterials. The highly porous structure of the material can impart properties such as a negative refractive index. Poly(dimethyl siloxane) (PDMS) is typically used in this application due to PDMS being commercially available and possessing desirable mechanical properties when crosslinked. However, there is a lack of control in the materials properties of the soft acoustic metamaterials. Here, the synthesis of PDMS-based polymerized medium internal phase emulsions (polyMIPEs) with tunable storage moduli (G') have been prepared using thiol-ene reactions between macromolecules. Changing the stoichiometric ratio of the thiol- or ene-containing PDMS controlled the materials properties of polyMIPEs with storage moduli values of ~38 to ~330 kPa being obtained. The surface area and pore size of the polyMIPEs were controlled by the volume of aqueous phase used in the emulsion formulation. The results demonstrate PDMS-based soft polymeric monoliths with well-defined materials properties using simple thiol-ene crosslinking techniques are possible. This work provides an example of the synthesis of soft polyMIPEs with possible applications in the metamaterials field as well as other areas of interest such as biomaterials and catalysis.

Current challenges and research goal

Current soft acoustic metamaterials are synthesized using limited commercial reagents with little to no modifications available. A narrow range of materials properties are accessible restricting the performance of these metamaterials. Our goal is to develop a polyMIPE system to synthesize porous polymeric monoliths using simple organic chemistry techniques to tune the mechanical properties and pore morphology of soft acoustic metamaterials.

