

Storage Moduli and Porosity of Soft PDMS PolyMIPEs Can Be Controlled Independently Using Thiol–Ene Click Chemistry

Tucker J. McKenzie, Paul S. Heaton, Kabir Rishi, Raj Kumar, Thomas Brunet, Gregory Beaucage, Olivier Mondain-Monval, and Neil Ayres*



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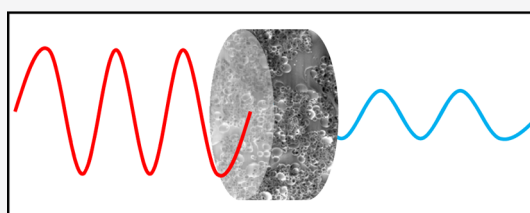


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Supporting Information

ABSTRACT: Porous elastomeric polymers have been used in a wide range of applications because of their unique characteristics such as biocompatibility, gas permeability, thermal stability, and hydrophobic and dielectric properties. Poly(dimethyl siloxane) (PDMS), a commercially available elastomer, has also been shown to exhibit specific acoustic properties. However, the material properties were limited because of a lack of control over the chemistry used to prepare the cross-linked PDMS elastomer. Here, the synthesis of PDMS-based polymerized medium internal-phase emulsions (polyMIPEs) with tunable storage shear moduli (G') has been performed using macromolecular thiol–ene reactions. Storage shear modulus values from ~ 38 to ~ 330 kPa were achieved by changing the stoichiometric ratio of the thiol-to-ene-functionalized PDMS, whereas the porosity of the polyMIPEs was controlled by the volume of the aqueous phase used in the emulsion formulation. Very low sound velocities (~ 40 m/s) through the porous materials were recorded using acoustic characterization. Therefore, this work provides an example of the synthesis of soft polyMIPEs with possible applications as acoustic materials.



INTRODUCTION

Porous elastomeric polymers are used in a wide range of possible applications including biomaterials^{1–5} and catalysis^{6,7} because of their elastomeric behavior, biocompatibility, gas permeability, thermal stability, and specific hydrophobic and dielectric properties.^{8,9} More recently, they were also shown to exhibit specific acoustic properties, including low-sound velocities through the materials (from 40 to 120 m/s).^{10–14} These soft acoustic metamaterials have been prepared from commercially available reagents such as poly(dimethyl siloxane) (PDMS) and lead to materials with negative acoustic indices when dispersed as small porous beads in a continuous matrix.^{11,13} These materials were also used to build flat acoustic devices, the so-called metasurfaces, owing to the very low and adjustable values of their acoustic velocities.¹⁰ However, the potential range of acoustic properties accessible using commercially available PDMS is limited.

One method to prepare highly porous materials is using emulsion templating with polymerized high internal-phase emulsions (polyHIPEs).^{15–18} This has been used to prepare porous PDMS materials.^{19–24} The term *high* is defined as when the volume fraction of the dispersed phase of the emulsion exceeds 74% of the global volume. An emulsion with 24–74% dispersed phase by volume is called a *medium* internal-phase emulsion (MIPE), and *low* internal-phase emulsions (LIPEs) contain less than 24% of the dispersed phase by volume.²⁵ Polymerized emulsions are formed after polymerization of a monomer in the continuous phase, and a porous network is obtained after removal of the dispersed phase. This method is

compatible with both hydrophilic and hydrophobic monomers depending on if a water-in-oil (w/o) or oil-in-water (o/w) emulsion is used.^{23,26} For example, free radical polymerization of styrene and a divinylbenzene cross-linker is often used in the synthesis of hydrophobic polyHIPE materials,²⁷ and hydrophilic monoliths have been prepared using acrylamide and *N,N'*-methylenebisacrylamide.²⁸ It has been suggested that a constraint with using free radical polymerization techniques is a lack of network homogeneity, leading to unpredictable material properties including irreproducible Young's modulus.^{29,30} A way to circumvent this constraint may be to use macromolecular orthogonal coupling reactions (or “click chemistry”),^{31,32} such as thiol–ene reactions.^{33,34} This reaction can occur between functionalized polymers³⁵ or small molecules,^{36–40} and macromolecular thiol–ene reactions have been reported using cross-linked silicones.³⁵ These reactions enable the properties of the final polyHIPE to be tuned based on stoichiometric ratios of the reactants and permit postpolymerization functionalization³⁷ or secondary click reactions.⁴⁰

In this study, we prepared emulsion-templated PDMS-based porous polymeric materials for potential acoustic applications

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using thiol–ene click-chemistry reactions to form polyMIPes. We have focused on the synthesis of polyMIPes, as porous PDMS acoustic metamaterials are typically prepared in the MIPE regime rather than the HIPE regime. We have investigated the effects of the thiol-to-ene ratio, the composition and amount of the dispersed phase, and the concentration of the surfactant. Significantly, for future metamaterial applications, it was found that changing the chemical composition of the polyMIPE results in porous cross-linked silicones that have predictable and tunable emulsion morphology and mechanical properties. Finally, the acoustic properties of the porous materials have been tested with respect to the modulation of sound velocity through the PDMS polyMIPes.

