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Development of Glassy Step Growth Thiol-Vinyl Sulfone Polymer Networks

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Abstract

Thermo-mechanical properties of neat phosphine-catalyzed thiol-Michael networks fabricated in a controlled manner are reported, and a comparison between thiol-acrylate and thiol-vinyl sulfone step growth networks is performed. When highly reactive vinyl sulfone monomers were used as Michael acceptors, glassy polymer networks were obtained with glass transition temperatures ranging from 30–80 °C. Also, the effect of side-chain functionality on the mechanical properties of thiol-vinyl sulfone networks was investigated. It was found that the inclusion of thiourethane functionalities, aryl structures, and most importantly the elimination of interchain ester linkages in the networks significantly elevated the network's glass transition temperature as compared to neat ester-based thiol-Michael networks.

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Supporting Information

Supporting Information, including detailed synthetic and experimental procedures, IR and DMA characterization, is available from the Wiley Online Library or from the author.

Keywords

thiol-Michael addition; step growth polymerization; temporal control; dynamic mechanical analysis

1. Introduction

The base- or nucleophile-mediated thiol-Michael addition, unlike the more traditional radical thiol-acrylate reaction, proceeds without any acrylate homopolymerization, and leads to a pure thioether product. As it is a step-growth process, this approach results in uniform as well as low shrinkage and shrinkage stress network polymers when multifunctional monomers are reacted.^[1-4] However, the majority of thiol-Michael cross-linking reactions yield elastomeric materials with low glass transition temperatures that fail quickly when subjected to larger mechanical stresses, mainly due to flexible thioether bonds formed in the reaction product. This behavior limits these materials in regards to their potential implementation in applications that require high toughness and hardness at ambient conditions. As such, thiol-Michael addition networks have been most widely implemented in hydrogel synthesis for biomedical applications to date.^[5-11]

Other areas where thiol-Michael cross-linking reactions have been used include applications such as mechanophotopatterning^[12, 13], microfluidics^[14], nano-, or microgel synthesis^[15, 16] and dual-cure systems with potential applications in optical, shape memory, and impression materials.^[17] Nearly all of these examples utilize thiol-acrylate reactions since a multitude of multifunctional acrylates are commercially available as substrates, and the thiol-acrylate reaction is facile to employ. One of the less frequently considered options, but also excellent Michael acceptors, are vinyl sulfone-containing monomers, which have been proven to be highly efficient reactants, e.g. in thiol-Michael hydrogel synthesis based on vinyl sulfone-functionalized PEG precursors.^[18] In a comparative study of the relative reactivities of vinyl sulfones and acrylates, the former were shown to exhibit much higher reaction rates which was attributed to the greater electron deficiency of the vinyl sulfone. Besides, an impressive selectivity was observed in a stoichiometric mixture of thiol, vinyl sulfone and acrylate where strongly preferential reaction with the vinyl sulfone was observed.^[19] Further, unlike the acrylate thioether ester, the thioether sulfone is hydrolytically stable, and the presence of polar sulfone groups should facilitate electrostatic interactions between dipoles, which is expected to positively affect the toughness and other mechanical properties. There are few examples describing the properties of thiol-vinyl sulfone step growth networks with increased content of sulfone groups, particularly in dense networks rather than hydrogels.^[20] Therefore, the motivation for this study was to assess the relative importance of the sulfone characteristics on the polymer network properties as compared to those of similarly cross-linked thiol-acrylates.

Incorporating an initiating system composed of a nucleophile-acid pair, that enables temporal control over the reaction between thiols and electron-deficient vinyls, we synthesized novel network polymers from multifunctional thiols and vinyl sulfone monomers. Since there is only one commercially available (in a gram scale) difunctional vinyl sulfone, i.e. divinyl sulfone (DVS), herein we also present a method to synthesize other vinyl sulfones of higher functionality either in thiol-Michael or oxa-Michael reactions. The new vinyl monomers, DVS, and acrylates of similar structural design were used to fabricate network polymers, which were subsequently evaluated for their viscoelastic behavior. Further, thiol-vinyl sulfone networks incorporating pendant functionalities were also prepared, and the effect of substituent groups on the network properties was assessed.