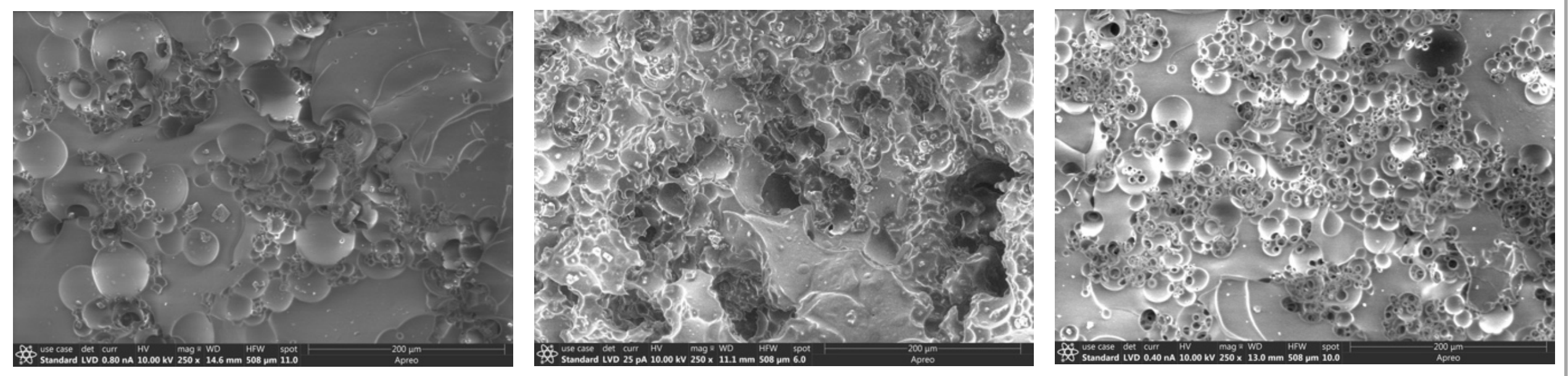
PolyMIPE experimental design



Typical polyMIPE

Crosslinked PDMS

Scanning electron microscope images



40% NaCl with 0.4% Silube

40% NaCl with 3.0% Silube

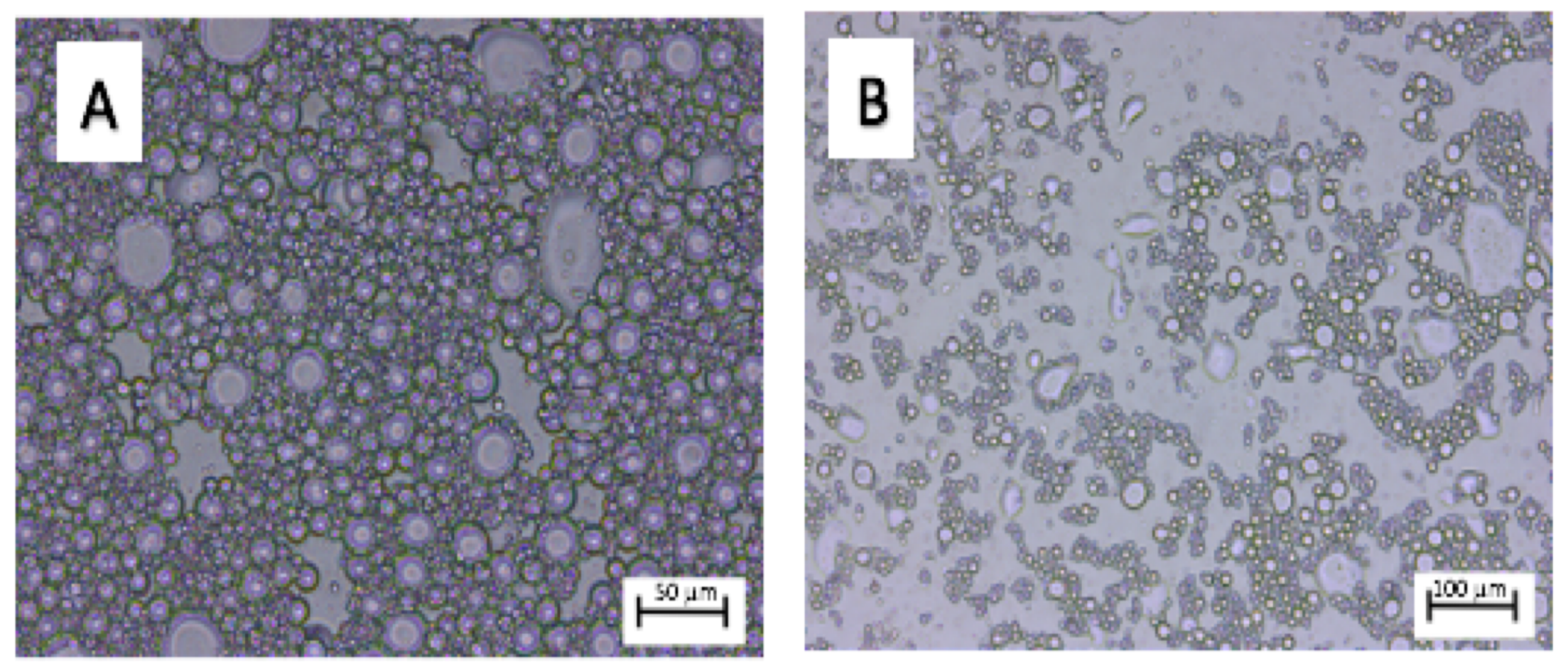
70% NaCl with 1.0% Silube

SEM images of cross sections of dried polyMIPEs with varied components of the system. Scale bar is 200 microns for each image.

