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# Deciphering Siloxane Bond Exchanges: from a Molecular Study to vitrimerization and recycling of Silicone Elastomers.

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KEYWORDS: siloxane exchange, dynamic networks, vitrimers, rheological model

**ABSTRACT:** The activity of various additives promoting siloxane equilibration reactions is examined and quantified on model compounds. We found in particular that the “superbase” phosphazene derivative  $P_4tBu$  can promote very fast exchanges (a few seconds at 90 °C) even at low concentration (<0.1 wt%). We demonstrate that permanent silicone networks can be transformed into reprocessable and recyclable dynamic networks by mere introduction of such additives. Annealing at high temperature degrades the additives and deactivates the dynamic features of the silicone networks, reverting them back into permanent networks. A simple rheological experiment and the corresponding model allow to extract the critical kinetic parameters to predict and control such deactivations.

## INTRODUCTION

Silicone elastomers feature high flexibility, high thermal stability, and both hydrophobic and oleophobic surface properties. They are used in a vast range of applications such as heat-resistant sealants or encapsulants, moulds, cosmetics, drug delivery or bio-implants<sup>1,2</sup>. While recent academic and industrial developments have led to silicone thermoplastic elastomers (SiTPEs), such as segmented block copolymers<sup>3-5</sup> or thermoplastic vulcanizates (SiTPVs),<sup>6,7</sup> the vast majority of silicone elastomers are still obtained through conventional cross-linking methods such as hydrosilylation, hydrolysis-condensation or radical reactions (essentially peroxides- or UV-induced)<sup>8</sup>. Unlike conventional cross-linked elastomers, recycling routes for silicone elastomers is practically and economically feasible through chemical depolymerization with acids, bases or fluorides<sup>9</sup>, which is particularly favored in the case of poly(dimethyl siloxane) by the equilibration between (macro)cyclic and linear forms and the high volatility of the smaller cyclic species ( $D_4$  to  $D_6$ ) that can be recovered by distillation and repolymerized.<sup>10-13</sup> Alternatively, covalent adaptable network (CAN) strategies<sup>14-21</sup> have been recently applied to silicone materials with the prospect of directly healing cracks or reprocessing the materials by grinding and molding steps. Three approaches can be distinguished: i) the use of dissociative crosslinks such as Diels-Alder adducts<sup>22</sup> or borate esters (the original “silly putty” formulation<sup>23</sup>) that provide viscoelastic or TPE materials, ii) the use of associative exchanges: UV-induced disulfide exchanges,<sup>24</sup> heat-activated transesterifications,<sup>25,26</sup> imine exchange,<sup>27</sup> vinylogous urethanes<sup>28</sup> or derivatives of Meldrum's acids<sup>29</sup> and iii) the direct and controlled catalysis of siloxane exchanges.

The latter has been known for over 70 years, with the pioneering work on siloxane bond equilibration of Osthoff in the 1950s.<sup>30-32</sup> The underlying admitted mechanism for bases or fluorides is the cleavage of the Si-O-Si bond by nucleophilic displacement, which forms a silanolate anion.

