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Direct Silyl Ether Metathesis for Vitrimers with Exceptional Thermal Stability

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Supporting Information

ABSTRACT: Vitrimers are a new class of polymeric materials that simultaneously offer the desired physical properties of thermosets and malleability/reprocessability of thermoplastics. Despite significant progress being made in the field of vitrimers, there exists a critical need for the development of robust dynamic covalent chemistries for the production of strong and thermally stable vitrimers. In this work, we discovered a new silyl ether metathesis reaction and used it for the preparation of vitrimers with exceptional thermal stability. In small-molecule model studies, we observed that silyl ether motifs directly exchange under anhydrous conditions catalyzed by a Brønsted or Lewis acid catalyst. For initial vitrimer demonstration, a commodity polymer, poly(ethylene-*co*-vinyl alcohol) (PEOH), was silylated with trimethylsilyl (TMS) groups followed by cross-linking with a bis-silyl ether cross-linker. The resulting thermoset showed exceptional thermal stability while maintaining malleability/reprocessability at elevated temperatures. The vitrimer properties such as recyclability and stress relaxation at various temperatures were carefully investigated. The material was reprocessable at 150 °C while also exhibiting good creep resistance at temperatures below its melting transition (T_m). This work demonstrates the silyl ether metathesis reaction as a new, robust dynamic covalent chemistry to introduce plasticity, reprocessability, and recyclability to thermosets.

Permanently cross-linked polymers (i.e., thermosets) have excellent mechanical properties, creep resistance, and chemical/solvent stability. However, a critical limitation of thermosets is that they cannot be reshaped, reprocessed, or recycled by heat or with solvent. In contrast, thermoplastic polymers are reprocessable, but normally have poorer chemical/solvent resistances and both lower mechanical strength and lower dimensional stability at elevated temperatures. To combine the desirable attributes of both thermoplastics and thermosets, dynamic covalent chemistries have been incorporated into covalent adaptable networks (CANs) to introduce plasticity and malleability under external stimuli.[1,2] The plasticity/malleability is imparted by dynamic covalent cross-links that can undergo associative or dissociative exchange mechanisms.[2] Of the associative exchange-based CANs, "vitrimers" have generated considerable interest as they offer increased mechanical properties and solvent resistance while maintaining malleability/reprocessability.[3]

Several dynamic covalent motifs have been employed in vitrimer designs, such as trans-amination of vinylogous urethanes,[4,5] transesterification,[3,6−8] olefin cross metathesis,[9,10] trans-carbamoylation,[11] triazolium trans-alkylation,[12] poly(alkylurea−urethane),[13] boronic ester or boroxine exchange,[14−16] imine exchange,[17] and acetal exchange.[18] Despite the rapid progress in this field, the dynamic covalent chemistries involved in the reported systems have major limitations as some motifs are thermally and/or oxidatively unstable, while others only suitable for a relatively narrow range of polymers. For further development, there is a critical need to develop robust dynamic covalent chemistries for making mechanically strong and thermally stable vitrimers.

Toward this goal, our lab has recently demonstrated silyl ether as an advantageous dynamic covalent motif for vitrimer design[19] due to its high chemical and thermal stability, facile accessibility, and general applicability. As one of the most ubiquitous chemical bonds in natural and synthetic materials, the Si−O bond is thermodynamically strong (BDE ≈ 535 kJ/mol).[20] Accordingly, silyl ethers show excellent stability toward heat and oxidation in contrast to many other dynamic covalent motifs including the promising boronic esters,[14,16] which are susceptible to deboronation and oxidation at elevated temperatures.[21,22] However, one of the major limitations of our initial silyl ether exchange vitrimer[19] as well as several other vitrimer systems[3,11,18] is the requirement of free hydroxyls on the polymers. The presence of free hydroxyls is undesirable because they can introduce side reactions such as dehydration and oxidation at elevated temperatures, as well as possible reactions with polymers (e.g., transesterification with polyacrylates).[23] This would be undesirable for general vitrimer applications that involve multiple cycles of reprocessing/recycling at elevated temperatures.