MIPE preparation and characterization

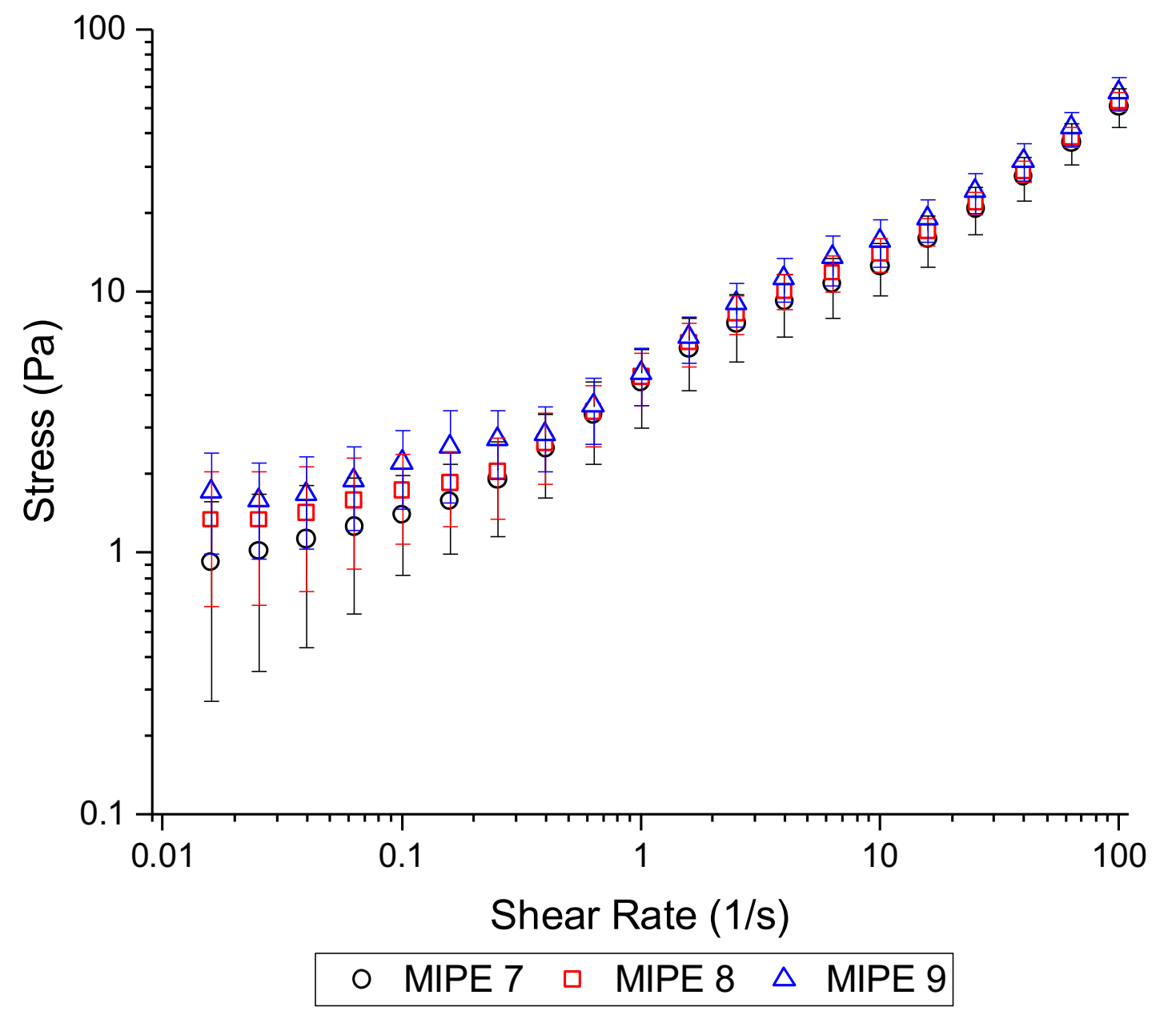
Emulsions were formed following the general experimental design without the addition of photoinitiator to make MIPEs 1-12.

MIPE	Thiol:Ene Ratio	Dispersed Phase	Surfactant Content
1	1:2	40% NaCl	0.40%
2	1:1	40% NaCl	0.40%
3	2:1	40% NaCl	0.40%
4	1:2	40% $CaCl_2$	0.40%
5	1:1	40% $CaCl_2$	0.40%
6	2:1	40% $CaCl_2$	0.40%
7	1:1	40% NaCl	1.00%
8	1:1	40% NaCl	3.00%
9	1:1	40% NaCl	5.00%
10	1:1	50% NaCl	1.00%
11	1:1	60% NaCl	1.00%
12	1:1	70% NaCl	1.00%