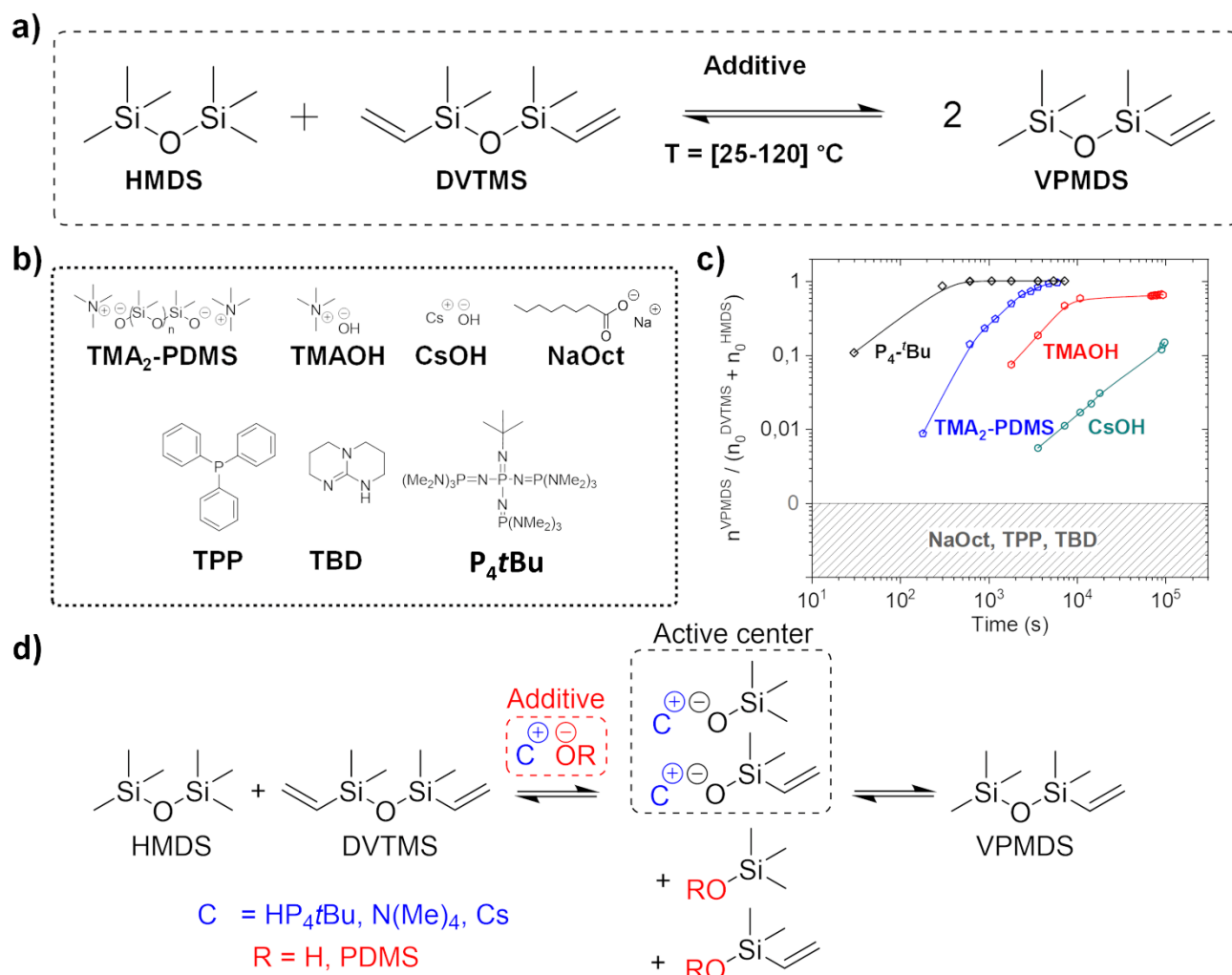
This silanolate moiety is further involved and regenerated through nucleophilic attacks on other Si-O-Si bonds. This equilibration reaction is also at the core of the equilibrium between rings and linear chains in PDMS polymers that occurs to a certain extent in anionic ring-opening polymerization (ROP) of silicones, and that started to be studied by Wright and Semlyen in the 70's.<sup>33,34</sup> Exploitation of such equilibration reactions in dynamic crosslinked silicone networks was however only brought up by McCarthy and Zheng in 2012.<sup>35</sup> They conducted an anionic ROP of octamethyl tetrasiloxane ( $D_4$ ) in presence of a bis- $D_4$  crosslinker initiated by an oligosiloxane functionalized with tetramethylammonium silanolate endgroups (TMA2-PDMS). In absence of quenching, the living silanolate group enables dynamic chain exchange and welding of fractured parts at 90°C for 24h. Although precise measurement of exchange dynamics or network relaxation times were not carried out, these materials were further studied by Seiffert and coworkers, using this time as catalyst tetramethylammonium hydroxide (TMAOH) at higher concentrations than McCarthy.<sup>36</sup> Using home-made piercing experiments that monitor the flow of dynamic networks, they found very fast relaxations, typically in the 1-2 s range, with only weak dependencies to catalyst concentrations or to temperature in the 5-60°C range. Exciting benefits of malleable silicone networks have also been explored by Xie and coworkers, who combined plastic deformation of micropatterned silicones with pyrolysis to obtain well defined silicon oxycarbide ceramics.<sup>37</sup> The malleable silicone network was obtained this time directly by adding sodium octanoate (NaOct) from a commercial two-component formulation undergoing platinum-catalyzed hydrosilylation (Sylgard 184 from Dow Corning). Much higher temperatures were however required for malleability, typically between 180 and 200°C. More recently, the group of Terentjev has also investigated the use of siloxane crosslinks for the reprocessing of liquid crystalline elastomers obtained after thiol-acrylate Michael addition between mesogenic diacrylates and isotropic dithiols.<sup>38</sup> Several additives were found