■ EXPERIMENTAL SECTION

Materials. The polymers [13–17% (mercaptopropyl) methylsiloxane]–dimethylsiloxane copolymer (thiolated-PDMS), vinyl-terminated PDMS (vinyl-PDMS), and (30–35% dodecylmethylsiloxane-[7–10% hydroxy(propethylenoxy (6–9) propyl) methylsiloxane]–(55–65% dimethylsiloxane) terpolymer (Silube J208-812) were purchased from Gelest (Morrisville, PA, USA) and used as received. The photo-initiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) and reagent-grade dichloromethane (DCM) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received.

Methods. Emulsion images were recorded using an Axio Vert.A1 inverted microscope (ZEISS), using ZEISS Efficient Navigation (ZEN) software. Samples were illuminated using bright-field microscopy. Each emulsion was placed between a glass microscope slide and glass coverslip. The coverslip was gently pressed on using the hand to limit vertical droplet–droplet stacking (Figure S1). The samples were observed before and after applying force and no difference in the droplet shape or size was seen. Rheological analysis was performed using oscillatory frequency sweeps (0.1–100 Hz; 24 °C) with a Discovery Series Hybrid Rheometer (DHR) (Model HR-2, TA Instruments) using 20 mm diameter parallel plates and controlled temperature using an advanced Peltier system. A sample size of ~0.2 mL of each emulsion was used. Emulsions for rheological analysis were prepared without a photo-initiator for ease of handling. PolyMIPes were prepared using UV irradiation of the emulsions by pouring the emulsion into a well of a 6-well tissue culture polystyrene plate to a height of ~4 mm. The sample was then irradiated ($\lambda_{\text{max}} = 365$ nm, 48 W, 6 min) from all sides in a mirrored enclosure. Total porosity measurements were obtained from dried polyMIPE samples using a home-built Archimedes balance. Pore morphology was obtained using a scanning electron microscope (Low-Vac) (FEI XL-30) equipped with an EDAX detector. Cross sections of the materials were cut from dried polyMIPes and fixed onto aluminum stubs, sputter-coated with gold/palladium, and imaged at an accelerating voltage of 15 kV. Mechanical properties of dried polyMIPes were obtained using a PerkinElmer dynamic mechanical analyzer (DMA-8000) and processed using Pyris software. Sections of dried polyMIPes for analysis were cut to ~3 mm thick, ~5 mm wide, and ~8 mm long. Rectangular tension frequency sweep experiments (0.1–70 Hz; 0.01 mm strain) were carried out on three separate samples for each polyMIPE formulation. Ultrasmall-angle X-ray scattering (USAXS) studies were carried out at the beamline 9 ID-C at the Advanced Photon Source at the Argonne National Laboratory.^{41,42} X-ray scattering data sets were reduced, desmeared to account for the slit smearing and analyzed using Indra and Irena packages in IGOR pro.⁴³ This type of USAXS analysis relies on considering the porous silicone matrix as an ideal two-phase system.⁴⁴ The scattering contrast between the two phases (silicone matrix and pores) arises because of a difference in scattering length density of air and the silicone matrix. The average structural details of the pores were estimated by fitting the reduced scattering intensity, $I(q)$

measured in cm^{-1} as a function of reciprocal space vector, q , measured in \AA^{-1} to Porod's law^{45,46} given in the following equation

$$I(q) = 2\pi\Delta\rho^2(S/V)q^{-4} \quad (1)$$

where $\Delta\rho^2$ (cm^{-4}) is the squared difference of the scattering length densities of the silicone matrix and air and (S/V) is the surface area-to-volume ratio of the pores. The scattering length densities of the two components were determined from the scattering contrast calculator available via the Nika package in IGOR pro.⁴⁷ The term (S/V) expressed in cm^{-1} can then be used to obtain the specific surface area expressed in m^2/g from the measured densities of the porous materials. For spherical entities such as pores, the Sauter mean diameter is used to represent the pore diameter.⁴⁸

$$d_p = 6(S/V)^{-1} \quad (2)$$

The acoustic characterization of samples was performed on the porous materials at ultrasonic frequencies. For each polyMIPE, two samples (32 mm in diameter) with different thicknesses d (1 and 2 mm) were used. Each sample was placed between two identical broadband ultrasonic (US) transducers (emitter and receiver, Olympus V301) with a diameter of 30 mm and a central frequency of 500 kHz. The US transducers were placed face-to-face and mounted on a linear manual stage, allowing the precise measurement of the sample thickness, that is, the propagation distances d with an uncertainty of about 100 μm . The emitting transducer was excited with short (broadband) pulses generated using a pulser/receiver (Olympus, S077PR) that was also used to amplify the electric signal recorded by the receiving transducer before its acquisition on a computer via an oscilloscope.

