Trialkylsulfonium-based Reprocessable Polyurethane Thermosets

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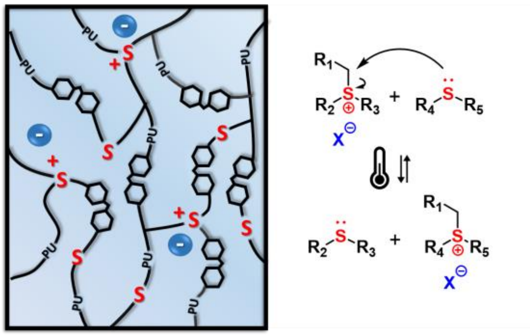
KEYWORDS. Vitrimer materials, recycling, salt-catalyzed, solvent-free, polysulfide



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ABSTRACT

We report the development of a solvent-free protocol to produce colorless, highly transparent, and glassy polyurethane-based networks containing thioether bonds using commercially available building blocks. These polyurethane networks are converted into reprocessable networks by partial alkylation of the thioether bonds, giving dynamic trialkylsulfonium bonds that are able to exchange via transalkylation at elevated temperatures, thus induce viscoelastic flow. Reprocessability of the trialkylsulfonium networks was demonstrated for three cycles without significant detoriation of material properties. Interestingly, these materials were found to be highly processable at elevated temperatures (~140 °C) and showed excellent creep suppression up to 100 °C, a combination that is rare among dynamic covalent polymer networks. The suppression of creep can be further controlled by changing the alkylating additive. In addition, as a result of their excellent transparency and high clarity, we investigated their optical properties to assess their potential use in smart coatings and optical devices.

INTRODUCTION

Although thermoset materials are indispensable in modern society, they also pose an important and ever-growing issue in terms of sustainability. Despite being preferred for their excellent dimensional stability and mechanical properties, thermosets are by far more challenging to recycle than their thermoplastic counterparts.[1] Today, the annual thermoset production is estimated to be approximately 65 million tons, posing a serious challenge for the recycling industry.[2] Polyurethanes (PU) are among the most widely produced thermoset materials and have found utility in a multitude of applications, ranging from coatings, adhesives, sealants and elastomers to foams or bulk structural components. Their success can largely be attributed to the simplicity and versatility of their production process, as well as the resulting diverse material properties.[3] Despite the significant progress in repurposing or recycling polyurethanes,[4,5] a satisfactory solution remains elusive to date. An attractive approach that is gaining traction in both industry and academia is the incorporation of dynamic covalent bonds within the polymer network.[6,7] The resulting so-called dynamic covalent polymer networks or covalent adaptable networks (CANs) are able to efficiently rearrange their network topology upon an external stimulus, such as heat.[8,9] CANs can roughly be classified into two types: dissociative and associative networks, based on their exchange mechanism and their extended response to elevated temperatures and solvents.[10] Vitrimers (i.e. thermally triggered associative CANs), exhibit a resilient rubbery state in rheological assessments, do not dissolve in a good solvent, and maintain their network connectivity at high temperatures, while showing significant stress-relaxation behavior.[11,12] Another distinctive feature of vitrimers is the correlation between viscosity and temperature, which follows an Arrhenius-type relationship.[10] However, it should be noted that many ‘dissociative’ CANs exhibit all or most of the features of vitrimers, if the breaking and forming of the bonds is fast or highly endothermic, which can prevent the depolymerization under a wide variety of circumstances. Indeed, the underlying exchange mechanism has a significant influence on the macroscopic flow behavior and therefore the processing conditions of these dynamic materials.[13] For this reason, an impressive array of dynamic covalent chemistries have been investigated and reported to date, such as furan-maleimides,[14] transesterification,[15] disulfide exchange,[16] imines[17] and triazolinedione- and boron-based chemistries,[18–21] all of which have been introduced into a PU-matrix.[22] However, compared to classic thermoset materials, dynamic covalent networks often showcase limited relevant thermomechanical properties like poor creep resistance[23] or suffer from other limitations such as external catalyst leaching or ageing,[24] the occurrence of side reactions under the high temperature processing conditions,[10] tedious syntheses or the need for exotic chemicals.[25]

In recent years, there has been an increasing interest in the field of transalkylation chemistry as a chemical framework for CANs. Drockenmuller, Montarnal and co-workers implemented it in polyionic triazolium-based polymer networks.[26–28] Interestingly, although their system was found to undergo a dissociative exchange mechanism, they were able to attain vitrimer-like flow behavior. They explained this phenomenon by showing that the rate-determining step was the dissociation of the alkyl triazolium, and that the reformation of cross-links occurred rapidly. This implicates that the apparent cross-link density of the network remained nearly constant over a wide temperature range.[28] Following this work, the group of Konkolewicz and the group of Guo have designed dynamic covalent networks based on the transalkylation exchange of quaternized amino-based salts, such as anilinium an pyridinium salts.[29–31] Heuts, Sijbesma and co-workers further exploited the power of quaternary ammonium salts as a transalkylation-based dynamic covalent chemistry platform, by designing a dynamic network using a divalent cross-linker, 1,4-diazabicyclo[2.2.2] octane. The obtained networks showed relaxation times at elevated temperatures that were significantly faster than many other reported CANs (< 6 seconds at 140 °C), despite being highly cross-linked.[32] Motivated by these promising results, other research groups have implemented the transalkylation of C-N bonds in polyurethane materials and were able to design ion-conducting polyurethane networks.[33,34]

In addition to quaternized ammonium salts, sulfonium salts can also undergo a dynamic covalent exchange (Figure 1). This exchange reaction was first reported by Goethals *et al.* in the early 1970s[35] and later exploited by our group for the synthesis of catalyst-free transalkylation-based vitrimers (Figure 1).[36] In this case, thioethers are expected to engage sulfonium salts in an S_N2-type exchange mechanism, thus constituting an associative pathway.