to induce relaxations in these networks, such as TMA<sub>2</sub>-PDMS, triphenylphosphine (TPP), triazobicyclodecene (TBD) and NaOct. TBD, also known to ring-open and polymerize effectively cyclic siloxane,<sup>39</sup> was found very effective. In this case also, very high temperatures from 190 °C to 210 °C were required, even in the case of tetramethylammonium-based catalysts that are yet known to degrade above 150 °C.<sup>40,41</sup> Last, Du Prez and coworkers recently investigated epoxy resins containing bisamine disiloxane hardeners and various catalysts (strong organic bases and silanolates). While studies of siloxane exchanges on disiloxane model molecules barely showed any effect of TBD (5 mol%) over 16 h at 120 °C, the addition of alcohols slightly accelerated the exchange. Mechanical relaxation of the epoxy networks containing 10 mol% TBD/Si and a large amount of hydroxyls issued from the epoxy-amine reaction showed however dramatically faster relaxations, down to about 5 s at 220 °C which eventually enabled reprocessing and thermoforming of composites.<sup>42</sup>

Given the historical and technological relevance of dynamic siloxane exchanges, the apparent discrepancy

within all these studies of the effect of network composition and the nature or concentration of catalysts on the exchange dynamics of siloxanes prompted us for a more thorough comparison of various catalysts using model compounds. Recognizing the importance of the effective solubility of catalysts in highly apolar environments and the economical necessity to use catalytic amounts of additives, we ensured in particular to study purely siloxane environments, either as small model molecules or as target dynamic networks.

While we found unexpectedly that several additives mentioned above do not promote sizeable siloxane exchanges, we also discovered that a phosphazene derivative, P<sub>4</sub>tBu (please see full name in the Materials section in SI), is extremely effective. Incorporation of this additive in both model and commercial silicone networks proved a highly efficient way to transform them into malleable dynamic networks. Last, we also discovered that at temperatures higher than 130 °C thermal degradation of P<sub>4</sub>tBu effectively deactivates the dynamic siloxane exchanges and the networks are reverted to non-dynamic networks. We empha-



**Figure 1.** a) Molecular study of the siloxane bond exchange. b) Library of additives used to induce the dynamic exchange. c) Kinetic study at 90 °C in presence of 100 ppm of additive. d) Mechanism involved for the siloxane bond exchange.

size that proper control of such deactivation and corresponding predictive mathematical modelling opens exciting perspectives for dynamic networks in general, and may solve the difficult compromise that must be made between fast dynamics required for (re)processing the networks at high temperatures and very slow dynamics required for effective creep-resistance at service temperatures.<sup>43</sup>

## RESULTS AND DISCUSSION

**Molecular study** of catalyzed siloxane exchanges. While the equilibration of siloxanes has been studied as early as the 1950s the kinetics of these reactions was never, to the best of our knowledge, studied explicitly with model compounds. We chose short disiloxane compounds bearing different substituents (hexamethyldisiloxane - HMDS and divinyltetramethyldisiloxane - DVTMS). The expected cross-exchange product (vinylpentamethyldisiloxane - VPMDS) is also commercially available and can be easily quantified by gas chromatography (GC, Figure S1 in SI). The established exchange mechanism involves the formation of a silanolate ion pair as the active catalytic center (See Figure 1d). In practice, the various molecules added to accelerate the siloxane exchanges may only be precursors (e.g. organic bases, hydroxides) to the silanolates species. For clarity throughout the manuscript we will refer to them as *additives*. HMDS and DVTMS were mixed in equimolar ratios in presence of various additives (Figure 1b) at low concentration (0.1 wt%) and in absence of any additional solvents. Samples withdrawn at different times from the reaction medium were analyzed by GC to quantify the evolution of the fractions of HDMS, DVTMS and VPDMS during the reaction. The resulting equilibration kinetics is displayed in Figure 1c. Surprisingly, no formation of VPMDS was observed after 24 hours of reaction when TPP, NaOct and TBD were used as additives. Widely used tetramethyl ammonium basic salts, TMAOH and TMA2-PDMS display characteristic equilibration times of ca. 2 h and 1 h, respectively, while CsOH is much slower (ca. 150 h). Such differences are significant given that TMA2-PDMS and TMAOH involve the same counter ions (tetramethylammonium) and should lead to the same silanolate active species after the first exchange with disiloxanes (see Figure 1d). We attribute thus the significant induction time with TMAOH to a poor solvation of this salt in the apolar disiloxanes and correspondingly to a slow conversion in tetramethyl ammonium silanolate. The same reasoning might also explain the lower activity of CsOH.

