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Branched Polymers for Enhancing Polymer Gel Strength and Toughness (Final Report)

by Robert H. Lambeth, Randy A. Mrozek, Joseph L. Lenhart, Yelena R. Sliozberg, and Jan W. Andzelm

ARL-TR-6338   **February 2013**

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14. ABSTRACT

The objective of this project is to develop robust and scalable synthetic methods to access polymer network and solvent macromolecules with complex chain architectures and highly branched molecular structures. The introduction of branching points in the polymer network and solvent will significantly enhance the strength and toughness of polymers gels through increased physical chain entanglements. In particular, we have focused on synthesizing and characterizing poly(dimethylsiloxane) (PDMS) based materials with well-defined chain lengths and branching points for use in polymer gels. This research has yielded four major accomplishments related to the proposal objectives including: (1) conducting successful synthesis of a "star shaped" PDMS solvent; (2) demonstrating greater than two times improvements in both strength and toughness of the polymer gel due to incorporation of the star shaped solvent; (3) identifying synthetic strategies for increasingly complicated chain structures, such as H, pom-pom, comb, and dumbbell shaped molecules; and (4) employing anionic polymerization to prepare additional "star shaped" PDMS solvents of varying molecular weight and arm number.

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1. Objective

The objective of this project is to develop robust and scalable synthetic methods to access polymer network and solvent macromolecules with complex chain architectures and highly branched molecular structures. The introduction of branching points in the polymer network and solvent will significantly enhance the strength and toughness of the polymers gels through increased physical chain entanglements. These tougher polymer gels will enable a host of critical Army technologies including electronics packaging and shielding; soft robotics and morphing materials; stretchable and conformable electronics, smart textiles, sensors, and membranes; combat casualty care; prosthetics; bio-inspired materials; responsive coatings; and tissue simulants for ballistics testing. In particular, we have focused on synthesizing and characterizing poly(dimethylsiloxane) (PDMS) based materials with well-defined chain lengths and branching points for use in polymer gels.

2. Approach

Nature commonly employs complex and entangled architectures to control signaling, transport, and mechanical properties in biological systems. Interestingly, these soft biomaterials are amazingly tough and durable, despite the high water content (*1*). Synthetic polymer gels represent bio-inspired surrogates for these biotissues and are typically very soft elastomers composed of physically or chemically crosslinked polymer chains. Gels are loosely crosslinked and typically contain high solvent loadings to impart the softness. Many variables impact gel properties including the polymer/solvent chemistry, polymer/solvent chain architecture and size, solvent loading, and the incorporation of various fillers and additives. This tunability offers the potential to implement synthetic gels in a very wide range of Army applications including electronics packaging, soft robotics, textiles, sensors, membranes, and prosthetics; bio-inspired materials; and soft tissue surrogates for ballistics testing. While the potential applications are promising, synthetic approaches have not achieved the intricacy of biological materials. Critical challenges hinder broad utility of synthetic gels in defense-related applications including poor environmental stability; poor toughness, durability, and fatigue resistance; inability to function in extreme environments, lack of multifunctionality; and limited materials availability, processability, and reliability. These challenges must be addressed before widespread integration of gel-based materials can be realized in the defense community.

The presence of solvent in a crosslinked polymer network produces a polymer gel that behaves mechanically as a "soft solid" that is easily deformable yet still recovers from an applied strain due to the elastic nature of the crosslinked polymer chains (*2*). Polymer gels have received

considerable attention for use in a wide range of applications including microvalves (*3, 4*), robotics (*5*), sensors (*6, 7*), electronic packaging (*8*), and biomedical technology (*9, 10*). A significant amount of this research effort has focused on water-based hydrogels. For example, hydrogels based on poly-(N-isopropylacrylamide) (PNIPAM) exhibit a volume shrinkage transition near 33 °C that has been exploited in the biological community for several applications including controlled release (*11*), cellular adhesion (*12*), and nucleic acid purification (*13*). However, widespread implementation of gel-based technology is often hindered by narrow operational temperature ranges, limited performance lifetimes, and poor toughness (*14*).

To avoid the operational limitations of water-based hydrogels, the solvent can be composed of low volatility organic molecules. The incorporation of organic solvent coupled with other critical material requirements has led to the design of non-aqueous gels with very broad temperature performance (*8, 15*). However, the solvent molecules often have a significant impact on the small strain mechanical properties and high loadings of small molecule organic solvents almost exclusively results in a gel with very low toughness. Several approaches have been investigated to enhance the strength, toughness, and durability of polymer gels. Examples include slip-link gels, polymer hydrogel nanocomposites, and double-network gels. While these approaches enhanced the mechanical properties of the gel through different toughening mechanisms, each required complicated processing not amenable to scale up limiting their broad utility.

Most research in polymer gels exploits a chemically or physically crosslinked polymer loaded with high fractions of a small molecule solvent (examples include physically crosslinked thermoplastic elastomer gels [*16*], chemically crosslinked polymer networks [*15*], hydrogels [*17*], and organogels [*18*]). Recent efforts from our laboratory demonstrated the importance of solvent molecular weight on the small strain rheological response and fracture behavior of the polymer gel. The impact of sol loading and molecular weight on the mechanical properties of a model end-linked PDMS gel that contains non-reactive PDMS soluble material was investigated. The networks were formed in the presence of non-reactive PDMS solvents with molecular weights from 1,250 to 423,000 g/mol, broadly spanning the molecular weight of entanglement for PDMS ($MW_{ENT} \sim 29{,}000$ g/mol) (*19*). The gels exhibited a strong frequency-dependent mechanical response when the solvent molecular weight $> MW_{ENT}$. In addition, scaling factors of shear storage modulus versus solvent loading displayed a distinct decrease from the theoretical value for networks formed in a theta solvent of 2.3 with increasing measurement frequency and solvent molecular weight. The frequency dependent shear storage modulus could be shifted by the ratio of solvent molecular weights to the 3.4 power to form a master curve at a particular solvent loading indicating that mobility of entangled solvent plays a critical role for the mechanical response. In addition, the incorporation of entangled solvent can increase the toughness of the PDMS gels.