To address this key limitation, we have been searching for new strategies for silyl ether exchange without the need of free hydroxyl groups. During our study, we discovered that silyl ether groups can directly exchange (i.e., silyl ether metathesis), which would completely eliminate the need for free hydroxyls (Figure 1). *To the best of our knowledge, this is the first report of direct silyl ether metathesis.* In addition to a new type of dynamic covalent chemistry, the thermal and oxidative stability of silyl ether functionality lends itself toward general design of thermally robust vitrimers. Different from anionic *siloxane* exchange, which is limited to polysiloxanes,[24,25] silyl ether groups can be easily introduced post-polymerization by

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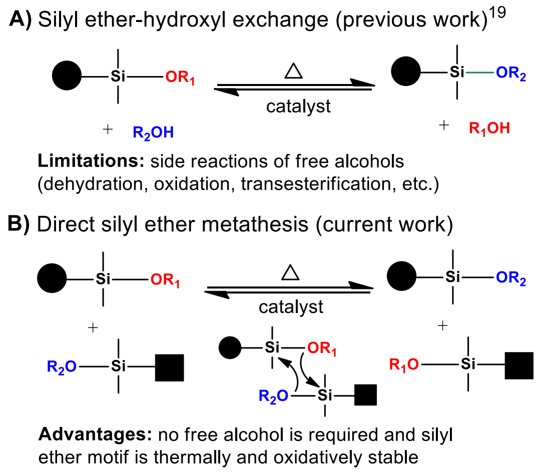


Figure 1. Differences between silyl ether−hydroxyl exchange and silyl ether metathesis for vitrimer design.

silylation of free hydroxyl,[26] methoxy,[27] and acetate[28] groups or by simple polymerization/co-polymerization with a silyl ether functionalized monomer.

First, the direct silyl ether metathesis reaction was discovered in our small molecule model studies. As shown in Figure 2A, an equimolar amount of ethyltributoxysilane ($\mathbf{B_3}$) and ethyltripentoxysilane ($\mathbf{P_3}$) were mixed in an anhydrous solvent with or without a catalyst. The mixtures were heated at different temperatures and the exchange between butoxy and pentoxy groups was monitored by GC-MS (see Supporting Information). At time zero GC-MS showed two peaks with equal intensity for the two starting materials. As exchange proceeded, two additional peaks appeared with the masses matching the exchange products $\mathbf{B_2P_1}$ and $\mathbf{B_1P_2}$, respectively. The intensity of the new peaks grew with time until reaching the expected 1:3:3:1 statistical distribution for $\mathbf{B_3}$:$\mathbf{B_2P_1}$:$\mathbf{B_1P_2}$:$\mathbf{P_3}$ at equilibrium. Without the addition of any catalyst, the exchange proceeded slowly, reaching full exchange after 16.5 h at 190 °C.