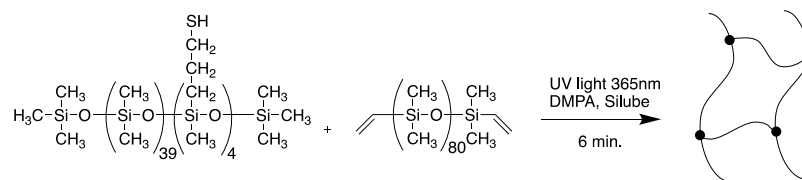
General MIPE Preparation. Water-in-silicone inverse emulsions were prepared using a modified literature procedure.¹³ An emulsion containing equal thiol-to-alkene functional groups was prepared by adding thiolated-PDMS (2.5 g, 2.86 mmol thiol-functional groups) and vinyl-PDMS (8.57 g, 2.86 mmol alkene-functional groups) in a glass vial and mixed on a vortex shaker. Silube (44 mg) (0.4 wt % compared to total weight of both PDMS components) was added and the mixture was further vortexed to ensure a homogenous continuous phase. A dispersed phase consisting of either 1.5% wt/vol NaCl or CaCl_2 solution in ultrapure Milli-Q water was added to the vial containing the continuous phase to a volume of 40% and vortexed to form the emulsion. Each emulsion was characterized using optical microscopy and rheology.

General PolyMIPE Synthesis. PolyMIPes were prepared using a modified literature procedure.¹³ The continuous phase was first prepared in an appropriately sized glass vial. For a polyMIPE with a 1:1 (thiol to alkene) functional group, thiolated-PDMS (2.5 g, 2.86 mmol thiol functional group) and vinyl-PDMS (8.57 g, 2.86 mmol alkene functional group) were added and vortexed slightly to mix. In a separate glass vial, DMPA (111 mg, 1.0 wt % with respect to the weight of the continuous phase) and Silube (44 mg, 0.4 wt % with respect to the weight of the continuous phase) were dissolved in approximately 0.3 mL of DCM. This solution was added to the continuous phase and vortexed until homogeneous. Nitrogen gas was bubbled through the reaction mixture to remove the DCM. The dispersed phase was then added as either a 1.5% wt/vol NaCl or CaCl_2 solution in Milli-Q water. These two phases were vortexed until a viscous emulsion formed. The emulsion was poured into a 36 mm-diameter well of a 6-well tissue-culture plate and irradiated with UV light ($\lambda_{\text{max}} = 365$ nm) for 6 min and allowed to stand further for 5 min. The resulting polyMIPE was removed and weighed before being placed into the vacuum oven and dried for ~48 h at 24 °C. The polyMIPE was weighed periodically to monitor water content loss. The final polyMIPes were characterized using dynamic mechanical analysis and scanning electron microscopy.

■ RESULTS AND DISCUSSION

We prepared polyMIPes using thiol–ene click reactions within a water-in-silicone emulsion, where the continuous phase

Scheme 1. Cross-linking Reaction between Thiolated-PDMS and Vinyl-PDMS



consisted of thiolated-PDMS and vinyl-terminated PDMS (Scheme 1). A commercially available surfactant, Silube, was used to stabilize the emulsions. We used the photo-initiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) in UV light to initiate the thiol–ene reaction.

We investigated four parameters to understand how the emulsion composition affected the properties of the resulting PDMS polyMIPes. These parameters were the thiol-to-ene ratio, the type of salt solution used as the dispersed phase, the volume of the dispersed phase added, and the concentration of the surfactant used to stabilize the emulsion. The details of each emulsion formulations are given in Table 1.

Table 1. Formulations of the 12 MIPes Prepared in This Study

| MIPe | thiol/ene ratio | volume of dispersed phase and salt ^a | surfactant content ^b (%) |
|------|-----------------|---|-------------------------------------|
| 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 |

^aThe dispersed phase consisted of a 1.5 wt % salt solution of either NaCl or CaCl₂. ^bThe surfactant concentration was added as a weight percent with respect to the total weight of the continuous phase.

We first varied the stoichiometric ratio of thiol-to-ene functional groups while keeping the dispersed phase (40% by volume of a 1.5 wt % sodium chloride solution and 0.4 wt % concentration of the surfactant with respect to the continuous phase) constant. This initial formulation was chosen based on previous work on PDMS-based polyMIPes.¹³

The emulsions were characterized before polymerization using optical microscopy and rheology. Optical microscopy images revealed a distribution of spherical droplets with the largest droplets being approximately 40–50 μm in diameter. This is shown in Figure 1 for MIPe 1. Optical microscopy images were similar for all the formulations and can be found in the Supporting Information (Figure S1). The spherical droplets of the aqueous dispersed phase packed together, with smaller droplets arranging themselves between larger droplets, as shown in Figure 1a. These droplets could be isolated into smaller aggregates by gently pressing on the glass cover slide to better visualize the distribution of droplet sizes, as shown in Figures 1b and S2 in the Supporting Information. MIPe 1 was diluted to 20% by volume using the excess continuous phase to