Further investigation about the nature of the silanolate active center was obtained by directly using lithium, sodium, or potassium silanolates. In the three cases no VPDMS was observed, thus demonstrating that highly dissociated ion

pairing is critical for the reactivity of silanolates. This prompted us to test bases with highly delocalized charge and excellent solubility in apolar media. In this regard, the  $P_4tBu$  “superbase” is known to form phosphazanium hydroxide  $[HP_4tBu]^+[HO]^-$  or alcoxides in presence of adventitious water or alcohols (See Scheme 1),<sup>44-46</sup> and is also amongst the most efficient known initiators for ROP of D4 cyclic siloxanes.<sup>7,41-45</sup>  $P_4tBu$  was indeed found extremely efficient for these siloxane equilibrations, with ca. 3 min of exchange time at 0.1 wt% and 90°C (Figure 1c). We assume that the traces of water enables the in situ formation of  $[HP_4tBu]^+[HO]^-$  initiator.

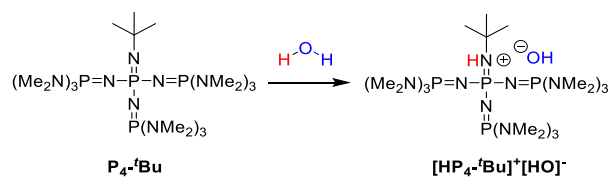
As expected, increasing the amount of additives and heating accelerates the exchanges kinetics. The corresponding mastercurve of exchange kinetics at different temperatures for TMA2-PDMS (Figure S2) demonstrates the absence of latent effects in these reactions (e.g. sudden increase of reactivity above a temperature threshold) and allows to determine for 0.1 wt% additive an exchange time about 900 s at 90°C and an activation energy  $E_a$ , of 92 kJ mol<sup>-1</sup>. The exchange kinetics also depend on the concentration, with a 10-fold acceleration from 0.05 wt% to 5 wt% of additive (Figure S3).

Above 110°C, however, the reaction becomes slower, which might be related to the thermal decomposition of the tetramethylammonium silanolate in trimethylamine and methoxysilane, or its subsequent condensation products as reported in the literature.<sup>35</sup> No clear evidence of such decomposition products were however identified on the gas chromatograms as trimethylamine is highly volatile. TMSOMe and DVSOMe might also condense readily to reform HMDS, DVTMS and VPMDS.<sup>45</sup> The deactivation of TMA2-PDMS at 120°C was further verified by pre-equilibrating the additive with HMDS for 2h before adding 1 eq. of VDTMS. In this case, no cross-exchanged VPDMS could be detected after 2h.

In comparison, the  $P_4tBu$  additive at 0.1 wt% shows much faster exchanges, ca. 75 s at 90°C (Figure S4) with comparable activation energy about 100 kJ mol<sup>-1</sup>.

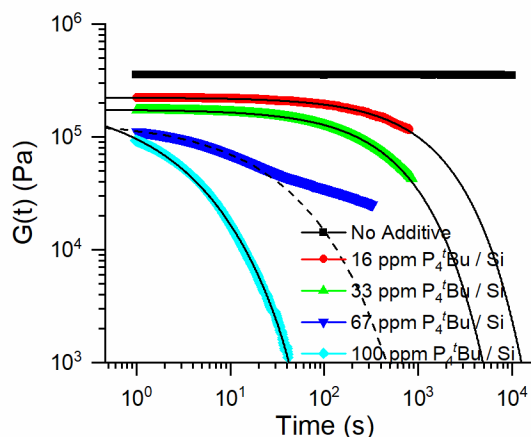
**Silicone vitrimers.** Model polysiloxane networks were prepared to further study the effect of these siloxane exchanges on relaxations. Liquid silicone resins (LSR)-like formulations have been implemented using divinyl-terminated poly(dimethylsiloxane) ( $M_w = 25\,000$  g mol<sup>-1</sup>), polymethylhydrosiloxane crosslinker ( $M_w = 1900$  g mol<sup>-1</sup>, SiH/Vinyls=2) and a Pt-based NHC derivative (300 ppm/vinyls)<sup>47,48</sup> that allows a complete curing within 15h at 75°C (please see complete description in the SI). The resulting networks do not display any detectable extractable fraction; they are permanent networks (see stress relaxations below) and relatively brittle ( $\epsilon_{break}$  about 100%) given the relatively low molar mass of the divinyl PDMS precursors.