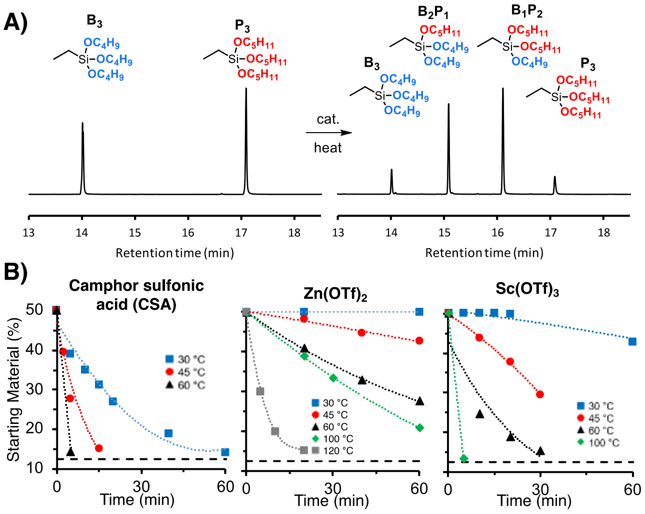
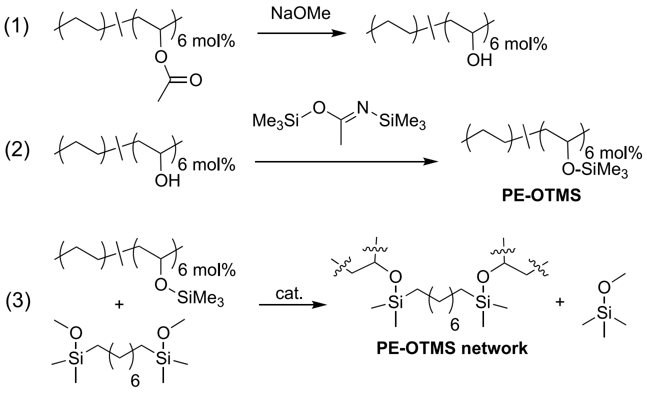


Figure 2. Silyl ether metathesis. (A) Representative GC chromatograms of the equilibration of $\mathbf{B_3}$ and $\mathbf{P_3}$ to $\mathbf{B_3}$, $\mathbf{B_2P_1}$, $\mathbf{B_1P_2}$, and $\mathbf{P_3}$ with catalyst. (B) Kinetics of silyl ether exchange using different catalysts and temperatures.

To accelerate the reaction, we added 5 mol% of a Brønsted acid (camphor sulfonic acid, CSA) or a Lewis acid ($Zn(OTf)_2$ and $Sc(OTf)_3$) catalyst (Figure 2B). Among the catalysts tested, CSA was found to be the most active catalyst and chosen for subsequent vitrimer studies. The exact mechanism for the direct silyl ether exchange is not clear at the moment. A simple proposal is direct exchange between silyl ethers, i.e., silyl ether metathesis (Figure 1B). Alternatively, the exchange can be facilitated by some transient reactive intermediates formed in the process. Notably, the GC-MS traces showed clean product distributions with no detectable byproducts (Figures 2A and S5−S7), indicating clean exchange between the silyl ether compounds.

Encouraged by the direct silyl ether metathesis reaction observed in model studies, next we applied this new dynamic covalent chemistry to vitrimer designs. For initial demonstration, a low molecular weight poly(ethylene-*co*-vinyl acetate) (EVA, 6 mol% vinyl acetate, MFI = 150 g/10 min) was chosen for its commercial availability and ease of processing. EVA was hydrolyzed quantitatively with sodium methoxide to yield poly(ethylene-*co*-vinyl alcohol) with 6 mol % alcohol. The free hydroxyls in the resulting polymer were fully silylated with N,O-bistrimethylsilyl acetamide to yield a trimethylsilyl (TMS) ether functional polymer (PE-OTMS) (Scheme 1). A divalent cross-linker, bis(methoxydimethyl)silyl octane, was synthesized from bis(chlorodimethyl)silyl octane via one step reaction with methanol. All the details for compound syntheses and characterizations can be found in the Supporting Information.

Scheme 1. Synthesis of PE-OTMS Polymer and Its Vitrimer



The vitrimer was prepared by dissolving PE-OTMS, the bis(methoxydimethyl)silyl octane cross-linker, and CSA in toluene at 80 °C. The cross-linker concentration was 3 mol% of the total −OTMS motifs and CSA concentration was held at 2 mol% of total −OTMS motifs. The excess of free −OTMS motifs on PE-OTMS backbone facilitate silyl ether metathesis with the silyl ether cross-links. After mixing, silyl ether metathesis between the cross-linker and PE-OTMS resulted in gelation. The gelled polymer was slowly dried and compression molded at 150 °C for 20 min at 400 psi for mechanical testing (see Supporting Information). The insoluble gel fraction of the samples was measured to be ~62% after incubating the processed polymer in hot anhydrous toluene for 16 h, indicating a relatively high degree of cross-linking within the samples.