One approach that has not been considered is the introduction of branched polymer and solvent molecules into the network. Examples of branched structures include t-shaped, h-shaped, pom-pom, barbwire (flexible main chain with rigid side chains), star, comb-shaped, dumbbell-shaped,

and a hybrid of multiple architectures illustrated in figure 1. The branched nature of the additive results in a range of diffusion timescales that are dependent on the molecular architecture (size and microstructure) when compared to linear polymers of similar molecular weight (*20*). Incorporation of these branched molecules into a polymer network will result in a reduced mobility in the network relative to a linear molecule of the same molecular weight. As a result, when the deformation rate becomes faster than the characteristic mobility time of the additive in the network, the additive cannot migrate away from the deformation zone. Deformations faster than the characteristic mobility time of the branched additive will result in an increase in the modulus, strength, and toughness of the network enabling tenability of the strain-rate-dependent mechanical response.
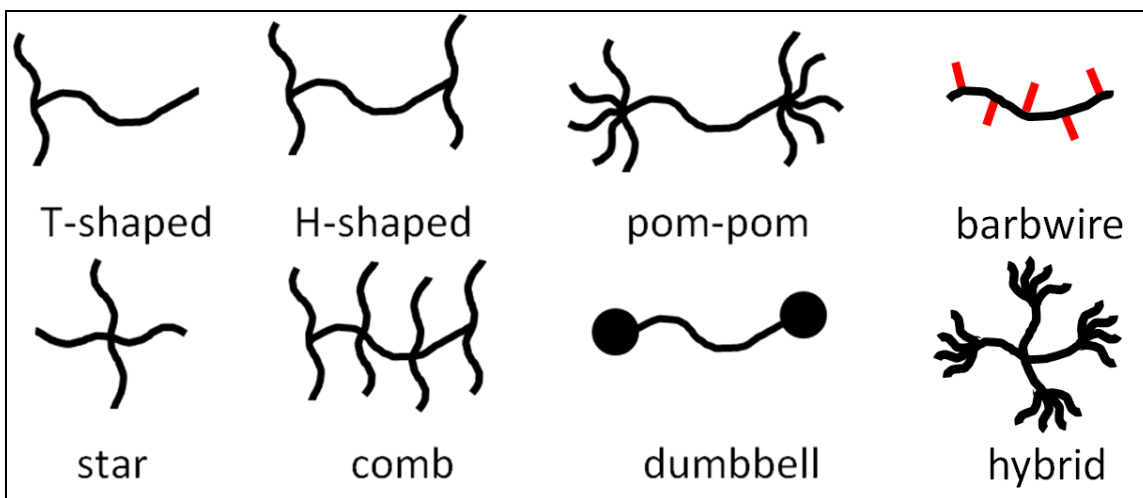
Figure 1. Examples of branched additive architectures.

During deformation as the result of a fracture event, the branched additive will enhance the toughness of the material through several mechanisms: (1) the decreased mobility of the additive will act as additional chemical crosslinking requiring a larger number of covalent bonds to be broken to facilitate further fracture propagation; (2) the inability of the additive to migrate away from the crack tip will produce a larger zone of plastic deformation requiring additional energy to maintain crack propagation; and (3) the larger plastic deformation zone will produce greater energy dissipation to limit crack propagation. The increased energy required to initiate, propagate, and maintain crack growth due to these mechanisms will lead to enhanced fracture toughness of the polymer network.

The incorporation of branched additives will enhance the strength and toughness, and/or produce a strain-dependent response regardless of the modulus of the material ranging from conformal soft polymers and polymer gels or biomaterials (G' ~ 100 Pa – 10 kPa) to structural resins (G' ~ >10 MPa). In particular, this approach will address the prohibitively low fracture toughness of soft polymeric materials that has prevented their widespread implementation into a variety of practical applications (*21*). Examples of soft polymeric materials include low modulus

network and elastomer (G' < 1 MPa); solvent-swollen polymer gels, polymer networks, or gel containing unreacted polymer precursors; and many biomaterials. The enhanced toughness of soft materials will facilitate implementation into a wide variety of applications including robotics, prosthetics, damping, biotissue simulants, tissue regeneration, biomedical implants, coatings, and sensors. In addition, tailoring the strain-dependent mechanical response will allow for the material to remain soft and conformable at low strain rates but stiffen upon high deformation rates. This strain-dependent mechanical response can be utilized in wearable textiles, prosthetics, and coatings, and provide materials with enhanced blast, shock, and fracture protection. Incorporation of branched additives in rigid structural polymers will further enhance their fracture toughness leading to implementation into additional applications and the reduction of size and weight in current applications.