All additives accelerating siloxane exchanges are bases and thus incompatible with the crosslinking reaction by Pt-catalyzed hydrosilylation. The additives were thus post-added in the PDMS networks by solvent-assisted diffusion in toluene. To ensure homogeneous dispersion, 8 mm x ca. 1.5 mm disks of the PDMS networks were impregnated with



**Scheme 1** Activation of  $P_4tBu$  by the adventitious presence of water in HMDS and DVTMS

the exact amount of additive solution in toluene required for swelling to the equilibrium (e.g. a 1:1 weight ratio of solution to PDMS sample), and left to dry at 40°C overnight. As  $P_4tBu$  shows promising results in terms of solubility and equilibration times in the above study involving molecular compounds, we focused our study on its use to induce siloxane bond exchanges in PDMS networks. A control experiment on the pristine PDMS rubber (Figure 2) demonstrates the absence of any relaxation at 90°C.

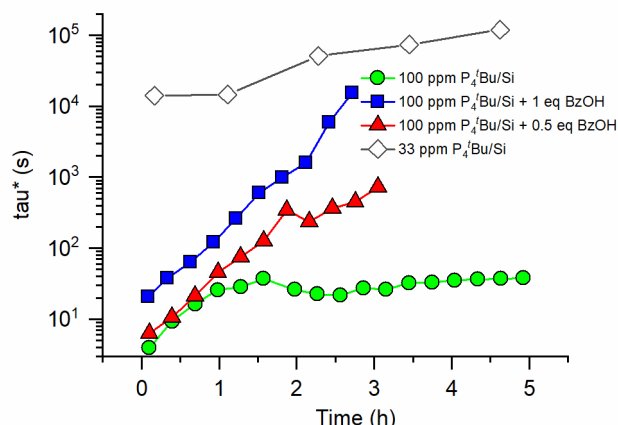


**Figure 2. Stress relaxation at 90°C (1% strain) of model silicone networks containing 0-100 ppm  $P_4tBu$ /Si.**

Adding  $P_4tBu$  to the networks in amounts from 16 to 100 ppm to Si atoms (e.g. from 0.01 wt% to 0.09 wt%) induces stress relaxation (Figure 2 – The corresponding frequency sweeps are shown in Figure S5 in SI), with corresponding characteristic times from 1700 to 3 s. Notably, these dynamic exchanges are complemented by a decrease in the plateau moduli (from about 350 kPa for the initial network to about 100 kPa for the highest  $P_4tBu$  loading) that substantiates the expected mechanism of this additive. First, Si-O-Si chains are cleaved by the phosphazanium hydroxides to yield phosphazanium silanolates acting as persistent active centers. Further exchanges within the network allow strand exchanges and stress relaxation. It should be noted that such reorganizations also trigger the formation of volatile cyclic siloxanes by back-biting reactions. Consequently, the crosslinked samples gradually depolymerize and evaporation takes place over time at 90°C. Figure S6 shows the weight loss of ca. 70 mg disks after annealing in open air at 90°C for 6h: significant losses > 25wt% are observed for  $P_4tBu$  concentrations above 100 ppm /Si. This limited stability illustrates a major drawback of fast dynamics in silicone networks and prompted us to characterize the time-dependent evolution of exchange dynamics.