The thermal and mechanical properties of the vitrimer were carefully investigated. The differential scanning calorimetry

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(DSC) trace for PE-OTMS showed a broad melting transition with the peak at 93 °C (Figure S12), consistent with the semicrystalline structure of the PE backbone. Thermogravimetric Analysis (TGA) demonstrated the vitrimer having exceptional thermal stability, with minimal loss below 400 °C and 5% loss of its original mass at 427 °C (Figure S14). To the best of our knowledge, this is the most thermally stable vitrimer reported so far. Because of no free hydroxyl groups, the current vitrimer has substantially higher thermal stability than our previous system using silyl ether−hydroxyl exchange.[19] The robustness of silyl ether moieties and lack of free hydroxyls should contribute to the high thermal stability.

Dynamic mechanical thermal analysis (DMTA) clearly showed a rubber plateau after the melting transition at ∼93 °C for the vitrimer in contrast to the linear polymer PE-OTMS which completely flowed after melting (Figure 3A). The vitrimer network retains mechanical strength after melting due to covalent cross-links. The molecular weight between cross-links (M_c) was calculated to be 9.61 kDa (see Supporting Information). Furthermore, introducing silyl ether cross-links significantly improved the vitrimer creep resistance as compared to the PE-OTMS linear polymer. The linear polymer crept rapidly at 80 °C under 0.1 MPa stress (Figure S17). On the contrary, the vitrimer showed negligible creep under the same condition (80 °C, 0.1 MPa) (Figure 3B). At temperatures above the T_m, the vitrimers exhibit an initial elastic response followed by a transition into a linear creep region whereby dynamic silyl ether exchange occurs. As expected, the vitrimers display faster creep at increasing temperatures due to the temperature-dependent silyl metathesis reaction.

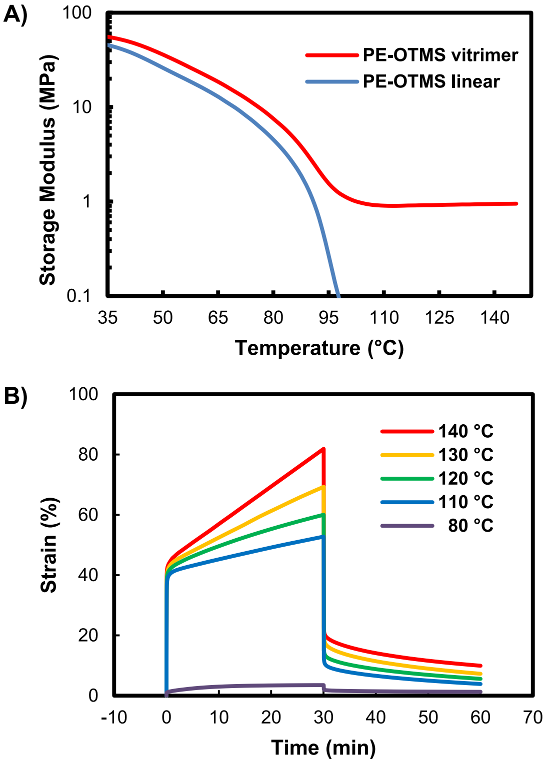

Figure 3. (A) DMTA analysis of both the linear and cross-linked PE-OTMS. (B) Creep tests of the PE-OTMS vitrimer at different temperatures under 0.1 MPa stress.

To further quantify the silyl ether exchange dynamics in bulk, the silyl ether vitrimers were subjected to stress relaxation testing at elevated temperatures (130−170 °C) by monitoring the decrease of stress over time at constant strain (Figure 4A).