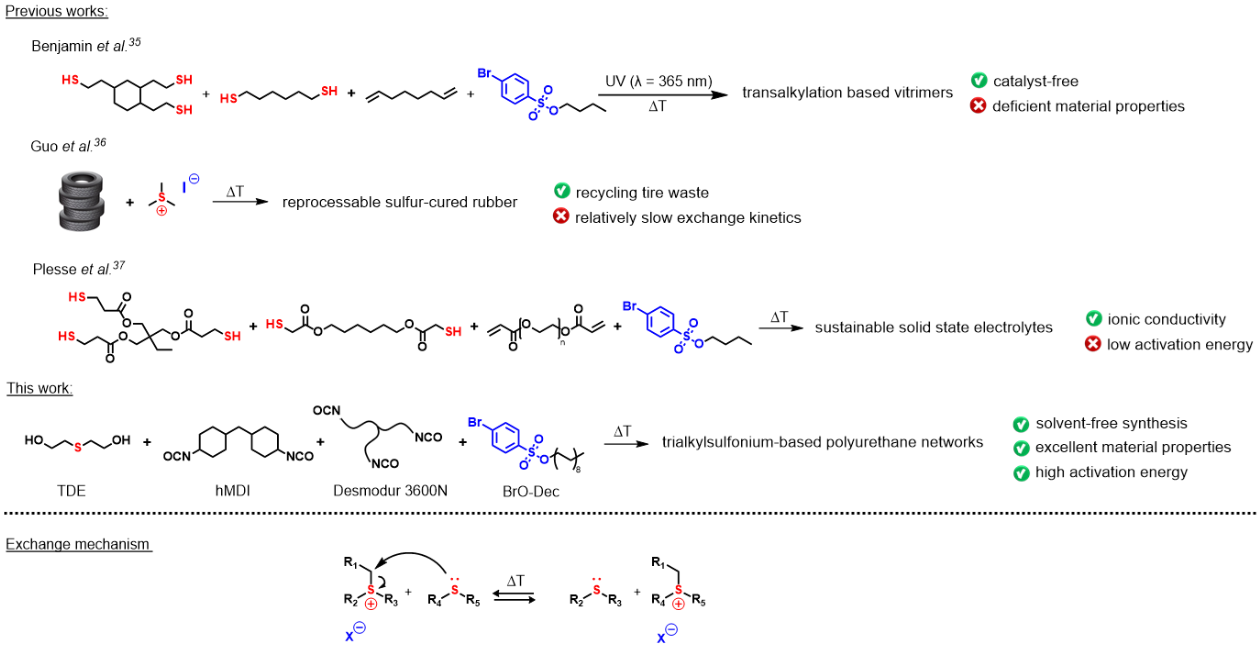


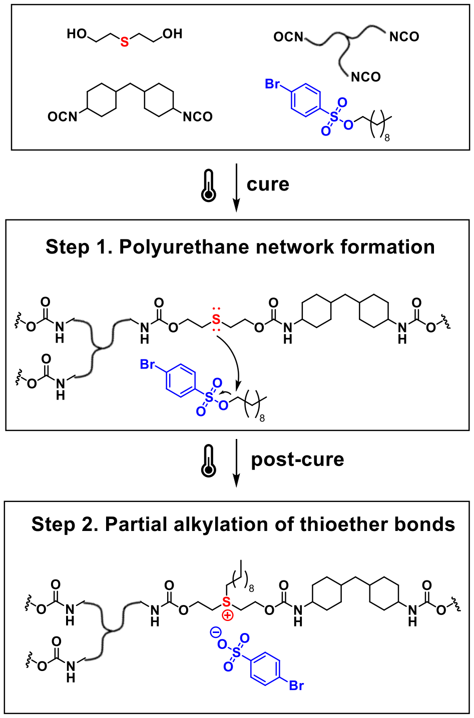
Figure 1: Comparison of the presented work with earlier reported works. Our group reported the synthesis of catalyst-free transalkylation-based vitrimers.[36] Guo and co-workers identified an opportunity in the recycling of sulfur-cured rubber waste.[37] Plesse and co-workers implemented this chemistry in the design of vitrimer ionogels towards solid-state electrolytes.[38] This research highlights the solvent-free synthesis of trialkylsulfonium-based reprocessable polyurethane networks, showing excellent material properties and a high activation energy for dynamic exchange. The bottom part of the figure shows the trialkylsulfonium-thioether bond exchange, which includes a S_N2-type reaction of sulfonium salts with thioether nucleophiles.

Alternatively, as was found for triazolium-based networks, a rapid bond exchange is obviously also possible by engagement of the counterion. This attractive exchange mechanism and the simplicity of the trialkylsulfonium salt dynamic chemical framework has led to a rapid uptake in the design of CANs. For example, Guo and co-workers identified an opportunity in the recycling of sulfur-cured rubber (Figure 1).[37] More recently, Vidal and Plesse implemented this chemistry in vitrimer ionogels towards sustainable solid-state electrolytes.[38] These materials maintained their conductive behavior after undergoing multiple healing processes (Figure 1).

Despite the great potential that lies in this dynamic covalent chemistry, it has never been implemented in a polyurethane matrix. Herein, we report our findings in the solvent-free preparation of polyurethane networks in which the dynamic bond exchange is governed by trialkylsulfonium exchange with thioethers. Through judicious selection of starting compounds, all of which are commercially available, we were able to obtain cured PU-coatings that possess high transparency, minimal coloration and glass transition temperatures up to 70 °C. Moreover, these properties could be preserved through reprocessing within acceptable limits. Also, we demonstrate that these polyurethane thermoset materials are highly resistant towards deformation at lower temperatures, while they show fast reprocessability at higher temperatures (Figure 1).

RESULTS AND DISCUSSION

One of the primary objectives of the present study was to develop a simple synthetic strategy for trialkylsulfonium-based CANs, using only commercially available building blocks. Hence, 2,2-thiodiethanol (TDE), bis(4-isocyanatocyclohexyl)methane (hMDI) and a polyfunctional aliphatic isocyanate (Desmodur N3600) (Figure 1) have been chosen to introduce the CS transalkylation chemistry into a classical formulation for polyurethane networks. Moreover, these compounds enable precise control over material properties (*vide infra*) and, as a result of the aliphatic nature of the isocyanates used, ensure minimal coloration, UV resistance, and thermal stability.[39] The final other essential reagent, which only needs to be added in a small amount to allow efficient bond exchange, is an alkylating agent. Many alkylating agents are commercially available, but it is generally known that such reagents are associated with serious health effects and safety issues.[40] Therefore, special care was taken to select a suitable one based on literature. Here, we synthesized the safe-to-handle decyl 4-bromobenzenesulfonate (BrO-Dec, see Figure S1-S5 for full characterization), which is non-volatile and has a relatively high melting point of 45 °C.[36] To screen for an optimal formulation, PU-networks containing sulfonium salts with varying cross-link densities have been synthesized (Table 1). For this, the sulfide-containing diol (TDE) was mixed with appropriate amounts of Desmodur N3600, hMDI, dibutyltin dilaurate catalyst (DBTDL) and the alkylating agent BrO-Dec in neat conditions and heated to 80 °C (Scheme 1). To ensure homogeneous distribution throughout the network, the latter was incorporated into the initial formulation at a 5 mol% ratio compared to the thioether bonds. This approach avoids on the one hand phase separation issues that may arise when the sulfide would be partially alkylated before the network synthesis and on the other hand alkylation of free hydroxyl groups as a possible side reaction. Full conversion of the isocyanate groups in the polymer matrix was verified using Fourier-transform infrared spectroscopy (FTIR), showing complete disappearance of the characteristic isocyanate stretching band at 2250 cm^{-1} (Figure S6 and Figure S7). These materials were then subjected to a thermal post cure at 130 °C for 1 h to ensure the covalent incorporation of the alkylating agent into the network (Scheme 1).