The enhancements from incorporating branched additives into a polymeric network are the result of the additive architecture, requiring no specific interactions, and can be used in any polymer network. This allows for a single additive to be used with a variety of network chemistries with similar solubilities. As a result, the branched additive production can be increased in scale to reduce the end cost of the product. While no specific interaction are required to obtain the aforementioned improvements, chemical functionalities that promote interaction of the additive with the network can provide further enhancements. Examples of chemical functionalities that promote interaction include hydrogen bond donors/acceptors, metal center ligands, and the production of covalent bonds. In addition, variations in chemical or mechanical properties could further improve toughness by acting similar to barbs on a fish hook, preventing disentanglement of the branches, to increase the zone of deformation and the extent of energy dissipation.

The primary challenge for implementation of this technology is the development of robust, simple, and scalable synthetic methods to access the branched polymer species with controlled branch architectures and molecular weight. Most approaches to branched polymers described in the literature require multiple synthetic steps and purifications, require very stringent reaction conditions, and are not amenable to scale up. As before, the model system consists of end-linked PDMS network swollen with non-reactive branched PDMS solvent molecules of varying architecture and molecular weight. In particular, we have focused on developing synthetic protocols for PDMS star polymers. Several different approaches were investigated accompanied by full molecular characterization. Upon development of synthetically viable approaches, the procedures were scaled up to produce enough material to formulate swollen PDMS network gels. The mechanical properties of the resulting gels were probed via stress-strain tensile measurements and tack adhesion testing.

3. Results

3.1   Year 1

3.1.1 Star Polymer Synthesis

The synthetic strategy chosen is based on coupling commercially available mono-functional (chain end functionalized) PDMS with a multi-functional core molecule to create a star-branched structure, as shown schematically in figure 1. Initially, thiol-ene linking chemistry was investigated to join the functional PDMS to a multi-reactive core. The reaction is highly versatile and quantitative, and can be conducted under a wide variety of conditions. The chemistry involves reaction between terminal thiols and terminal alkenes to form a thioether. In our case, an ene-terminated PDMS was reacted with a multi-functional thiol core in the presence of a photoactive radical initiator. The reaction products were characterized by Fourier transform infrared (FTIR) spectroscopy and ^{1}H nuclear magnetic resonance (NMR) (figure 2). Each characterization method indicated complete attachment of the ene-functionalized polymer to the thiol core. ^{1}H NMR spectroscopy indicated complete consumption of vinyl end groups in the end functionalized PDMS as evidenced by the complete disappearance of the resonances associated the vinyl group from 5.70–6.20 ppm. Reaction of the thiol group was monitored by FTIR, which confirmed complete consumption of the thiol group as well.
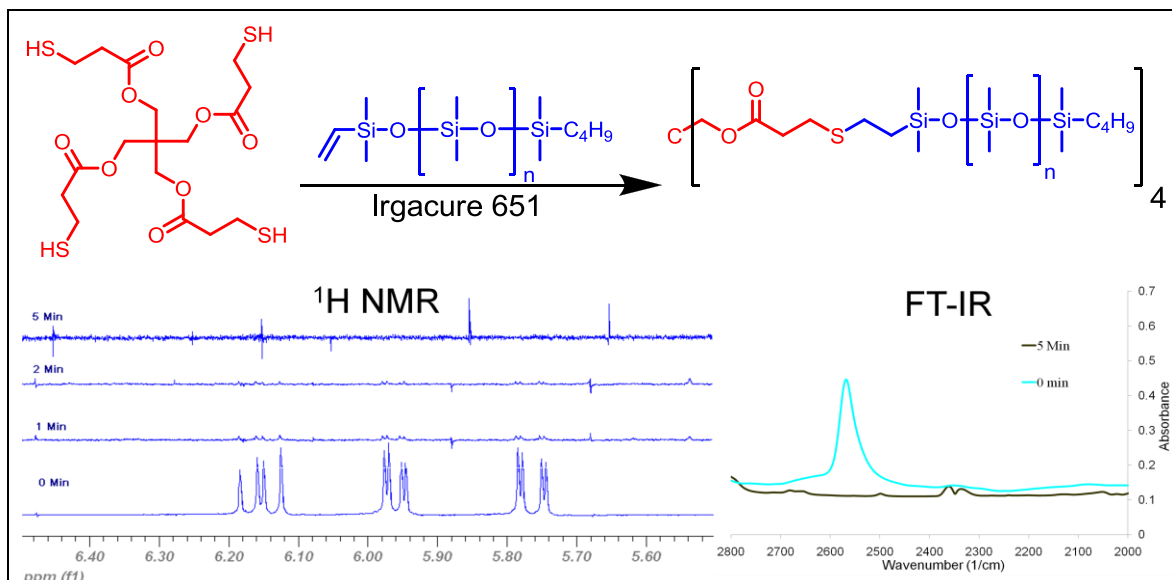

Figure 2. Synthetic scheme for PDMS star polymer via thiol-ene coupling chemistry (top). ^{1}H NMR analysis of vinyl-terminated PDMS showing complete disappearance of resonances associated with vinyl functionality after a 5-min reaction time (left). FTIR analysis of tetra-thiol showing disappearance of thiol peak after 5 min (right).

After studying the reaction on gram scale, it was scaled up to 50-g batches and used to formulate the PDMS network gels. However, the gel did not cure in the presence of the PDMS star polymer. We reasoned the platinum catalyst used for curing the gel was being poisoned and rendered inactive either by impurities present from the reaction or unreacted thiol groups. The reaction products were subsequently rigorously purified by multiple precipitations and extractions and any potentially unreacted thiol groups capped by reaction with a large excess of ethyl vinyl ether. Despite these added steps, attempts to cure the PDMS were met with uniform failure. It is possible the thioether linkages formed from the thiol-ene reaction are coordinating and deactivating the catalyst as a number of platinum (II) thioether complexes are known in the literature.