2. Experimental section

2.1. Multifunctional monomers

Trimethylolpropane triacrylate (TMPTA), ethylene glycol diacrylate (EGDA), divinyl sulfone (DVS), trimethylolpropane tris(3-mercaptopropionate) (TMPTMP), pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) were used as received. 1,3-Bis[1-(ethenylsulfonyl)ethane]propane sulfide (DVS-344), *trimethylolpropane tris*[(1-ethenylsulfonyl)ethane] (TVS-488), and 1,3,5-tris(3-mercaptopropyl)-1,3,5-triazine-2,4,6-trione (TTT-SH) were synthesized.

2.2. Network fabrication and IR characterization

All network polymers were prepared from neat thiol and vinyl monomers mixed in a stoichiometric ratio of thiol to vinyl functional groups. The monomer compositions incorporated triphenylphosphine/methane sulfonic acid (TPP/MsOH) as an initiating system at a fixed component ratio of 1wt% of TPP and 0.2 wt% of MsOH. First, TPP and MsOH were mixed thoroughly with the thiols. Then, vinyl sulfone or acrylate monomers were added to the thiol and mixed vigorously for 30 sec. The homogeneously mixed liquid compositions were injected between two glass slides separated by 1 mm thick glass spacers and left for 20 minutes to polymerize at ambient conditions. After the reaction, the polymeric films were thermally annealed for 1 h at 60 or 100 °C (TTT-SH/DVS). All post-cured samples were analyzed for vinyl double bond conversion. The intensity of the double bond peak absorbance at 6160 cm^{-1} was confirmed to disappear completely after thermal annealing in all tested samples. An exemplary PETMP/DVS real time kinetic plot showing the rapidness of vinyl conversion as well as the complete disappearance of the double bond signal after post-cure is depicted in Figure S1 and S2.

3. Results and Discussion

The thiol-Michael reaction is known to proceed efficiently and rapidly even with minimal catalyst loadings, especially in concentrated mixtures of multifunctional monomers.^[1-3] The rapidity of this reaction presents several issues with respect to controlling the reaction, particularly in bulk mixtures that react rapidly and result in cross-linked network polymers that can be formed in less than a few seconds (see Figure S1). This lack of temporal control limits the thiol-Michael network implementation in materials chemistry applications that require resin processing such as molding or casting. In the present investigation we facilitated thiol-Michael network synthesis by implementing the recently developed two component initiating system that leads to predictable induction times in thiol-vinyl mixtures.^[21]

Specifically, the reaction was catalyzed by triphenylphosphine used in combination with methanesulfonic acid. This initiating system delayed the reaction onset and enabled thorough mixing and handling of monomers prior to rapid cross-linking polymerization. Consequently, homogenous polymeric films were carefully prepared even from highly reactive vinyl sulfone monomers. To compare the properties of thiol-acrylates with thiolvinyl sulfones, network polymers from stoichiometric mixtures (per functional group concentration) were prepared from commercial thiols (PETMP and TMPTMP), commercial acrylates (TMPTA and EGDA) and vinyl sulfones (commercial DVS and synthesized DVS-344 and TVS-488). The new vinyl sulfone monomers were synthesized by thiol-Michael and oxa-Michael reactions (Figure 1).

The monomer functionalities along with a summary of the DMA results are shown in **Table 1**. Three representative DMA plots showing the shift in T_g in thiol-acrylate, thiolvinyl sulfone and ester-free thiol-vinyl sulfone polymers are depicted in **Figure 2**. The remaining DMA plots can be found in the supporting information in Figure S3.