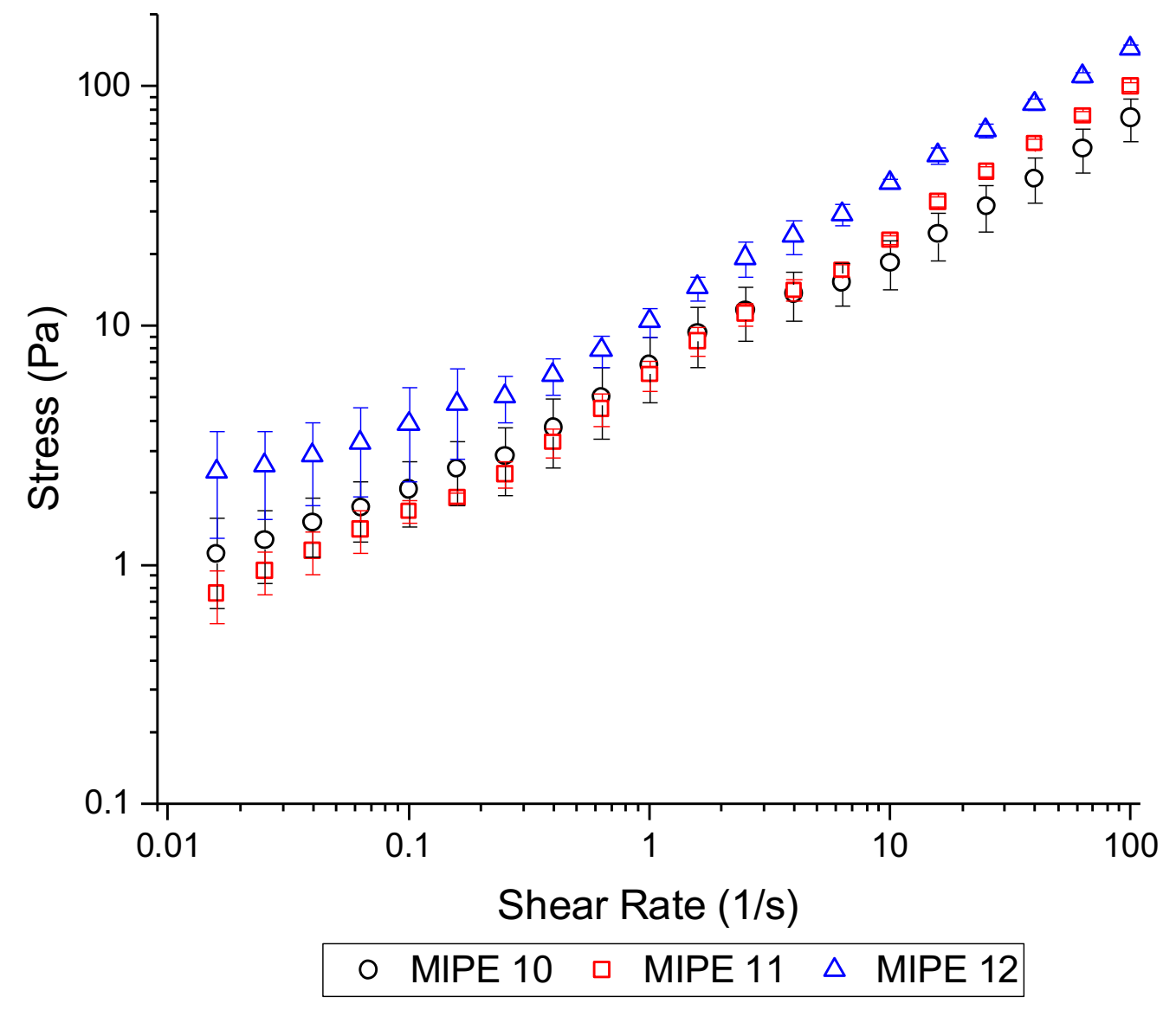
Optical microscopy images show dispersed droplets in all MIPEs where (A) is before and (B) is after applying pressure to glass slides.