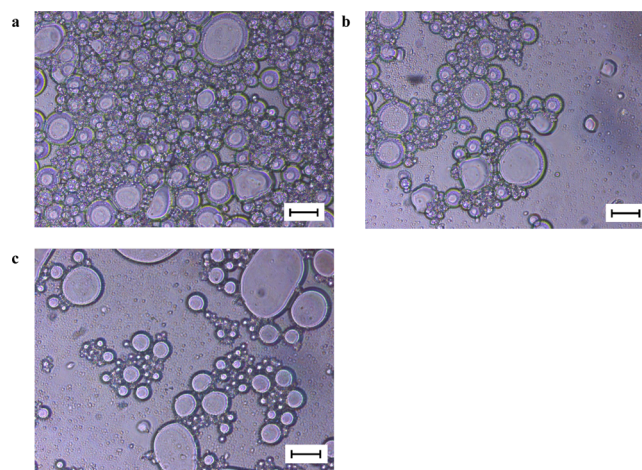


Figure 1. Optical microscopy images of MIPe 1. (a) As-prepared emulsion. (b) Emulsion droplets spread over the slide by pressing gently on the cover slide. (c) Optical microscopy image of 20% by volume dilution. The scale bar is 50 μm in all images.

observe if the droplets remained aggregated under dilute conditions. Aggregations of polydisperse-sized droplets could be seen following dilution, as shown in Figure 1c, indicating there are heterogeneous clusters of droplets in the emulsions.

When the emulsions were characterized using rheology, there was little difference in either stress versus shear rate (Figure 2a) or viscosity versus shear rate (Figure S3) plots upon changing the composition of the continuous phase (MIPes 1–3, Table 1). These data suggest that changing the composition of the continuous phase with respect to the ratio of the two PDMS reagents does not alter properties of the final emulsion. In Figure 2, the data are an average of three separate emulsions for each formulation.

We next explored if the type of salt dissolved in the aqueous phase had an effect on the emulsions. The dissolved salt in the dispersed phase slightly increases the polarity of the solution, making it more insoluble with the oil phase and allowing for stable emulsions to be formed more readily.^{4,49,50} We repeated the formulations described in MIPes 1–3 using a 1.5 wt % calcium salt solution as the dispersed phase. In our case, the rheology behavior was similar for all formulations, as shown in Figure 2a. In Figure 2a, the data for emulsions MIPe 1–6 are plotted to demonstrate that a similar behavior is seen both within each series (i.e., 1–3 and 4–6) and between the series. Therefore, there is no effect in the emulsion properties when using either NaCl or CaCl₂ salt solutions.

Our initial emulsion formulations were based on reported syntheses of PDMS-based polyMIPes for microfluidics applications that used a remarkably low level of the surfactant.¹³ However, many reports of polyHIPE and polyMIPe syntheses use much higher amounts of the surfactant, sometimes as high as 20 wt % of the emulsion.^{50,51} Considering this, we used increasing concentrations of the

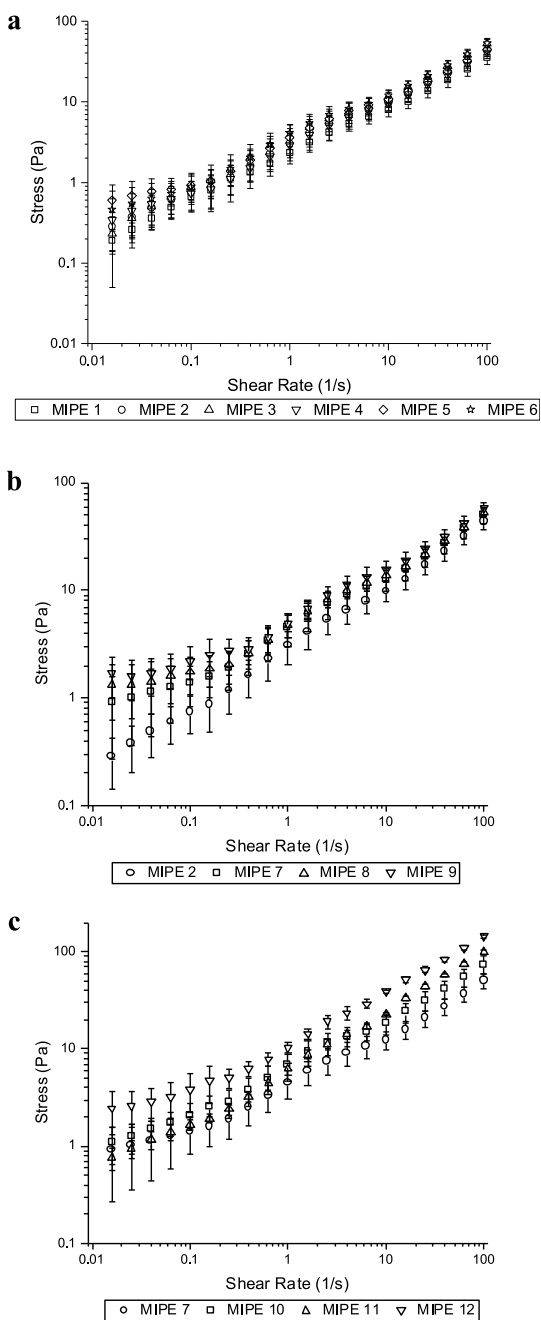


Figure 2. (a) Stress versus shear rate of MIPEs 1–3 and MIPEs 4–6 comparing emulsions with sodium chloride and calcium chloride dispersed phases, respectively, (b) where the surfactant concentration was varied, and (c) with increased volumes of the sodium chloride dispersed phase. The formulations for each MIPE are provided in Table 1.

surfactant in our emulsions, specifically 0.4, 1.0, 3.0, and 5.0% by weight with respect to the continuous phase, and characterized the resulting emulsions using rheology (Figure 2b). At these concentrations, the stress versus shear rate plot showed an inflection point in the data at low shear rates, implying a yield stress of ~ 1 Pa as the surfactant concentration in the MIPE increased.