Scheme 1: Schematic overview of the synthetic protocol towards PU-networks containing trialkylsulfonium salts. In Step 1, network formation is realized by reaction between isocyanates and hydroxyl groups. This causes the alkylating additive (BrO-Dec) to be physically incorporated in the network. In Step 2, a post-cure at elevated temperature entails the partial alkylation of thioether functionalities *via* an S_N2-type substitution pathway with BrO-Dec.

Formation of the trialkylsulfonium salts was assessed by X-ray Photoelectron Spectroscopy (XPS, Figure 2A). The characteristic S 2p peak is appearing at 161.9 eV, together with an additional shoulder at 165.8 eV. The latter can be ascribed to either the S=O of the brosylate’s sulfonate moiety or to the formation of the trialkylsulfonium salts (S$^+$).[41,42] To address this ambiguity, a series of Raman analyses were performed (Figure 2B). Most parts of the spectra of the alkylated PU networks were identical to the reference (non-alkylated) material, except for the appearance of the aromatic ν(C=C-C) band at 1578 cm^{-1}. In other words, this indicates the inclusion of the alkylating agent in the materials. Of greater interest is the distinct shift observed in the sulfonate ν(SO_3) band, shifting from 1098.2 cm^{-1} to 1119.4 cm^{-1}. This displacement arises as a result of the formation of the brosylate's sulfonate anion. It must be pointed out that no observable difference exists between the Raman spectra acquired subsequent to the first curing step and the additional thermal post-cure step. Nonetheless, in the pursuit of ensuring complete covalent integration of the alkylating additive into the materials, the supplemental thermal curing step was maintained. In what follows, the synthesized polyurethane networks containing integrated trialkylsulfonium salts (PUTS) will be referred to as PUTSX-Y% in which in the X is a serial number referring to the (theoretical) cross-link density (1 for the formulation with the highest amount and 5 for the lowest amount of polyisocyanate crosslinker), and the suffix Y represents the mole percentage of alkylating additive with respect to the thioether bonds in the network. All PU-networks were prepared in a stoichiometric ratio between reactive OH and NCO moieties (index 100).

Table 1: Composition and properties of PUTS-materials containing 5mol% of BrO-Dec relative to thioether functionalities.

Sample Code	TDE [equiv.]	hMDI [equiv.]	Desmodur [equiv.]	Swelling Degree[a] [%]	Gel Fraction[a] [%]	T_g[b] [°C]	$T_{TGA-95\%}$[c] [°C]
PUTS1-5%	1	0.4	0.4	87	94	16	278
PUTS2-5%	1	0.55	0.3	230	94	39	269
PUTS3-5%	1	0.7	0.2	276	96	60	262
PUTS4-5%	1	0.75	0.17	338	96	64	265
PUTS5-5%	1	0.8	0.13	394	94	68	263

[a)] Swelling ratio and gel fraction in THF obtained from four sample measurements at room temperature for 24h. [b)] Glass transition temperature (T_g) determined from the second heating curve of DSC-experiments. [c)] TGA onset-temperatures after 5% weight loss ($T_{TGA-95\%}$).

Since we aimed to synthesize PU-materials that are mechanical rigid at room-temperature, but can readily be reprocessed at elevated temperatures, a thorough thermal analysis was conducted. As can be seen in Table 1, despite PUTS5-5% having the lowest cross-link density it also possesses the highest glass transition temperature (T_g) (68 °C). This can be attributed to the inherently more flexible Desmodur 3600N (crosslinker) and to the rigid nature of the hMDI building block (acting as a chain extender). Furthermore, both PUTS3-5% and PUTS4-5% showed phase separation as evident from the cooling curves in the corresponding DSC thermograms (Figure S8). This behavior is commonly observed and often intentionally sought after in polyurethane materials and is caused by combining two phases which are generally not miscible.[43] One phase primarily comprises a high-T_g polymer (hMDI, transition at high temperatures in cooling curves) and serves as the crosslinking nodes within the continuous, soft, elastomeric phase. It also provides the material with enhanced mechanical strength through intermolecular interactions (such as H-bonding).[44,45] The other elastomeric phase is predominantly constituted by a low-T_g amorphous polymer caused by Desmodur 3600N and gives a transition at lower temperatures in cooling curves. Interestingly, based on the chemistry and ratio of the monomers involved, (micro)phase separation can be minimized.[43,46] Also, it is important to note that urethane linkages themselves are well-known to exhibit some dynamic covalent behavior at elevated temperatures (typically >150 °C), even in the absence of catalysts.[39,47,48] Leading to regenerated isocyanates that can participate in multiple side reactions and alcohol moieties that can be irreversibly alkylated at elevated temperatures, thereby deactivating dynamic exchange. For this reason, although aliphatic urethane linkages are considered more stable than their aromatic counterparts, reprocessing of the PUTS-materials has been carried out at 140 °C. Consequently, in order to enable swift dynamic exchange and mitigate the influence of chain rigidity at the reprocessing conditions, the monomer formulations were carefully chosen to obtain materials with T_g at, or below, 70 °C. At room temperature, these materials behave as mechanically robust glassy materials, as also evidenced by their brittle breaking patterns (Figure S9). Thermogravimetric analysis (TGA) revealed excellent thermal stability with 5% weight loss temperature ($T_{TGA\text{-}95\%}$) above 260 °C (Figure S10). Swelling experiments were then conducted in tetrahydrofuran (THF) at room temperature to qualitatively evaluate the network integrity and connectivity (Figure S11). As anticipated, PUTS5-5% – having the lowest cross-link density – swelled the most, and vice-versa for PUTS1-5%. Further, all materials showed gel fractions above 94%, indicating the formation of nearly defect-free networks. It should be noted that even for a dissociative exchange mechanism, these materials cannot shift to a depolymerized state, as only the BrO-Dec can dislodge itself from the network.