Rheology of MIPEs with respect to concentration of surfactant



Frequency sweep rheology of MIPEs 7-9 showed increasing the concentration of surfactant produced yield-stress fluids above 1%.

Rheology of MIPEs increasing volume of dispersed phase



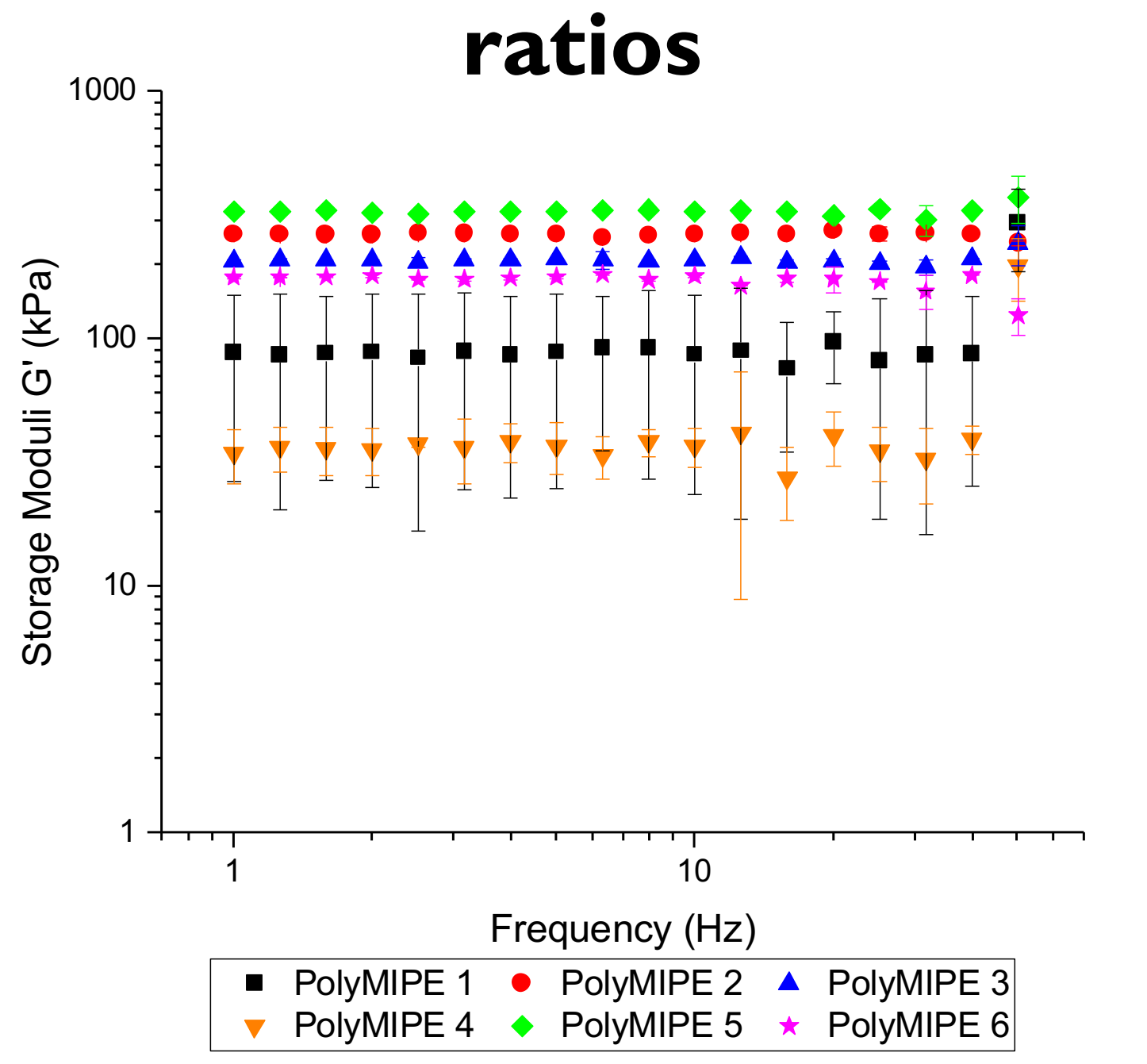
Frequency sweep rheology of MIPEs 10-12 showed increasing the volume of dispersed phase produced yield-stress fluids above 50%.