Finally, we systematically increased the amount of the dispersed phase in the formulation. In these experiments, we maintained the stoichiometric ratio at 1:1 thiol-to-ene, while changing the sodium chloride solution dispersed phase from

40% by volume to 50, 60, and 70% by volume. The concentration of the surfactant was held constant at 1.0% to ensure that stable emulsions were formed. Rheology data from these emulsions (Figure 2c) revealed a yield stress of ~ 2 Pa, and emulsions with the highest volume of the dispersed phase possessed the highest yield stress. However, we were unable to form emulsions with higher than 70% volume of the dispersed phase using 1.0 wt % surfactant with our current protocols.

We prepared polyMIPEs from the emulsions by adding a photo-initiator, DMPA, to the continuous phase to initiate thiol-ene reactions upon irradiating with UV light. All of the MIPE formulations produced porous monoliths after thiol-ene polymerization and were characterized using SEM, total porosity, surface area analysis, and dynamic mechanical analysis (DMA). The SEM images of the polyMIPEs are presented in Figure 3.

Figure 3a–c shows polyMIPEs prepared from MIPEs 1–3. The polyMIPEs appear to be similar with respect to pore size and interconnectivity of pores. The pore interconnectivity is particularly visible on the most porous samples. Interestingly, there appears to be sections of nonporous cross-linked PDMS present too, as highlighted by the arrow in Figure 3a,b. The presence of nonporous PDMS is expected when considering the optical microscopy images of dilute emulsions where upon dilution with the continuous phase, droplets maintained an aggregated state. Therefore, clusters of water droplets are formed before polymerization and appear as clustered porous sections in the polymerized materials after drying. This observation is again seen in Figure 3d–f where the dispersed phase salt is changed to a CaCl_2 solution, representing polyMIPEs 4–6. Similar to the rheology of the emulsions, these images do not show significant differences in polyMIPEs using NaCl or CaCl_2 solution dispersed phases. This gives further evidence that changing the salt in the dispersed phase does not impact the resulting polyMIPE. The polyMIPEs in Figure 3g–i were prepared from MIPEs 7–9. When the surfactant concentration was increased to 3 and 5%, there appeared to be more interconnectivity between the pores with fewer regions of nonporous PDMS. Figure 3j–l shows polyMIPEs from MIPEs 10–12 where the volume of the dispersed phase was increased to higher than 40%. These images show an increase in the number of pores in the polyMIPEs while maintaining the interconnected morphology. The areas of nonporous PDMS also appear to decrease in a qualitative analysis of the SEM images.

We calculated the surface area and average pore sizes using USAXS, and total porosity calculations of the polyMIPEs were obtained using eq 3 where ρ is the average density of the bulk PDMS (0.975 g/mL), ρ^* is the density of individual polyMIPE samples, and Φ is the total porosity. The results are also presented in Table 2.

$$1 - \frac{\rho^*}{\rho} = \Phi \quad (3)$$

Using the Sauter mean size, d_p , from USAXS for the pore diameter and the calculated porosity from eq 3, the specific surface area (S_s) can be calculated with eq 4, assuming that all pores are spherical and exhibit the same average diameter d_p .

$$S_s = \frac{6\Phi}{(1 - \Phi)\rho d_p} \sim 10^{-2} \text{ m}^2/\text{g} \quad (4)$$