Next, we turned our attention to another type of coupling chemistry to attach the mono end functionalized PDMS to a central core. The reaction investigated was a platinum catalyzed hydrosilylation between an ene-terminated PDMS linear polymer and a tetra-functional silane core molecule. This transformation is the same reaction used to cure the PDMS gels thus we were confidant the chemistry would be compatible for curing the gels. The reaction was characterized by size exclusion chromatography (SEC), which suggested nearly complete attachment of the mono vinyl terminated PDMS to the central core molecule (figure 3). The reaction was scaled up and a PDMS gel was prepared in the presence of the product. The gel appeared to be fully cured and the strength and toughness of the gels was evaluated relative to a linear PDMS solvent molecule.
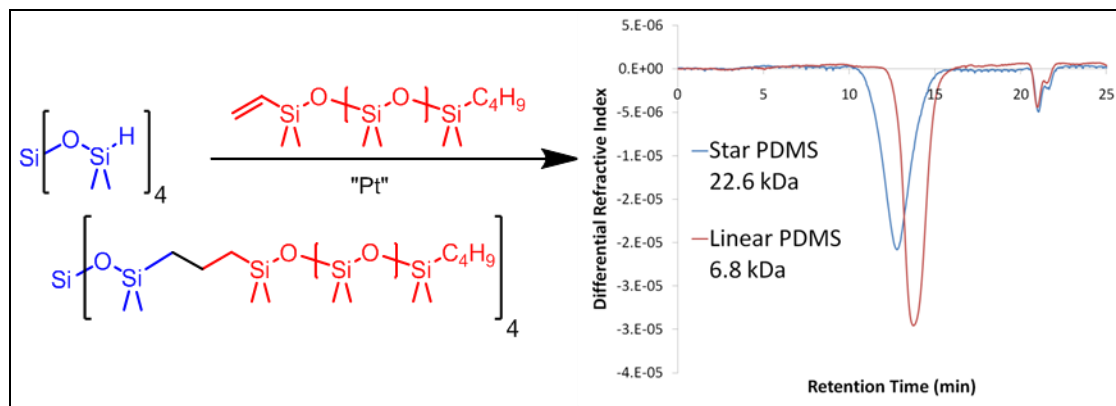
Figure 3. Synthetic scheme for platinum catalyzed hydrosilylation reaction (left). SEC analysis of the reaction showing shift of star polymer to higher molecular weight relative to linear peak with uniform peak shape and nearly 4-fold increase in molecular weight (right).

3.1.2 Tensile Testing

Tensile testing was performed using an MTS Synergie load frame at 10 in/min and a 500 N load cell on gel samples in a dogbone geometry. Figure 4 shows the stress-strain behavior of gel samples containing 50% of the star-branched additive and 50% of a small molecular weight linear chain (1,100 g/mol). The stress-strain tensile data exhibited a twofold enhancement of the

strength (stress at break) and a threefold enhancement in toughness (integral of stress-strain curve) with the star-shaped additive relative to the small linear solvent.
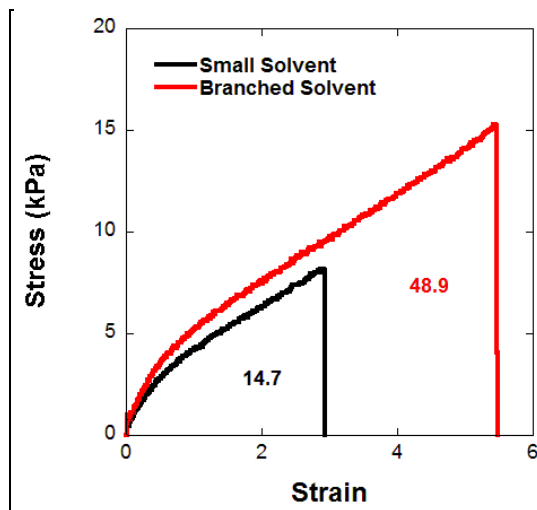

Figure 4. Comparison of stress-strain tensile data for PDMS gels with either 50 vol.% of the star-branched additive or 50 vol.% of a small linear chain PDMS additive (1,100 g/mol). The strength (stress at break) increased twofold and the toughness (integral of the stress-strain curve) increased by threefold for the gel containing the star-branched additive compared to a linear small molecule solvent.