polyMIPE preparation and characterization

polyMIPE	Total Porosity	Surface Area (m^2/g)	Average Pore Size (microns)
1	38 ± 2%	0.0586	164
2	39 ± 2%	0.0567	173
3	38 ± 2%	0.0727	136
4	36 ± 2%	0.0494	195
5	38 ± 2%	0.0635	153
6	42 ± 2%	0.0616	150
7	40 ± 2%	0.081	123
8	44 ± 2%	0.0402	249
9	42 ± 2%	0.0352	272
10	49 ± 2%	0.1151	104
11	60 ± 2%	0.2557	56
12	66 ± 2%	0.3743	48

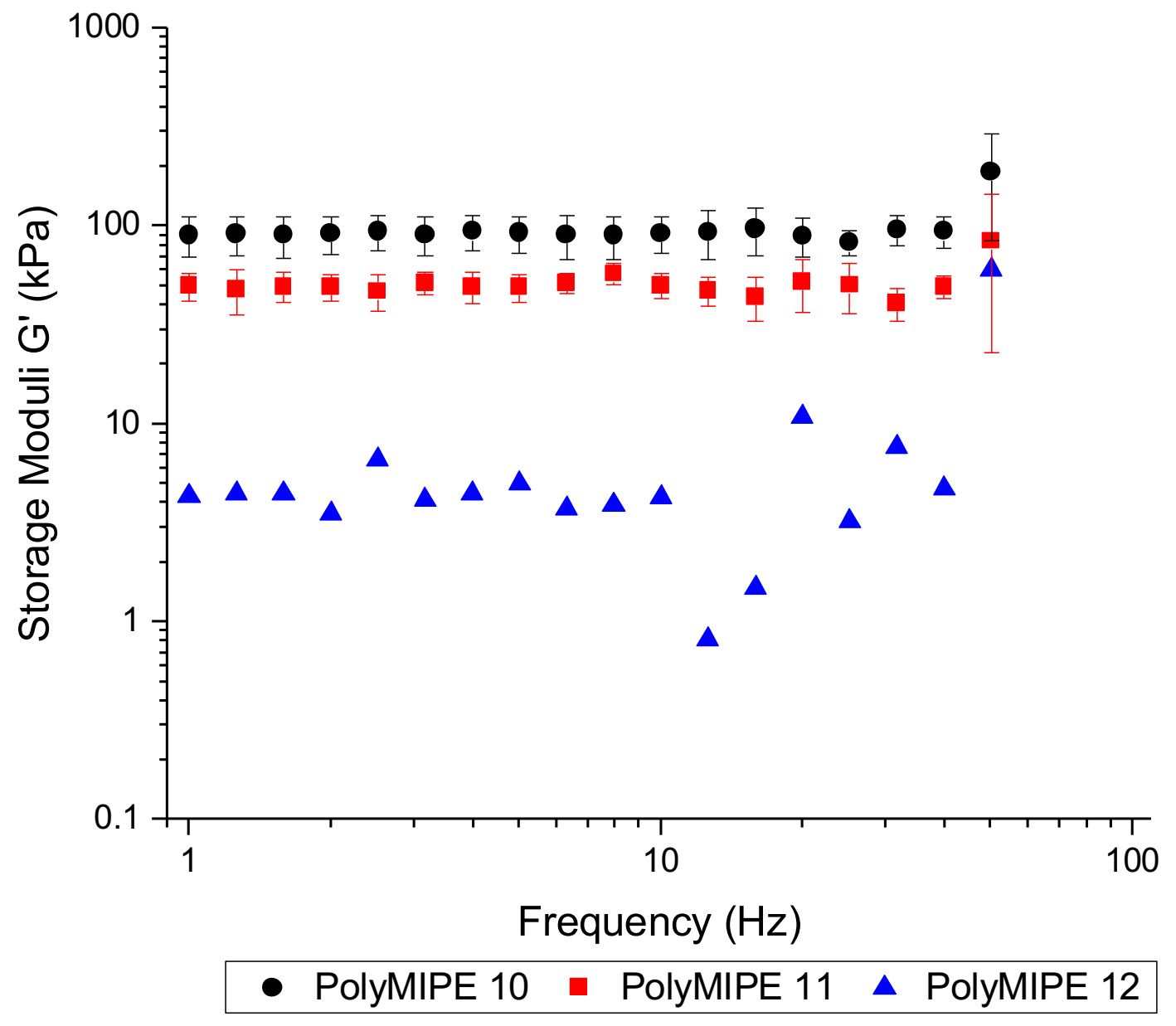
The general polyMIPE protocol was followed to obtain four different sets of polyMIPEs based on varying different components of the system.