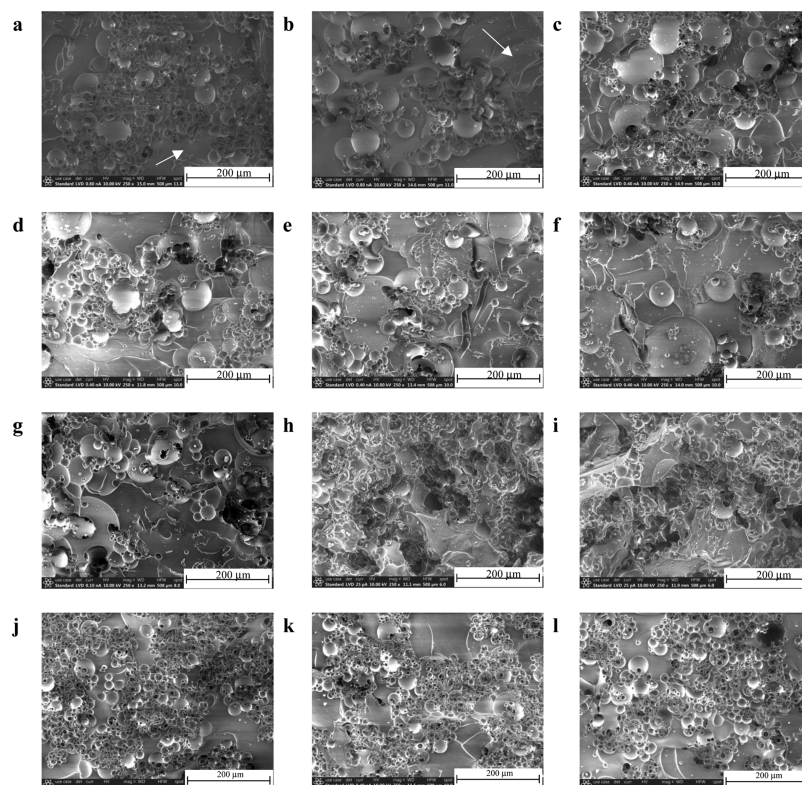


Figure 3. SEM images of cross sections of dried polyMIPes with varied components of the system. (a–c) PolyMIPes 1–3, (d–f) polyMIPes 4–6, (g–i) polyMIPes 7–9, and (j–l) polyMIPes 10–12. The scale bar is 200 μm for each image. Areas of nonporous cross-linked PDMS are present in all polyMIPes. Examples are highlighted by a white arrow in images (a,b). The formulations for each polyMIPe are provided in Table 1.

Table 2. Surface Area and Pore Dimensions of the PolyMIPes

| polyMIPe | measured density (g/mL) | average pore size ^a d_p (μm) | total porosity ^b (%) ($\pm 2\%$) | surface area ^a (m^2/g) |
|----------|-------------------------|--|---|---|
| 1 | 0.6247 | 164 | 38 | 0.0230 |
| 2 | 0.6100 | 173 | 39 | 0.0227 |
| 3 | 0.6066 | 136 | 38 | 0.0277 |
| 4 | 0.6223 | 195 | 36 | 0.0177 |
| 5 | 0.6174 | 153 | 38 | 0.0246 |
| 6 | 0.6499 | 150 | 42 | 0.0297 |
| 7 | 0.6007 | 123 | 40 | 0.0333 |
| 8 | 0.5988 | 249 | 44 | 0.0194 |
| 9 | 0.6249 | 272 | 42 | 0.0163 |
| 10 | 0.5015 | 104 | 49 | 0.0569 |
| 11 | 0.4205 | 56 | 60 | 0.1654 |
| 12 | 0.3337 | 48 | 66 | 0.2487 |

^aCalculated from USAXS data. ^bCalculated using eq 3.

PolyMIPes 1–9 possess a porosity of approximately 40%, which corresponds to the volume of the dispersed phase of 40% used to prepare these polyMIPes. This similarity between the dispersed phase initial volume fraction and the final porosity indicates that no contraction of the materials occurred during drying. This lack of contraction in the polyMIPes is due to interconnected pores, which allows for the removal of water throughout the materials upon drying.^{13,52} A systematic increase in total porosity was observed for polyMIPes with increasing volume of the dispersed phase up to 70%. The porosity of these PDMS polyMIPes is unaffected by chemistry of the continuous phase, identity of the salt, or concentration

of the surfactant, and only by the volume of the dispersed phase.

The polyMIPes were characterized using DMA to obtain the storage moduli (G'), and the results are shown in Figure 4. Tan delta (δ) values were also obtained using DMA, and the values were consistently less than one (data not shown), which is representative of elastic materials. No variation in the storage moduli was observed over the frequency range used. The DMA results for polyMIPes 2, 3, 5, and 6 are shown in Figure 4a. The observed trend of storage moduli in the DMA results was comparable upon changing the stoichiometric ratio of the PDMS polymers in the continuous phase regardless if NaCl or CaCl_2 was used in the dispersed phase (Figure 4a), suggesting that the salt used in the dispersed phase has no effect on the storage moduli of the final polyMIPes. PolyMIPes 1 and 4 were prepared using a 1:2 thiol-to-ene ratio and were the two materials with the lowest storage moduli (~ 90 and 35 kPa, respectively); in fact, although the storage moduli of these polyMIPes were consistently lower than the other materials prepared, these polyMIPes did not produce materials with consistent behavior in the DMA. Therefore, we have only reported results from the averages of the materials with higher thiol-to-ene ratios. PolyMIPes 2, 3, 5, and 6 with thiol-to-ene ratios of 1:1 or 2:1 resulted in G' values similar to each other (between ~ 200 and 320 kPa) and consistently higher than that for polyMIPes 1 and 4. This is similar to literature reports of cross-linked silicone networks prepared using thiol-ene chemistry, where material properties increased with higher ratios of thiol-to-alkene, from which it was concluded that excess thiol functional groups were necessary to overcome imperfections during the formation of the network.³⁵ In our work, we did not observe this exact trend. We found that our