3.1.3 Tack Adhesion Testing

Tack adhesion testing was performed on an Anton Paar rheometer using a tack probe with a circular cross section 8 mm in diameter. The tack probe was brought into contact with the gel sample under a force of 1.5 N for 120 s followed by drawing the tack probe away from the sample at a rate of 1 mm/s. The results were similar to the tensile data where the ultimate force was significantly larger and the work of adhesion (toughness) exhibited a threefold increase relative to the small linear additive (figure 5).
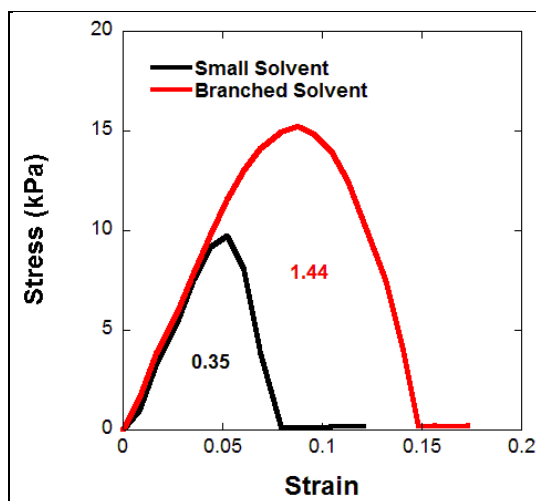
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Figure 5. Comparison of the stress-strain tack adhesion data for PDMS gels with either 50 vol.% of the star-branched additive or 50 vol.% of a small molecule PDMS additive (1,100 g/mol). Similar to the tensile testing, the adhesive strength (maximum stress) and toughness/work of adhesion (integral of the stress-strain curve) are significantly improved for the gel containing the star-branched solvent when compared to a sample containing the small molecule additive.

3.1.4 Computational Modeling

As shown in the preceding examples, the mechanical properties of polymeric networks can be significantly modified through the incorporation of additives with topological constraints and/or entanglements. To identify the most promising of the substantial number of potential additives, we are developing computational models. Direct atomistic modeling of the mechanical response of these systems is still unobtainable because of the slow dynamics and limited size of atomistic models. Coarse-graining models are being used to bridge this vast temporal and spatial scale. Conventional coarse-graining methods may use soft-repulsive interaction potentials between particles made of a large number of polymer monomers. Although the soft potential has substantial benefits allowing for long-time simulations, it also leads to unphysical crossing of the polymer chains making simulation of mechanical properties unrealistic. We addressed this issue by introducing a repulsive potential between bonds that prevents unphysical chain crossing. The models of polymer gel incorporating polymer network and a solvent composed of polymers exhibiting various shapes and lengths were built by applying recent U.S. Army Research Laboratory (ARL)-developed coarse-graining strategy. We have applied several coarse-grain techniques using both hard- and soft-repulsive potentials. In the latter care, a newly developed bond potential was also implemented. The polymer models were subjected to Molecular Dynamics simulations using the Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) program and the stress-strain relations were calculated with varying strain-rates (figure 6). A fracture model of polymer networks, dependent on the network deformation, was

introduced and applied to study toughness of polymeric gels. The computational modeling supports the observed improvements through the addition of branched and entangled solvent. In addition, the computational modeling suggests the most significant benefit from a "molecular barb-wire" architecture, where an entangled linear polymer has several short rigid side-chains resulting in a dramatic reduction in mobility.
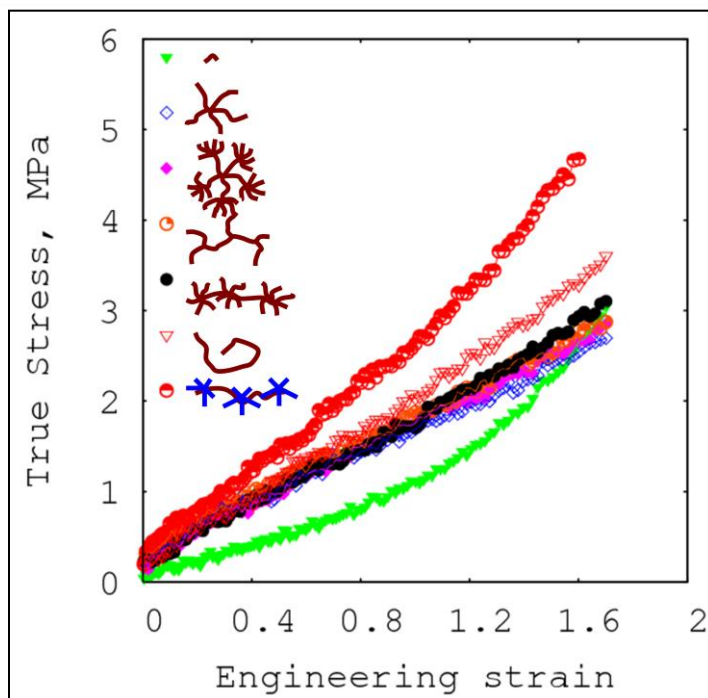

Figure 6. Computational modeling of the impact of solvent size
and architecture on the stress-strain behavior of a polymer
network.

3.2 Year 2

To expand the scope of our study, we sought to prepare more branched polymers of various molecular weights and architecture. The hydrosilylation reaction used to prepare the four-arm star polymers described previously is only effective with low molecular weight precursors. As the molecular weight of the vinyl terminated polymer increases, the concentration of the reactive groups decrease, leading to lower conversions (*21*). To overcome this limitation, we explored the use of chlorosilane coupling to prepare the branched polymers. The chlorosilane bond is highly reactive towards nucleophiles and generally leads to quantitative conversion. In addition, there are a number of commercially available chlorosilane compounds from which a variety of polymer architectures can be derived.