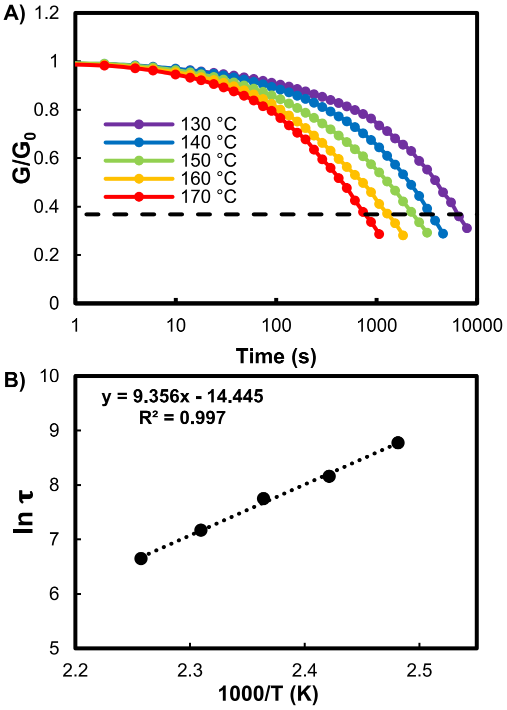

Figure 4. (A) Stress relaxation study of PE-OTMS vitrimer. Stress relaxation experiments were performed using 5% strain in tensile mode. (B) An Arrhenius treatment was performed on the stress relaxation data to yield an energy of activation of 77.8 kJ/mol.

Consistent with the creep data, we observed faster stress relaxation at higher temperatures. The characteristic relaxation time, τ^*, is defined as the time required for the normalized modulus to decrease to e^{-1} (∼37%) from the initial value. The relaxation time decreased from 6456 to 770 s as the temperature increased from 130 to 170 °C. As silyl ethers appear to undergo direct exchange with temperature dependency, they should follow the characteristic vitrimer Arrhenius behavior as defined by eq 1:[4,8,29]

$$\tau^* = \tau_o \exp\left(\frac{E_A}{RT}\right) \tag{1}$$

By performing Arrhenius treatment to the stress relaxation data (Figure 4B), we can calculate the energy of activation for the silyl ether exchange. Plotting $\ln(\tau)$ vs $1000/T$ yields a straight line with the slope correlating to an energy of activation of 77.8 kJ/mol. The activation energy for our CSA-catalyzed silyl ether exchange is comparable to the 81 kJ/mol value previously reported for amine-catalyzed silyl ether−hydroxyl exchange by our lab.[19]

Another important parameter of vitrimers is the topology-freezing transition temperature (T_v), the temperature at which the network topology is frozen through kinetic trapping of its internal dynamic chemistry. Following the reported protocols,[3] the T_v of the silyl ether vitrimer is calculated to be 45 °C. This transition temperature sits between the glass transition temperature ($T_g \approx -125$ °C)[30] and melting temperature ($T_m \approx 93$ °C) for the PE backbone. Despite the relatively low

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T_v, the vitrimer shows good creep resistance up to 80 °C (Figure 3B). This is due to the crystallinity of the polymer backbone which quenches the silyl ether exchange reaction. For future studies, we plan to modify the bulkiness of substituents on silyl ether group to further tune the T_v.

The chemical cross-linking also significantly enhanced the mechanical properties of the polymer. Tensile stress−strain tests showed a 5-fold increase in Young's modulus from 19.2 ± 1 to 101 ± 19 for the PE-OTMS polymer and vitrimer, respectively (Figures 5C, S15, S16). The ultimate tensile strength also increased from 5.5 ± 0.6 to 8.3 ± 0.2 for the PE-OTMS polymer and vitrimer, respectively. Finally, we tested the reprocessability of the silyl ether vitrimers. A vitrimer sample was repetitively diced into small pieces, melt pressed at 150 °C (Figure 5B), and subjected to mechanical and gel fraction tests. The mechanical properties—including the Young's modulus, tensile strength, elongation at break, and toughness—remain almost constant for the repetitively reprocessed samples (Figure 5A). The gel fractions for the reprocessed samples also remain nearly constant (Table S1 in the Supporting Information).