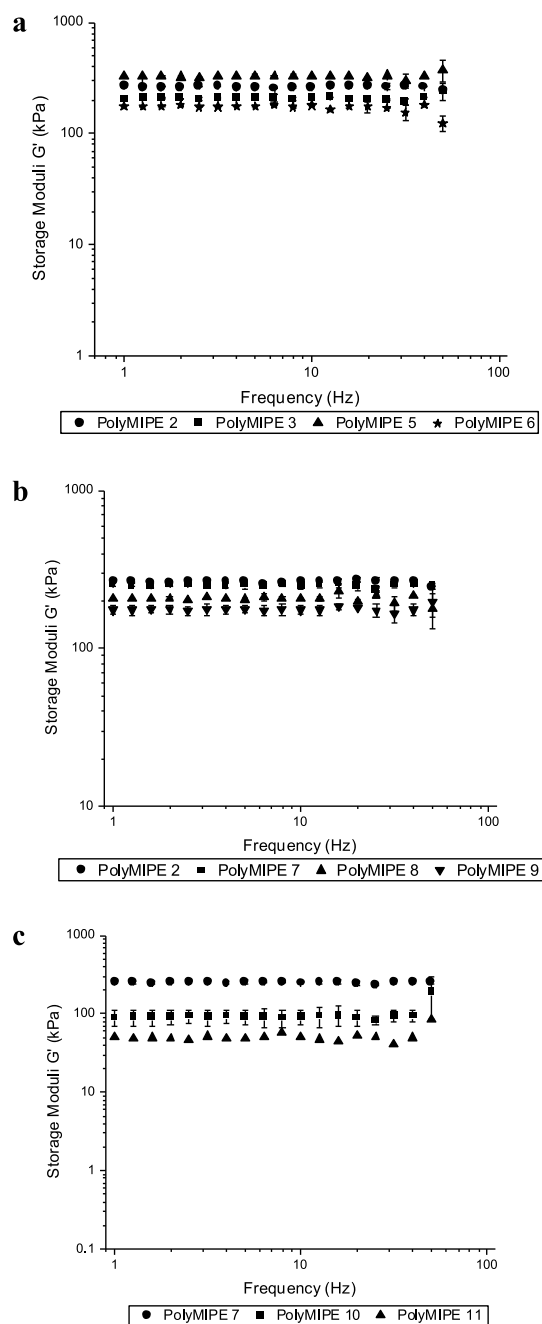


Figure 4. (a) Storage modulus versus frequency plots of polyMIPes 2, 3, 5, and 6 comparing emulsions with sodium chloride and calcium chloride dispersed phases, (b) polyMIPes 2 and 7–9 showing materials with varied concentrations of the surfactant, and (c) polyMIPes 7, 10, and 11 with increased volumes of the sodium chloride dispersed phase. The formulations for each polyMIPe are provided in Table 1 and are plotted as an average of three replicates except for polyMIPes 1, 4, and 12.

system had the highest storage moduli using 1:1 thiol-to-ene ratios. The DMA results in Figure 4a therefore show that the mechanical properties of the polyMIPes can be controlled by changing the molar ratio of thiol-functionalized to ene-functionalized PDMS in a given formulation, while simultaneously maintaining the morphology and porosity of the material.

The surfactant concentration had little effect on the storage moduli and only a slight decrease was observed for the highest

surfactant concentration (Figure 4b). The surfactant was not purposefully removed after synthesis and therefore may act as a plasticizer reducing the modulus of the polyMIPe if it remains within the network. We did observe differences in G' with polyMIPes using an increasing amount of the dispersed phase (polyMIPes 7 and 10–12) because of the increasing porosity of the materials, as is expected theoretically.^{30,53} The DMA results from this series of polyMIPes are shown in Figure 4c, and polyMIPes prepared with 70% volume of the dispersed phase (polyMIPe 12) did not give consistent results when characterized by DMA (although the recorded storage moduli were consistently lower than that from polyMIPes 7, 10, and 11). Therefore, the DMA results from this polyMIPe are omitted from plot, as shown in Figure 4c.

The acoustic properties of the polyMIPes were characterized at ultrasonic frequencies to test the potential of these materials as acoustic metamaterials. Unfortunately, measurements could not be performed on the samples having the lowest shear moduli (polyMIPes 1, 4, and 12) as they were too delicate to be manipulated between the transducers. An image of the instrumentation with a polyMIPe sample between a transmitter and receiver is shown in Figure S4. The transmitted signals through the samples were recorded as a function of time; as an example, the data from polyMIPe 10 are presented in Figure 5. We deduced the sound speed in the sample from

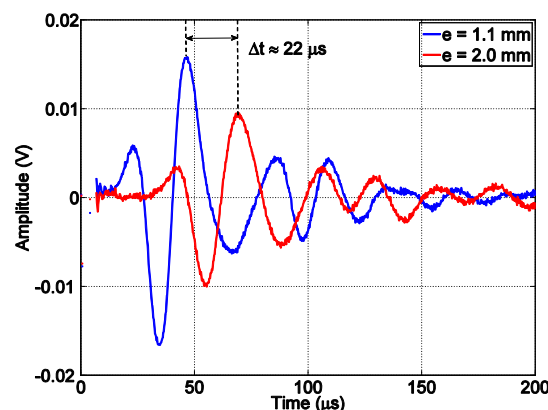


Figure 5. Transmitted signals through polyMIPe 10 with a porosity of 49% for two different thicknesses: $d = 1.1$ mm and $d = 2$ mm for longitudinal waves.

the difference of time-of-flight and found a value of the longitudinal phase velocity $c_L \approx 40 (\pm 20)$ m/s. This is a remarkably low value of the sound velocity and suggests that these polyMIPes can be used as acoustic metamaterials. We found that the sound velocity does not vary as a function of the porosity or the shear storage (G') modulus of the other polyMIPes within the accuracy of our experimental measurements, and values between 30 and 70 m/s were recorded.