Initially, we focused on preparing multi-arm star polymers using the chlorosilane coupling approach for comparison to the star polymers prepared via hydrosilylation. Commercially available mono-hydroxyl terminated PDMS (M_n ~ 10 kDa) was reacted with tetra- and hexyl-

functionalized chlorosilane compounds in the presence of triethylamine (figure 7). The reaction products were characterized by SEC (figure 8), which showed nearly complete coupling of the mono-hydroxyl terminated PDMS to the multi-functional chlorosilane.
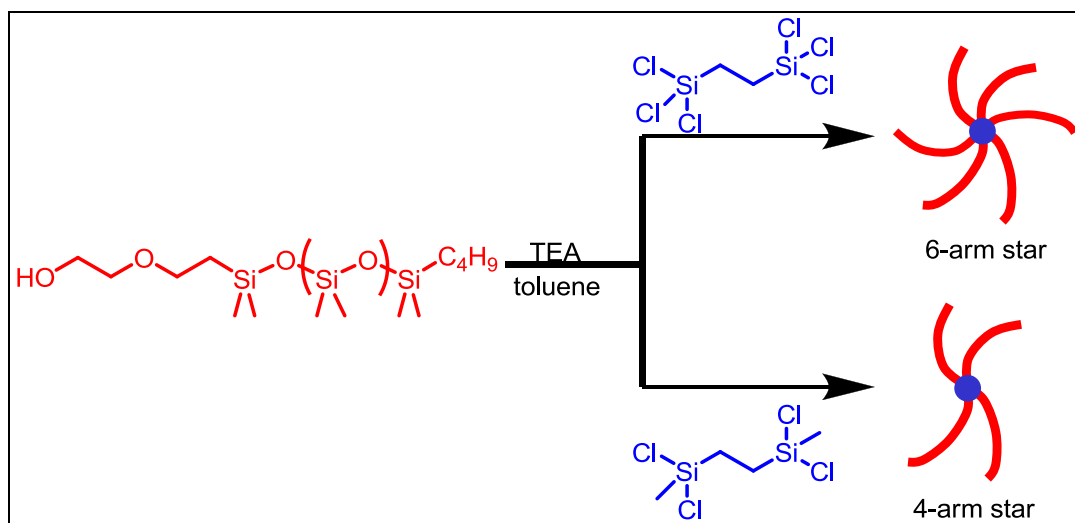

Figure 7. Synthetic scheme for preparation of four- and six-arm star polymers via chlorosilane coupling.
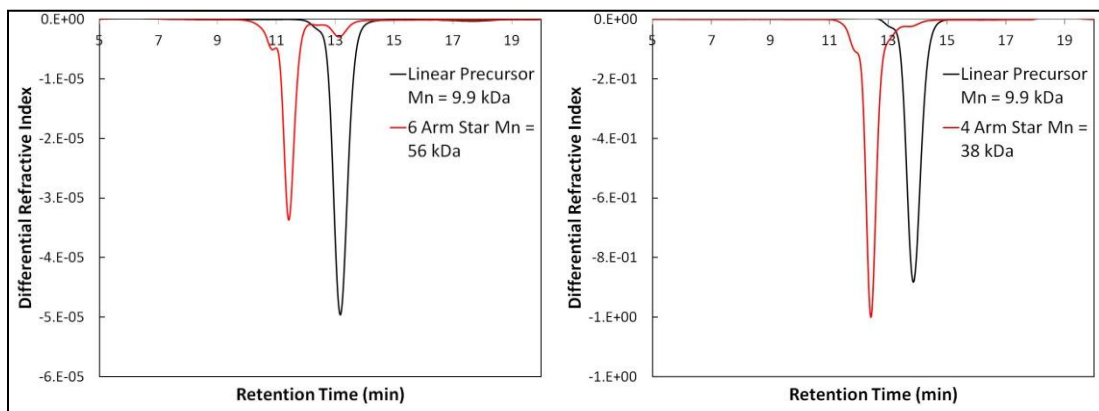

Figure 8. SEC analysis of chlorosilane coupling to form four- and six-arm star polymers.

Despite the success of using the chlorosilane coupling approach to prepare the star polymers, we were limited by the commercial availability of high molecular weight linear polymer precursors. The highest molecular weight available commercially is only 10 kDa. In order to expand the scope of the study to include higher molecular weight polymers, it was necessary to prepare linear precursors ourselves. There are a variety of methods to synthesize PDMS. We initially choose to explore organocatalytic ring opening polymerization (ROP) of hexamethylcyclotrisiloxane (D3) (figure 9) (*22*). It was shown to be a robust method to produce polymers of predictable molecular weight and end group functionality from cyclic carbosiloxane monomers, while avoiding side reactions that accompany other methods such as anionic polymerization.

The polymerization was initiated by pyrene butanol which is highly ultraviolet (UV) active and provides an analytical handle to analyze the resulting polymers. Only chains containing the pyrene butanol would be observable by UV analysis and could potentially help differentiate between polymer species initiated by impurities such as water. The polymerization is catalyzed by 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) which activates the initiator and subsequent propagating silanol through hydrogen bonding. We initially targeted a molecular weight of 33 kDa and monitored the polymerization over time by SEC. A typical result is shown in figure 10.
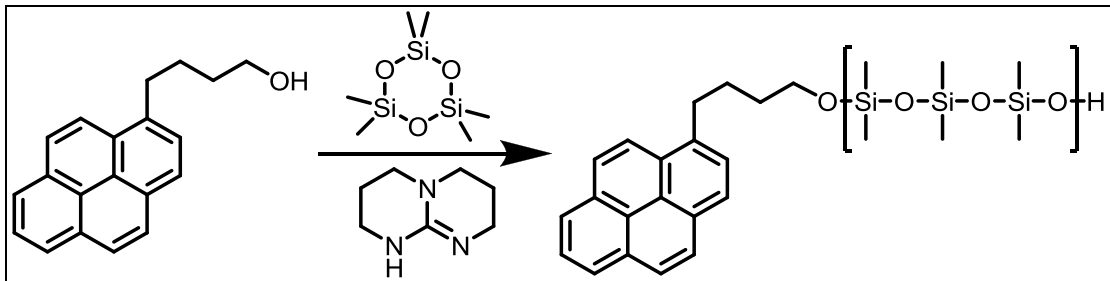