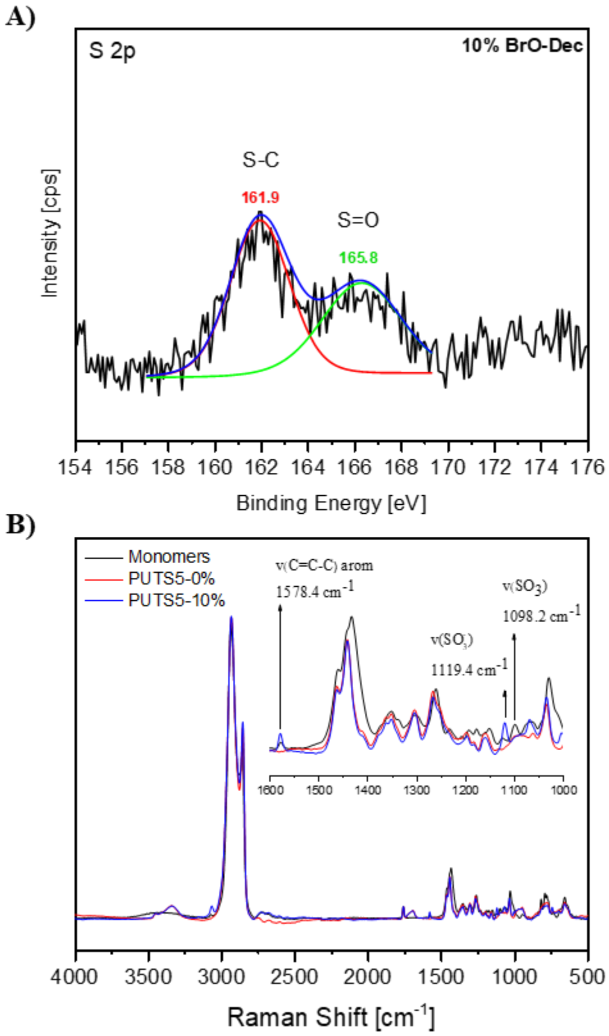


Figure 2: A) XPS spectrum of PU-material containing 10 mol% of BrO-Dec. A shoulder at 165.8 eV can be observed, which can be attributed to both sulfonium and sulfonate groups. **B)** Normalized Raman spectra of the monomeric mixture (including BrO-Dec) and the materials containing respectively 0% and 10 mol% of BrO-Dec. A distinct shift of the Raman peak corresponding to the sulfonate *v*(SO_3) band is observed towards higher wavelengths upon curing, indicating the formation of the brosylate's sulfonate anion and the covalent integration of the alkylating additive into the material.

Another interesting aspect to probe in the developed PU-networks is the influence of the alkylating agent on the thermal properties of the materials. Since the alkylating additive ultimately binds to the network structure, it alters the polymer backbone and introduces ionic charges, which should ultimately affect the properties of the material.[49,50] To investigate this, the lowly cross-linked PUTS5 materials with varying amounts of BrO-Dec were prepared, namely, PUTS5-2%, PUTS5-5% and PUTS5-10% containing 2, 5 and 10 mol% of alkylating additive respectively, while PUTS5-0% was prepared as a reference material. Next, potential phase separation occurring as a result of the introduced ionic charges (after the alkylation post curing step) was investigated by scanning electron microscopy (SEM). Even though cationic groups incorporated into polyurethanes are generally known to give rise to an increased phase separation,[43,51,52] no phase separation could be detected even in the case of PUTS5-10% that contained the highest concentration of trialkylsulfonium salts (Figure S12). This result can potentially be ascribed to the inherent soft character of the formed sulfonium salts and the predominance of H-bonds throughout the matrix inhibiting ionic aggregation. The same materials were also analyzed by DSC (Figure 3A and Figure S13) and TGA (Figure 3B).

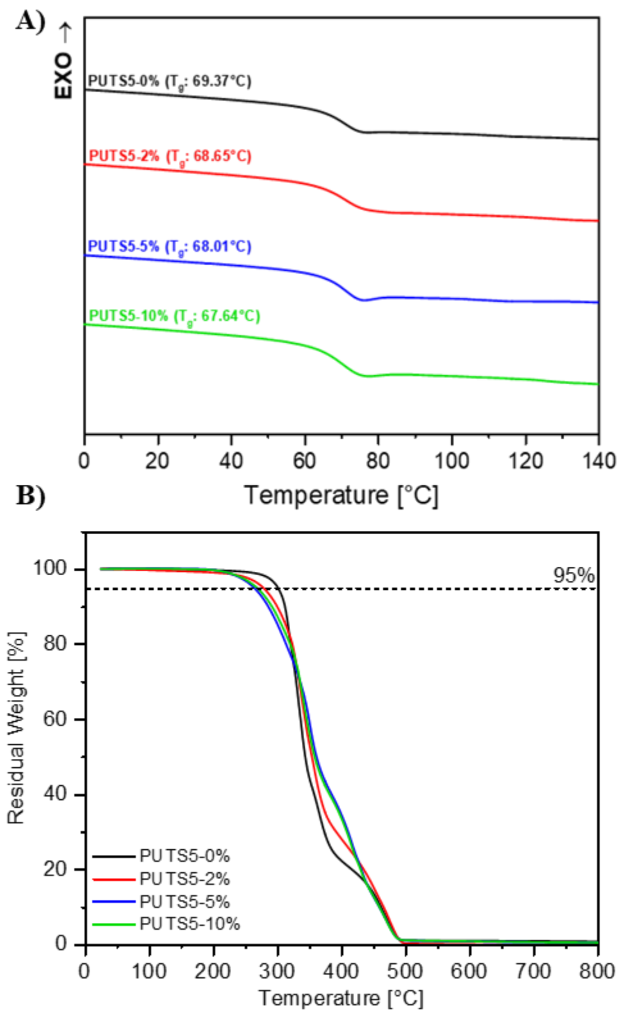


Figure 3: Thermal analysis of PUTS5 networks with increasing amount of BrO-Dec. **A)** Stacked second heating traces demonstrating minor changes in T_g. **B)** TGA analysis revealing $T_{TGA\text{-}95\%}$ values around 260 °C for all materials.