Dynamic mechanical analysis of thiol-ene ratios



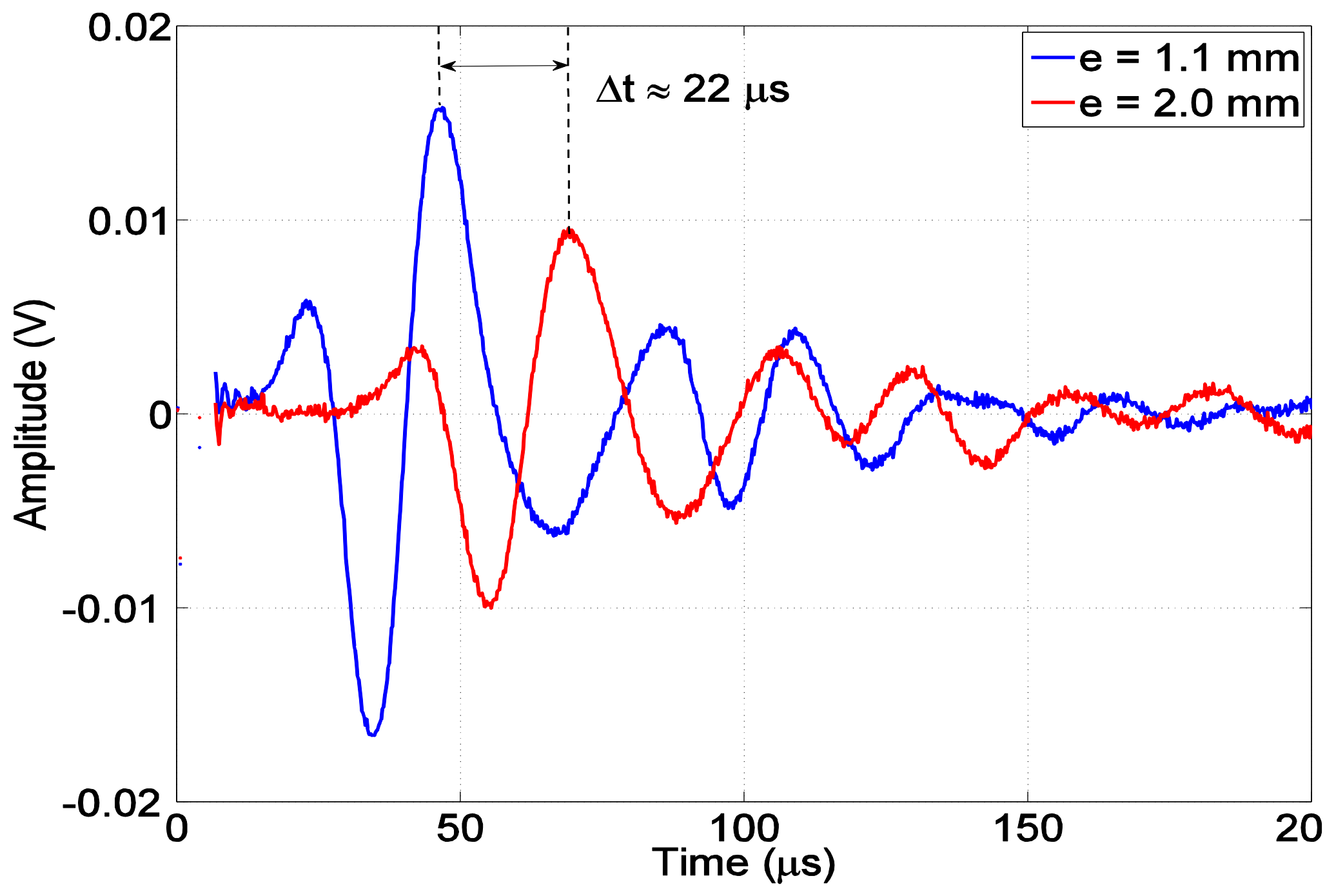
Thiol-ene ratios were proven to tune mechanical properties while changing the chemistry of the salt did not.