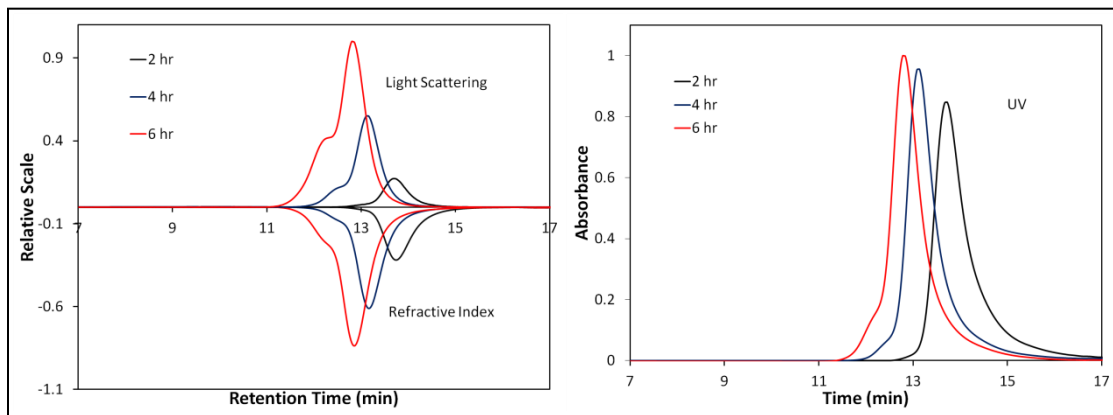Figure 9. Organocatalytic ROP of D3 initiated by pyrene butanol and catalyzed TBD.

Figure 10. SEC analysis with light scattering and refractive index (left) and UV (right) of organocatalytic ROMP of D3.

In all of the polymerizations attempted, a significant shoulder was observed in all three detectors in the high molecular weight region of the SEC trace, especially at longer reaction times. Since a high molecular weight impurity appeared in the UV signal, it meant the UV active pyrene initiator was present in the impurity. This suggests the impurity is the result of backbiting, where the active propagating undergoes a silyl ether interchange reaction with another polymer chain causing scrambling. To test this, we performed a control experiment where a preformed mono-hydroxyl terminated PDMS was combined with the TBD catalyst (not shown). If transetherfication was occurring, it would be expected to observe a broadening of the molecular weight distribution with time. However, the molecular weight distribution remained constant for at least 24 h. This result was consistent with previous control experiments, which demonstrated

silyl ether interchange did not occur when using the TBD catalyst (*22*). We performed multiple rigorous purifications to remove any impurities present in the starting materials. In addition, we experimented with reaction conditions varying the concentration of reactants, order of addition of reagents, and tried several other initiators but were unsuccessful in preparing a polymer with a monomodal molecular weight distribution.

Next, we turned our attention to preparing the polymers via anionic polymerization of D3 (figure 11). This method is commonly used to prepare well-defined PDMS chains (*23, 24*). Anionic polymerization requires very stringent reaction conditions excluding water and oxygen and is usually conducted using high vacuum techniques for which our lab currently does not the capability to do. In addition, at high conversions, the backbiting reaction described above occurs thus the polymerization must be terminated early (~85%). We performed the polymerizations in a mostly dry (<1.0 ppm H_2O and O_2) glove box atmosphere with a target Mn = 50 kDa at 100% conversion. The polymerization was monitored over time and analyzed by SEC (figure 11). The polymers produced had narrow molecular weight distributions (<1.1) and only a small shoulder in the high molecular weight region, possibly due initiation by trace amounts of H_2O or from backbiting.
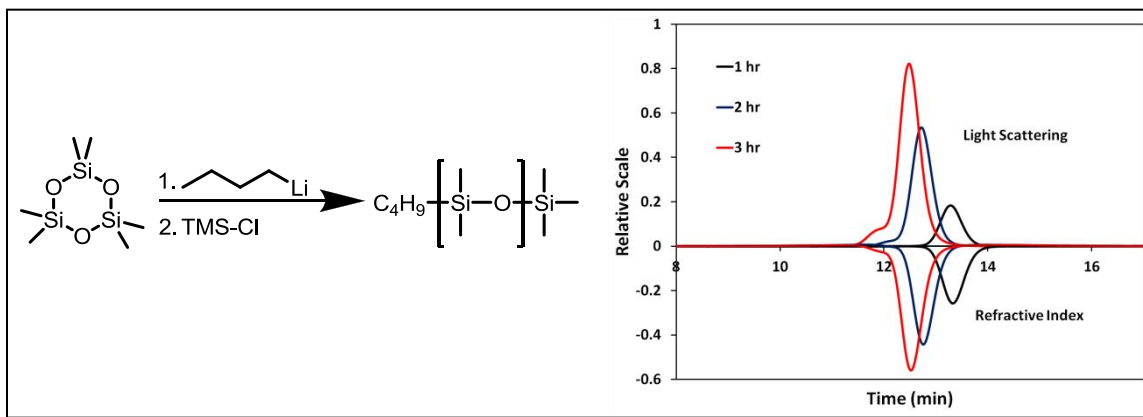

Figure 11. Synthetic scheme for anionic polymerization of D3 (left). SEC analysis over time by light scattering and refractive index.