From the data in Table 1 and Figure 2, it can be seen that all thiol-vinyl sulfone polymers exhibit significantly higher glass transition temperatures (T_g) than similarly cross-linked thiol-acrylates. For example, the acrylate polymer with the highest rubbery plateau (and thus cross-link density), i.e. PETMP/TMPTA ($E_R=16$ MPa) still has a T_g much lower than any of the less cross-linked thiol-vinyl sulfone polymers. Because DVS is a relatively low molecular weight monomer, and the distance between vinyls in its structure is limited, it results in the formation of dense networks with short (low molecular weight) chains between cross-links. Therefore, direct comparison of DVS-based networks with any of the thiol-acrylate networks is of limited value. It is more appropriate to compare the properties of two other thiol-Michael polymers, one incorporating the synthesized DVS-344 and the other based on EGDA – the lowest molecular weight diacrylate, i.e. PETMP/DVS-344 and PETMP/EGDA system, respectively (i.e., entries 5 and 6 in Table 1 and two DMA plots in Figure 2). From this comparison, it becomes evident how critical the polar interactions between sulfone groups are in the mechanical behavior of these materials. In spite of the much longer vinyl linking chain (11 atoms compared to 6 atoms of EGDA) and the high thioether content in the PETMP/DVS-344 formulation, the presence of the two sulfone functional groups makes the network quite rigid as evidenced by its T_g , which is much higher than ambient, while the PETMP/EGDA system has a T_g below 0 °C. On the other hand, increasing the cross-linking density in thiol-vinyl sulfone network, but at the same time decreasing the overall concentration of sulfone groups, does not lead to significant improvements in T_g as evidenced by the PETMP/TVS-488 results. These examples also indicate how detrimental flexibility of interchain ester functionalities is to the mechanical properties of step growth polymers.

To verify this hypothesis a trithiol devoid of ester groups (TTT-SH) was synthesized and used in a thiol-Michael reaction with DVS (Figure 2). As can be seen, the resulting network polymer has an impressive glassy T_g of over 80 °C. Additionally, the full-width at half maximum (FWHM) value remains quite low (12°C) which is indicative of its homogenous network structure. As there are no ester groups, this network structure will exhibit an increased resistance to hydrolysis in water. There are few examples in the literature describing glassy polymers (with T_g 's usually in the range of 60 °C) made from neat step growth polymerization reactions. Here, it was demonstrated that thiol-vinyl sulfone cross-linking polymerizations could yield materials with high glass transition temperatures, and with that, the thermal stability and mechanical strength are also improved.

Using a methodology similar to that of Hoyle and co-workers^[22] for assessing the importance of side chain groups on enthalpy relaxation in thiol-ene networks, we incorporated different pendant functionalities into a model thiol-vinyl sulfone network to assess their impact on thermomechanical properties with only minimal effects on the remainder of the network characteristics.

Because of their polarity, sulfone functional groups should be good hydrogen bonding acceptors, and combining the effects of electrostatic dipole-dipole interactions with stronger directional hydrogen bonding in the network is reckoned to lead to further property enhancement.

An idealized morphology of a model thiol-vinyl sulfone network, formed from PETMP and DVS monomers in which statistically one thiol group was reacted with a monofunctional monomer, is depicted in **Scheme 1**.

These networks feature a fixed amount of pendant functional groups of different types while having only minimal deviations in the cross-linking densities of the primary network structure. This approach enables distinguishing of behavioral and property changes arising from different types of interactions. The DMA results and the schematics of the side chain structures are presented in **Table 2** and Figure S4.

Indeed, even ester functionalities that are pendant to the network rather than in the backbone lead to significant decrease in the network T_g and contributed negatively to network homogeneity as evidenced by their significantly larger FWHM values, i.e. broader tan delta peaks (see also Figure S5). The PETMP/DVS network (entry 1 in Table 2), which has no additional pendant ester groups, is more homogenous than most of the thiol-vinyl sulfone-monoacrylate networks (entries 3, 6, 7). On the other hand, introducing thiourethanes, and with that hydrogen bonding donors, increases the resulting network T_g 's (entries 4, 5, 9). Interestingly, the presence of pendant aromatic rings together with thiocarbamate linkages resulted in the network with the highest T_g (51 °C) of all tested compositions. Despite lower cross-linking density, these networks have a T_g even higher than the stoichiometric PETMP/DVS system (Table 1). It appears that the hydrogen bonding interactions and π - π stacking of the phenylic rings both exert an even stronger reinforcing effect than the covalent linkage in the neat PETMP/DVS system. Also, of all acrylate-modified networks the one containing phenyl acrylate exhibits the highest T_g of 28 °C. On the other hand, the presence of weak hydrogen donors in the moiety of pendant thioether ester or amide group (entries 7 and 8) does not contribute much to network rigidity as the T_g 's are slightly higher but the differences are not significant. Also apparent is the plasticizing effect of hydrocarbon chains in both the thioether ester and thiocarbamate pendant functionality (i.e., entries 5 and 6).