Dynamic mechanical analysis of increased volume of dispersed phase



The polyMIPE highest volume of dispersed phase produced materials with the lowest mechanical properties

Acoustic analysis results of polyMIPE 10

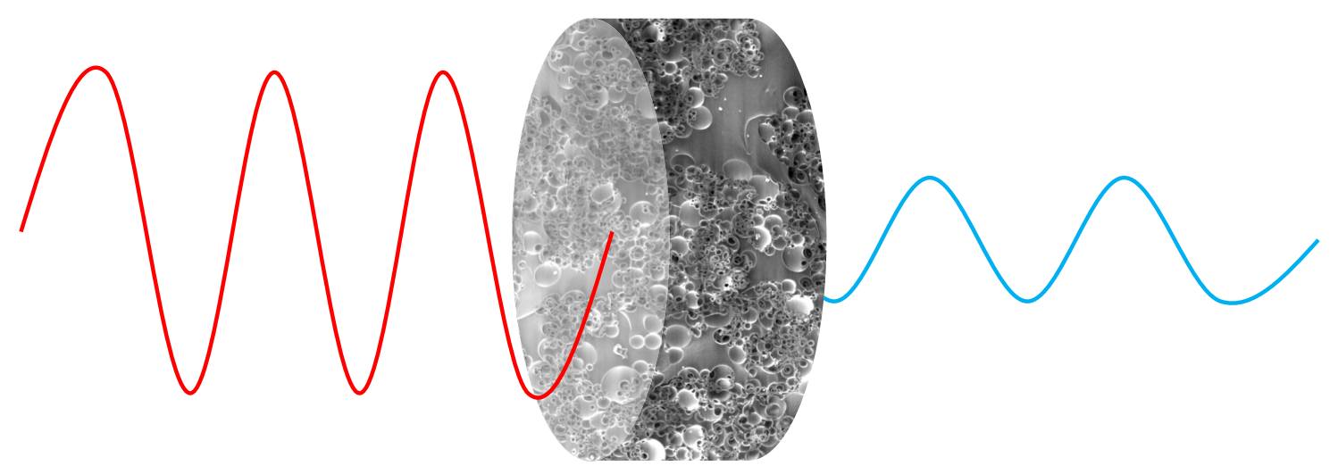


Longitudinal sound speed was calculated to be ~40m/s

Conclusions

While the ratio of the thiolated-PDMS to the vinyl-terminated PDMS does not affect the properties of the initial emulsion or porosity of the resulting polyMIPE, the storage moduli of the material is directly controlled by the stoichiometric ratio of the PDMS reagents.

The materials properties of the polyMIPEs could also be directly controlled by the amount of surfactant used to stabilize the emulsion and the volume of dispersed phase.



Acknowledgments