With a satisfactory method in place to synthesize high molecular PDMS chains, we attempted to prepare a star polymer using anionic polymerization terminated by multifunctional chlorosilanes similar to the strategy outlined in figure 7. The linear chains had a target Mn = 25 kDa at 100% conversion. The polymerization was terminated with a tetrafunctional chlorosilane. A small aliquot was removed from the polymerization for analysis prior to termination. SEC analysis (figure 12) showed the linear polymer had an Mn of 17.3 kDa (PDI = 1.08) and the star polymer had an Mn of 67.3 kDa (PDI= 1.14).
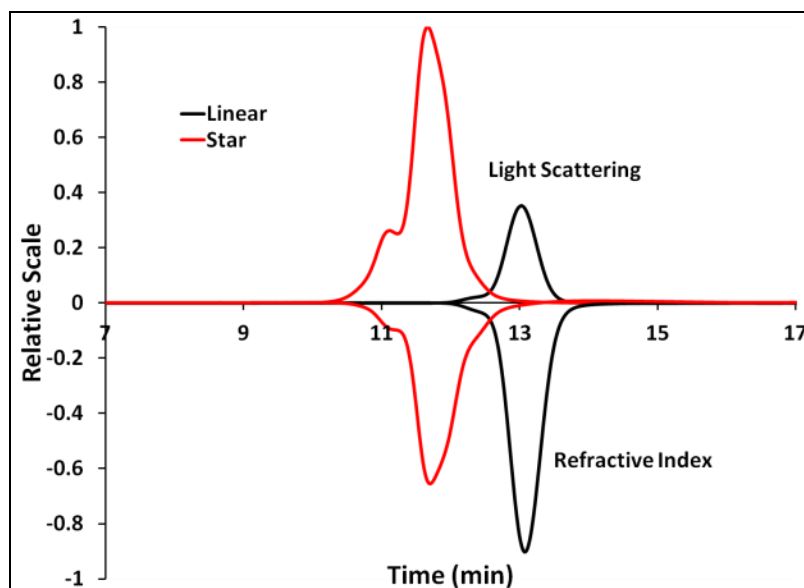
Figure 12. SEC analysis of star polymer synthesis via termination of anionic
polymer of D3 with multifunctional chlorosilane.

4. Conclusions

The design, synthesis, and characterization of branched polymer additives for enhancing polymer gel strength and toughness is reported. Several methods for synthesis of four-arm star PDMS based on coupling of vinyl-terminated PDMS to a multifunctional core were investigated. Thiol-ene coupling chemistry was shown to be an effective method for quantitative attachment of the polymer chains to the central core molecule. However, the thioether linkages that were formed appeared to be incompatible with the chemistry used to cure the gel. The platinum catalyzed hydrosilylation between a vinyl-terminated PDMS linear polymer and a tetra-functional silane core molecule was also investigated. Gel permeation chromatography (GPC) analysis of the reaction products suggested near complete attachment of the polymer chains to the central core molecule. The reaction was scaled up and a PDMS gel was prepared in the presence of the product. The gel appeared to be fully cured and the strength and toughness of the gels was evaluated relative to a linear PDMS solvent molecule. Mechanical testing of the gels was performed via tensile testing and tack adhesion. The stress-strain tensile data exhibited over a two times enhancement of the strength (stress at break) and a threefold increase toughness (integral of stress-strain curve) when comparing the star-branched solvent with a linear solvent. Similar observations were also made when comparing the tack adhesion of the gels prepared in the presence of the different solvent molecules. Computation modeling of various branched polymer additives further confirmed the improvements observed and suggested additional branched architectures to investigate that were not previously conceptualized.

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Synthetic efforts were expanded to include a wider range of molecular weights and architectures for study. Chlorosilane coupling was determined to be an efficient method to prepare four- and six-arm star polymers from low molecular weight, commercially available mono-hydroxyl terminated polymers. Due to the limited availability of high molecular weight precursors, organocatalytic ROP was explored as method to prepare high molecular weight precursors. This method proved difficult to prepare polymers without significant high molecular weight impurities. Anionic polymerization proved to be a more robust technique to prepare well-defined PDMS and was coupled with chlorosilane coupling strategy to produce a well-defined star polymer. We are currently refining our synthetic techniques and procedures to further eliminate impurities in the polymer. Scale up of these methods will enable mechanical testing of wider array of branched polymer additives.

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6.   Transitions

The research is being continued under the Tissue Simulants program in the Materials for Soldier Protection technical area. A patent application (Mrozek, R. A.; Lenhart, J. L.; Lambeth, R. H.; Andzelm, J. W. Novel branched additives for polymer toughening, Patent Disclosure [S/N 61/645,286]) was submitted and a peer-reviewed journal article (*Polymer* **2011**, *52*, 3422-3430) was also accepted.

List of Symbols, Abbreviations, and Acronyms

ARL   U.S. Army Research Laboratory

D3   hexamethylcyclotrisiloxane

FTIR   Fourier transform infrared

GPC   gel permeation chromatography

LAMMPS   Large-Scale Atomic/Molecular Massively Parallel Simulator

NMR   nuclear magnetic resonance

PDMS   poly(dimethylsiloxane)

PNIPAM   poly-(N-isopropylacrylamide)

ROP   ring opening polymerization

SEC   size exclusion chromatography

TBD   triazabicyclo[4.4.0]dec-5-ene

UV   ultraviolet

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