DSC analyses show minor changes in T_g with varying degrees of alkylating additive. Conversely, TGA reveals that, as can be expected, the PU-networks with more reactive trialkylsulfonium bonds show a slightly lower but still acceptable onset of degradation with $T_{TGA\text{-}95\%}$ values around 260 °C for all materials. Furthermore, by comparing the TGA thermograms of samples containing varying amount of BrO-Dec, a three-step degradation process can be observed (Figure S14).

To assess the reprocessability of our transalkylated PU-networks, the PUTS5-materials were broken down into smaller pieces and reprocessed by compression molding at 140°C (*vide supra*).

The alkylated networks could be reprocessed at least three times in contrast to the non-alkylated, reference PUTS5-0% material as is visualized in the images presented in Figure S17. This illustrates the requisite of sulfonium-thioether exchange to induce sustained dynamicity into the system under the applied reprocessing conditions. Reprocessing of the alkylated materials over multiple steps did not result in any significant change in network properties, such as, the chemical composition, absence of color, T_g, $T_{TGA\text{-}95\%}$, swelling degrees, and gel fractions (Figure 4 and Figure S18).

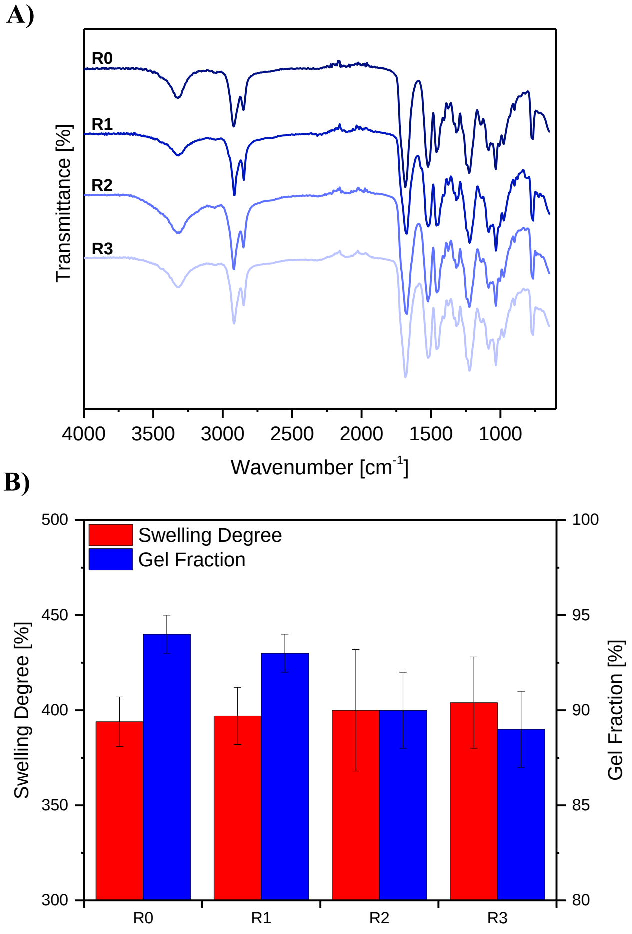


Figure 4: A) FTIR-spectra of PUTS5-5% samples showing no substantial changes in the chemical composition upon multiple recycling steps by compression molding at 140 °C for 45 min using 2 tons/m^2. **B)** Swelling and gel fraction of PUTS5-5% after subsequent recycling steps.

Supramolecular interactions (such as H-bonding) play a critical role in the morphology and overall properties of PUs. In order to visualize the importance of these interactions within the synthesized materials, we relied on high temperature FTIR spectroscopy for the determination of H-bonding. It is well-known that the wavenumber of ν(N-H) and ν(C=O) bands indicates the H-bonding strength: the lower the wavenumber, the stronger the H-bonds.[53] At room temperature (RT), the ν(N-H) can be found at 3323.9 cm^{-1} while the ν(C=O) can be found at 1684.3 cm^{-1}, visualizing the H-bonded states (Figure 5). These absorption bands gradually shifted to higher wavenumbers upon increasing temperature (from RT to 160 °C), due to the elongation of the hydrogen bonds. However, hydrogen bonds could still be detected, even at 140 °C .

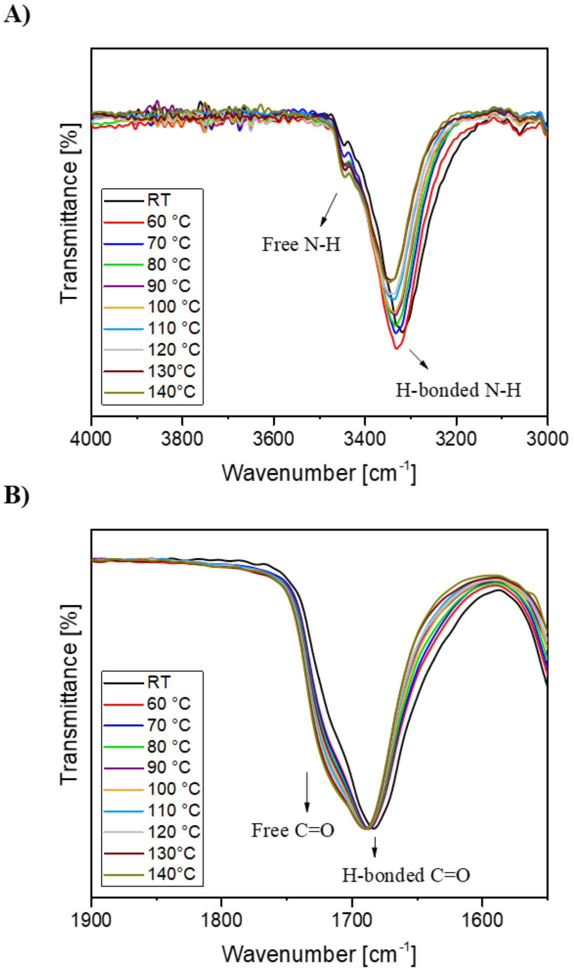


Figure 5: Variable temperature FTIR spectra for PUTS5-5% in the range of 3600 − 3100 cm^{-1} (**A**) and 1850 – 1550 cm^{-1} (**B**) from 30 to 140 °C with a temperature increment of 10 °C. The spectra are normalized by using the absorption intensity of $-CH_3$ at 2963 cm^{-1} as an internal reference.