Based on the examples shown in Table 2, the following conclusions can be drawn: (1) the presence of ester groups considerably lowers the polymer T_g , (2) incorporation of stiff thiocarbamates introduces secondary hydrogen bonding interactions and through that change, also increases the polymer T_g , and (3) the thiol-vinyl sulfone network properties are readily modified/tuned by inclusion of aliphatic or aromatic moieties as well as other functional groups. Therefore, eliminating all ester functionalities from thiol-Michael network increases the T_g and simultaneously improves the network's hydrolytic stability, among other properties. Additionally, polymers with these characteristics are likely to exhibit improved toughness due to the presence of secondary interactions, as well as stiff thiourethane linkages, which are known to strengthen the covalent network.^[23-25]

4. Conclusion

In this report new thiol-Michael step growth polymers incorporating vinyl sulfone monomers were synthesized, and their viscoelastic properties were compared with those of similarly cross-linked thiol-acrylates. It was shown that neat thiol-vinyl sulfone networks

containing high weight fractions of sulfone groups exhibit significantly improved glass transition temperatures, which are much higher than ambient. This approach is quite unique for pure thiol-Michael polymers, which often are soft materials with T_g rarely approaching ambient. It was also shown that the combination of sulfone structural effects, π electron interactions, and hydrogen bonding significantly shifted the transition temperatures toward higher values. However, decreasing the concentration of interchain ester linkages in the network seemed to have the strongest impact on the properties.

To demonstrate that as demonstrated in Figure 2, a liquid mixture of a trithiol monomer and divinyl sulfone was reacted to yield a glassy polymer with no ester interchain groups and a T_g of 82 °C. As it is a neat thiol-Michael network polymer, it possess the attributes of step growth reactions such as high functional group conversion and uniform network structure. Additionally, it is expected to show an increased resistance to hydrolytic degradation. Although, thiol-vinyl sulfone network polymers still require more detailed characterization, these materials are promising as a new class of highly reactive resins yielding glassy materials that may find applications in the areas that were not considered before such as dental materials, protective coatings, optical devices, and energy absorbing materials, to name a few.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.
Chemical structures of multifunctional monomers used in this study.

Figure 2.

Storage modulus and tan delta plots for neat thiol-acrylate (PETMP/EGDA), thiol-vinyl sulfone (PETMP/DVS344) and ester-free thiol-vinyl sulfone (TTT-SH/DVS) networks. The monomer ratios are: thiol:vinyl = 1:1 based on the functional group content.

Scheme 1.

The methodology of thiol-vinyl sulfone network modification. The model network was composed of PETMP/DVS/X in molar ratios of 2/3/2 with the X being a monofunctional acrylate, vinyl sulfone, isocyanate or free thiol.

Table 1

DMA results for neat thiol-Michael networks. All samples were prepared from mixtures containing equivalent amount of thiol and vinyl functional groups. Values in parentheses represent standard deviations of three replicates.

Entry	Thiol	# SH	Alkene	# C=C	T _g (°C)	Rubbery modulus (MPa)
1	PETMP	4	DVS	2	47 (2)	12 (1)
2	PETMP	4	TMPTA	3	20 (1)	16 (1)
3	TMPTMP	3	DVS	2	28 (1)	8 (1)
4	TMPTMP	3	TMPTA	3	11.0 (0.3)	11 (1)
5	PETMP	4	EGDA	2	−5.1 (0.8)	5 (0)
6	PETMP	4	DVS-344	2	38.5 (0.3)	8 (1)
7	PETMP	4	TVS-488	3	41 (1)	11 (1)

Table 2

DMA results for thiol-vinyl sulfone networks modified with pendant group functionalities. The curing conditions are as stated in the experimental section. Values in parentheses represent standard deviations of three replicates.

Sample #	Pendant group structure	T_g (°C)	E'_R (MPa)	FWHM (°C)
1		34.2 (0.8)	8 (1)	10.4 (0.4)
2		33.7 (0.5)	6 (1)	11.2 (0.8)
3		20 (1)	7 (1)	13.3 (0.4)
4		37.5 (0.4)	7 (1)	11.2 (0.5)
5		32 (1)	6 (1)	14 (1)
6		13 (2)	6 (1)	19 (2)
7		22.5 (0.6)	7 (1)	16 (1)
8		21.0 (0.4)	7 (1)	18.4 (0.5)
9		52 (1)	6 (1)	10.4 (0.2)
10		28.3 (0.9)	6 (1)	10.0 (0.4)