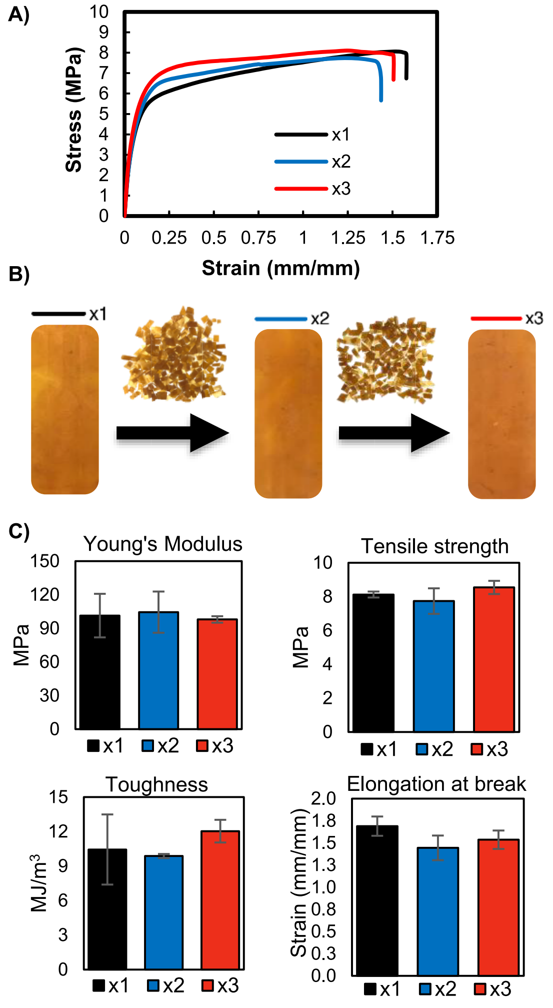

Figure 5. (A) Tensile test for the reprocessed samples x1, x2, and x3. (B) PE-OTMS samples were diced into small pieces, compression molded and reprocessed three times. (C) Mechanical properties of the recycled vitrimer (in triplicates).

In summary, we report our discovery of a new silyl ether metathesis reaction and its application for vitrimer design. Owing to the thermal and oxidative stability of silyl ether motifs, this new dynamic covalent chemistry was demonstrably suitable for making mechanically robust and thermally stable vitrimers. Compared to previously reported transesterification[3] and silyl ether−hydroxyl exchange[19] for vitrimer designs, the current silyl ether metathesis avoids free hydroxyls which are susceptible to side reactions such as dehydration and oxidation at elevated temperatures. Indeed, the PE-OTMS vitrimers show exceptional thermal stability as shown by TGA (Figure S14). To the best of our knowledge, this represents the most thermally stable vitrimer motif reported to date. Facilitated by silyl ether metathesis, the silyl ether vitrimers are fully reprocessable at elevated temperatures. The exceptional thermal stability of the silyl ether motif should open the door to the design of high-performance vitrimers with high thermal mechanical stability through tuning both the silyl ether bulkiness (T_v) and polymer backbones (T_g or T_m). Silyl ethers can be easily prepared by silylation of polymers bearing hydroxyl or its derivatives, copolymerization of monomers having silyl ether groups, or radical grafting with a silyl ether-containing a silyl ether motif. With the excellent attributes and synthetic feasibility of silyl ethers, we envision this new dynamic covalent chemistry can be generalized for various vitrimer syntheses, and studies are currently underway toward this direction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b08876.

> Experimental details, including synthesis, model reaction studies, sample preparation and characterizations, as well as thermal and mechanical studies, Figures S1−S20, and Tables S1−S3 (PDF)

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Notes

The authors declare no competing financial interest.

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