We performed calculations of the expected profiles of the velocity versus porosity using the Kuster and Toksöz⁵⁴ model to gain further insight into the experimental observations. It has been previously shown that this model well describes samples with very low G_0 values.¹⁴ In the Kuster and Toksöz model, the acoustic longitudinal velocity is a function of only three parameters: the porosity Φ , elastic bulk (K_0), and shear storage moduli (G_0) of the nonporous matrix. Therefore, we measured the shear storage moduli of nonporous materials prepared using the same PDMS formulations as the

polyMIPes. The storage moduli of the nonporous materials were found to range from 110 to 1170 kPa. The value of K_0 is typically 1 GPa for this type of matrix. In Figure 6, we plot the

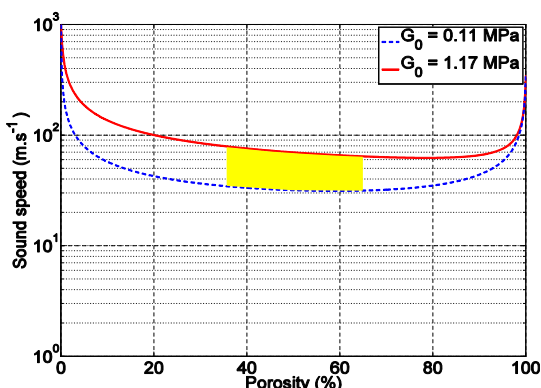


Figure 6. Evolution of the acoustic longitudinal velocity as a function of porosity for different values of the shear storage modulus G_0 of the nonporous matrix. Calculations are obtained from the Kuster–Toksöz model. The yellow domain represents the expected acoustic velocity values for the different samples, which are comprised between 30 and 70 m/s.

expected evolution of the velocity versus porosity profile for different values of the shear storage modulus of the nonporous polymer matrix that are comprised between 110 and 1170 kPa.

The curves obtained from the calculations for these values of the shear moduli and porosity values between 0.36 and 0.66 are in good agreement with the measured value of the acoustic velocity (~ 40 m/s) and does not significantly depend on the porosity and on the shear modulus in these ranges of shear moduli and porosity values (from 40 to 60%). This is shown in the yellow shaded area in Figure 6, which is the expected domain of sound velocity for the different materials presented in this study. From this graph, we expect the acoustic velocity of these samples to be between 30 and 70 m/s. Therefore, the results are in reasonable agreement with the predictions of the Kuster–Toksöz model. Additional work is under progress in our laboratory to more precisely determine the velocity and the acoustic attenuation of these materials.

CONCLUSIONS

This work has demonstrated the synthesis of soft polyMIPes using a macromolecular thiol–ene reaction to prepare porous networks. 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, but the stoichiometric ratio of the PDMS reagents does control the storage moduli of the materials. The material properties of the polyMIPes could also be directly controlled by the amount of the surfactant used to stabilize the emulsion and the volume of the dispersed phase. Acoustic measurements show that the materials exhibit very low values of the sound velocity (~ 40 m/s), a value rarely attained in any solid materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.0c00217>.

Optical microscopy images of emulsions; optical microscopy images of emulsions after applying different

pressures to the microscope slides to limit droplet stacking; viscosity versus shear rate plots of emulsions; and images of the acoustic characterization setup (PDF)

AUTHOR INFORMATION

Corresponding Author

Neil Ayres – Department of Chemistry, The University of Cincinnati, Cincinnati, Ohio 45221, United States; orcid.org/0000-0001-8718-2502; Phone: +01 513 556 9280; Email: neil.ayres@uc.edu; Fax: +01 513 556 9239

Authors

Tucker J. McKenzie – Department of Chemistry, The University of Cincinnati, Cincinnati, Ohio 45221, United States
 Paul S. Heaton – Department of Chemistry, The University of Cincinnati, Cincinnati, Ohio 45221, United States
 Kabir Rishi – Department of Chemical and Materials Engineering, The University of Cincinnati, Cincinnati, Ohio 45242-0012, United States; orcid.org/0000-0002-3159-031X
 Raj Kumar – University of Bordeaux—CNRS, Centre de Recherche Paul Pascal, Pessac 33600, France
 Thomas Brunet – Institut de Mécanique et d'Ingénierie, University of Bordeaux—CNRS—Bordeaux INP, Talence 33402, France
 Gregory Beaucage – Department of Chemical and Materials Engineering, The University of Cincinnati, Cincinnati, Ohio 45242-0012, United States
 Olivier Mondain-Monval – University of Bordeaux—CNRS, Centre de Recherche Paul Pascal, Pessac 33600, France

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.macromol.0c00217>

Notes

The authors declare no competing financial interest.

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