Adding to the hydrogen bonds, which are formed between urethane groups, also ionic interactions between the sulfonium cations and brosylate anions or a synergetic effect of both could take place.

In a next step, small-strain amplitude oscillatory shear (SAOS) measurements at different temperatures were performed in order to obtain a deeper understanding of the dynamic behavior of the alkylated polyurethane networks.[54] Frequency sweep measurements were performed on PUTS5-5% between 140 °C and 115 °C (Figure 6A) using a shear strain of 0.4%, which was well within the linear viscoelastic region (LVE-region) of the networks (Figure S19). The frequency sweeps were then combined in a master curve by shifting them towards a reference temperature (140 °C).[55] To ensure the validity of the time-temperature superposition principle for the materials, Van Gurp-Palmen diagrams were first constructed by plotting the phase angle δ as a function of the absolute value of the complex modulus $|G^*| = (G'^2 + G''^2)^{0.5}$ (Figure 6B). All measurements conducted over a range of temperatures, converged onto a single line, indicating that – despite the complex composition – the materials show a rheological simple behavior, and thus that a master curve can indeed be constructed.[56,57]

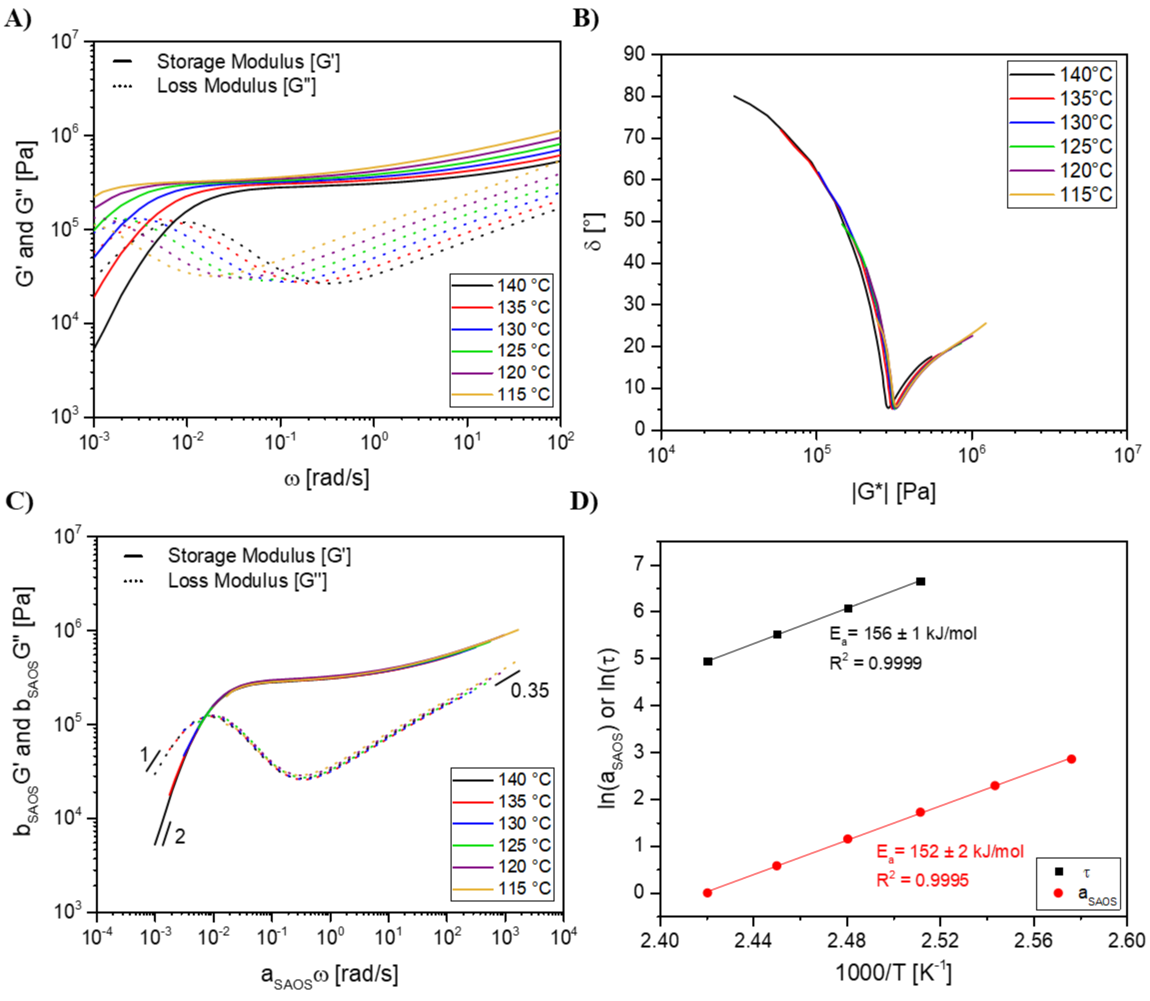


Figure 6: Linear viscoelastic measurements of PUTS5-5%. **A**) Combined frequency sweeps and **B)** Van Gurp-Palmen diagrams to verify the time-temperature superposition principle. **C)** Master curve constructed by shifting the frequency sweeps towards 140°C. **D)** Arrhenius plot of the time-temperature superposition shift factors (a_{saos}) for PUTS5-5% and relaxation times (τ) derived from unshifted frequency sweep data. Linear regression revealed a similar apparent activation energy for both a_{saos} (152 ± 2 kJ/ mol) and τ (156 ± 1 kJ/ mol).

The horizontal shift factors (a_{saos}), used to construct the master curves, are expected to follow $a_{saos} = \omega_{ref} / \omega_T$ and are generally used to indicate the averaged variation of relaxation times with temperature. To accommodate for matrix effects commonly observed for polyurethane materials (such as varying change of entropic force, density etc.), an additional vertical shift factor b_{saos} =

G_{ref} /G_T was considered.[58] It should be noted that the employed vertical shift factors were nevertheless small, ranging between 0.94 and 1.06 over the full range (a summary of the shift factors to construct the master curves can be found in Table S1). The resulting master curve is depicted in Figure 6C. Perfect overlap was observed throughout the expanded frequency interval. Left of the (relatively small) rubbery plateau at low frequencies a cross over between the storage (G') and loss (G") moduli was observed, indicating a transition from an elastic (solid) state to a more viscous (liquid) state. At frequencies lower than this cross-over point, the G' and G'' curves are observed to be proportional to ω^2 and ω respectively, revealing terminal relaxation was achieved in the material and that a Maxwell model can be applied. Furthermore, at high frequencies, a constant increment of G'' appeared with a slope of 0.35, which is a typical indication of internal chain dynamics as described by the sticky Rouse model.[59] Additionally, by fitting the a_{saos} values to an Arrhenian-type equation (equation S5), an apparent activation energy of 152 ± 2 $kJ.mol^{-1}$ was estimated. A similar activation energy (156 ± 1 $kJ.mol^{-1}$) was attained by fitting the relaxation times of the unshifted frequency sweeps to the Arrhenius equation (Figure 6D).

Following this, creep experiments were performed to evaluate the material response at long time scales upon application of a constant stress. Indeed, while the vitrimer concept provided an attractive strategy to introduce both reprocessability and solvent resistance to polymeric materials, it renders them vulnerable for creep at service temperatures.[23,60-63] To investigate the creep endurance of the synthesized materials, a series of consecutive creep experiments were performed at elevated temperatures with a constant shear stress of 1 kPa applied over the course of 10^4 s while the resulting strain was monitored as a function of time (Figure 7A). To verify if the terminal regime for which relationships between rheological quantities and molecular parameters is reached at a given temperature, the creep compliance (J(t)) is plotted as a function of time (t) in a doublelogarithmic plot (Figure S23).[64] For none of the measured materials, linear time scaling of steady-state flow could be attained within the measured time intervals. This indicates that terminal relaxation is not reached and thus that an accurate estimation of the overall creep ($\dot{\varepsilon}$) and zero-shear viscosity (η_0) is not feasible. Similarly to the SAOS measurements, the creep compliance data at various temperatures can be superimposed smoothly to create a master curve as visualized in Figure 7B. A notable correlation between the alkylating agent additive loading and the power law scaling was observed (Figure S24). Assuming that a higher power scaling for a given material under the same measurement conditions and time interval can be related to a higher sensitivity towards creep, increasing the quantity of alkylating agent and thus the concentration of reactive functional groups (i.e. sulfonium salts) in the polymer networks generally results in a higher power law scaling and thus a higher sensitivity towards creep.

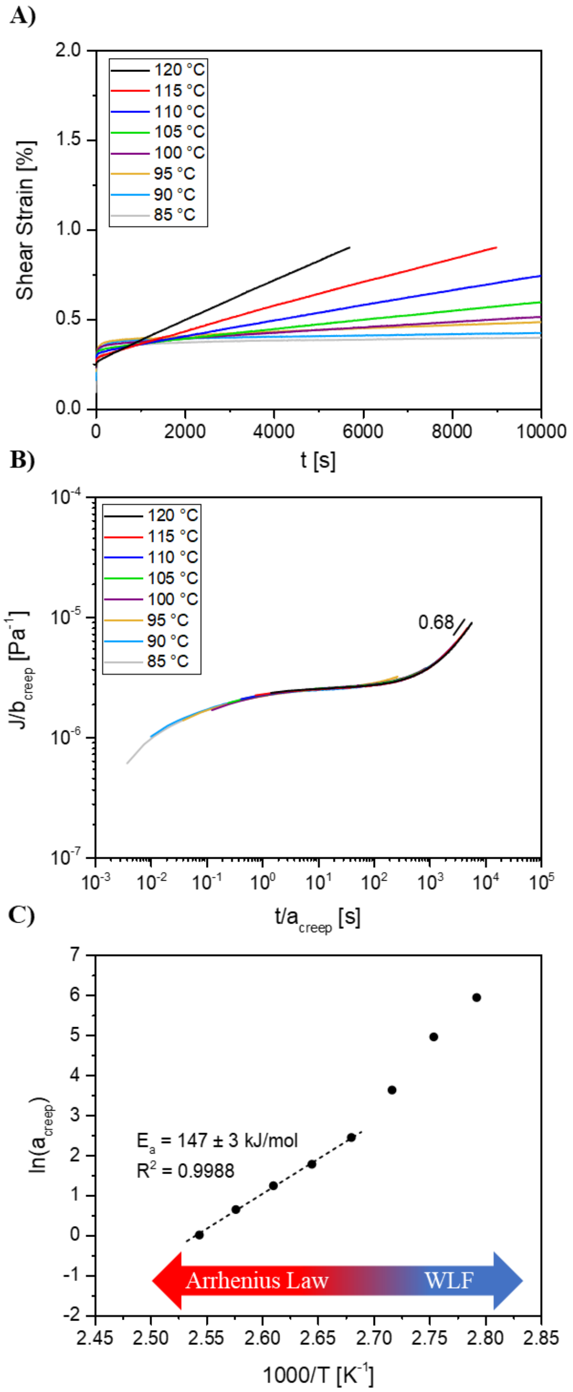


Figure 7: Raw strain (**A**) data of **PUTS5-5%** at different temperatures. **B)** Master curve constructed by shifting the creep compliance data towards 120°C. A power law scaling of only 0.68 was observed, indicating that the terminal relaxation regime was not reached. **C)** Arrhenius plot of the time-temperature superposition shift factors for PUTS5-5% reveals WLF behavior at low temperatures (>100 °C). Linear regression confirms the activation energy attained from the SAOS experiments (147 ± 3 kJ/ mol).

Furthermore, upon considering the relationship between the applied horizontal shift factors a_{creep} and temperature, it is possible to determine the apparent activation energy. Since the tested temperature window is now in close proximity to the T_g (65°C), polymer chain motion becomes a more dominant factor in the topology rearrangements, as described with the Williams-Landel-Ferry theory.[10,65] Indeed, a dual regime can be distinguished from the Arrhenius plot of the time-temperature superposition shift factors for PUTS5-5%, revealing WLF dominated behavior at low temperatures (> 100 °C) and an Arrhenian behavior at higher temperatures (Figure 7C and Figure S25).[66,67] Linear regression of the horizontal shift factors above 100°C to equation S6 confirmed the activation energy attained from the SAOS experiments. This activation energy (147 ± 3 kJ/mol), which is characteristic for the overall exchange process, was significantly higher than previous reported materials in literature (61 – 115 kJ mol^{-1}).[36–38] The difference can be ascribed to the prevalence of H-bonding within the developed PU-networks (*vide supra*). Indeed, physical cross-linking imposes restriction on the segmental relaxation of polymer chains.[68-71] This effect is further enhanced by the predominance of rigid segments throughout the polymer matrix.[72,73] Furthermore, hydrogen bonding is a well-known factor that slows down S_N2-reactions by lowering the intrinsic nucleophilicity of solvated nucleophiles.[74] Additionally, this significantly different activation energy can also be ascribed to, or aided by the different polarity of the polymer matrix.[75-77]

Prompted by the pivotal work of Drockenmuller, Montarnal and co-workers on the influence of the counter anion on the exchange kinetics and material performance, we prepared a dynamic material PUTS5-5% Br-Dec in which 1-bromodecane (Br-Dec) was used instead of decyl-4-bromobenzenesulfonate (BrO-Dec) as alkylating additive.[26-28] This implies that the only varied molecular parameter within the formulation is the nature of the counter anion. Significant changes in thermomechanical properties could not be observed, in comparison to the PUTS5-5% material

(Figures S26-27). However, these materials were found to be more challenging to reprocess and exhibited substantially longer relaxation times and lower power law scaling (i.e. better creep resistance) (Figure S24 and Figure S28). This slower dynamic behavior can be explained by several factors (or a combination thereof), such as the manifestation of clustering effects and stronger supramolecular interactions due to differences in ionic strength and the more nucleophilic nature of the bromide anion. The latter could in turn result in nucleophilic substitution reactions on alkyl side chains of a sulfonium salt as a side reaction. Also, the lower mobility of the trialkylsulfonium salts throughout the polymer matrix could be taken into account.

After studying the dynamic behavior of the PUTS-materials, their potential use in optical applications was evaluated. In general, a high refractive index and optical transparency are absolute requirements for optical applications.[78] The refractive index was determined at 20 °C and a relatively high refractive index value of around 1.54 was observed, which is in the same order as conventional glass. Thereafter, the transmittance within the visible light region was measured for PUTS5-10% and PUTS5-0%, the networks with the highest content of sulfonium salts and without any salt. An average transmittance of 84 % was recorded for both samples which closely matches to the transmittance of glass (89 %) and of common polymer glasses found in the literature (Figure 8).[79,80] Encouraged by these promising results, we then monitored the transmittance after reprocessing. Initially, a notably lower transmittance (57 %) was attained but this could be ascribed to the existence of visible healing trails or other inhomogeneities on the surface that were formed during the reprocessing experiments, causing light diffraction (Figure S30). Nevertheless, while subjecting the reprocessed PUTS-samples to a focused thermal heat treatment, these unwanted trails gradually erased over time, leading to an almost complete recovery of the transmittance values (80%).

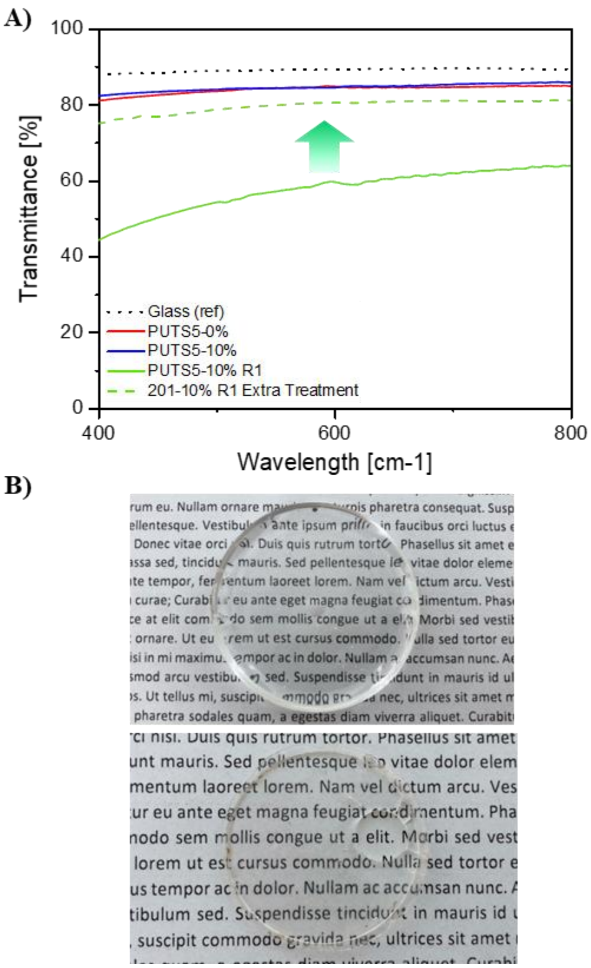


Figure 9: A) Transmittance as a function of wavelength of glass, PUTS5-0%, PUTS-5-10% R0 and PUTS5-10% R1. Although PUTS5-10% R0 contains the highest fraction of alkylating additive, it has a comparable transmittance with the reference material PUTS5-0%. B) Picture of PUTS5-5% before (top) and after reprocessing (bottom), both exhibiting high transparency and little coloration.

CONCLUSION

In summary, this study demonstrated the successful solvent-free synthesis of colorless and highly transparent glassy PU-networks containing trialkylsulfonium salts, starting from readily available compounds. The obtained cross-linked materials were subjected to an in-depth characterization, revealing excellent transmittance in the visible light region that are in close correspondence to that of glass and other common polymer glasses. Additionally, we observed efficient stress-relaxation at elevated temperatures and creep resistance at relatively high temperatures and high activation energy. These viscoelastic properties could be tuned through the loading of the alkylating additive and the nature of the anionic counter ion. Significantly, the material properties and transmittance were not detrimentally affected by thermal reprocessing. The presence of trialkylsulfonium salts is expected to enhance the adhesion to metallic substrates, rendering them an appealing option for various applications including smart coatings, as well as optical and optoelectronic applications.[81,82] In any case, the trialkylsulfonium transalkylation chemical platform seems to hold good promise for the development of innovative PU-materials.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge.

Materials and instrumentation; synthesis and characterization of the alkylating agent and PUTS-networks; NMR, Fourier-transform infrared (FTIR), Raman, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and rheology data; swelling experiments, SEM-pictures.

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Notes

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