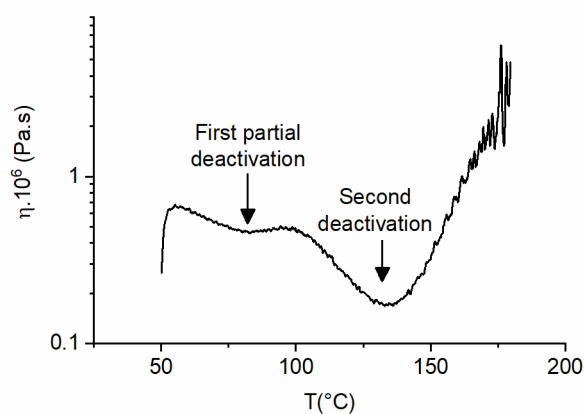
**Deactivation of exchange reactions.** We carried out repeated stress relaxations (1% strain) to measure the evolution of characteristic relaxation times (Figure 3). The network containing 100 ppm  $P_4tBu$  displays an initial increase of relaxation times that levels off to about 30 s after 1h. We hypothesized that this change is due to slow and partial deactivation of the silanolate groups due to impurities in the network, probably water.<sup>49</sup> We verified this by adding

controlled amounts of benzyl alcohol (BzOH, 0.5 and 1 eq. to  $P_4tBu$ ); the corresponding deactivations proceed to much larger extents, effectively yielding kinetics comparable to networks initially loaded with ca. 33 ppm of  $P_4tBu$ /Si.



**Figure 3. Evolution of relaxation times at 90°C in model silicone networks containing various amounts of  $P_4tBu$ /Si and BzOH.**

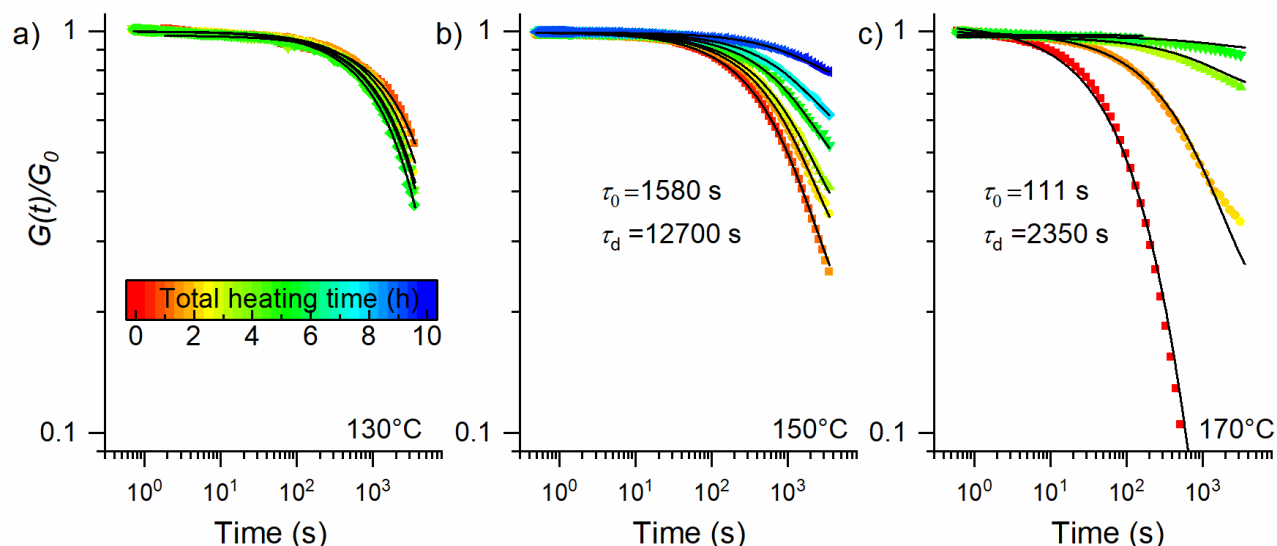
Extended uses of such exchange deactivations can be found at elevated temperatures, when thermal degradation of the silanolate salts occurs. A rapid screening of the time- and temperature-evolution of deactivation was found by monitoring the creep behavior while applying a heating ramp to the material (Figure 4). While the viscosity is expected to continuously decrease upon heating, temporary idleness around 80-100°C corroborates a partial deactivation. A subsequent dramatic increase of viscosity above 140°C indicates a second and total deactivation, which would effectively transform the highly dynamic networks into quasi-permanent networks.



**Figure 4. Evolution of apparent creep viscosity in model network containing 100 ppm  $P_4tBu$  during a 1°C min<sup>-1</sup> heating ramp.**

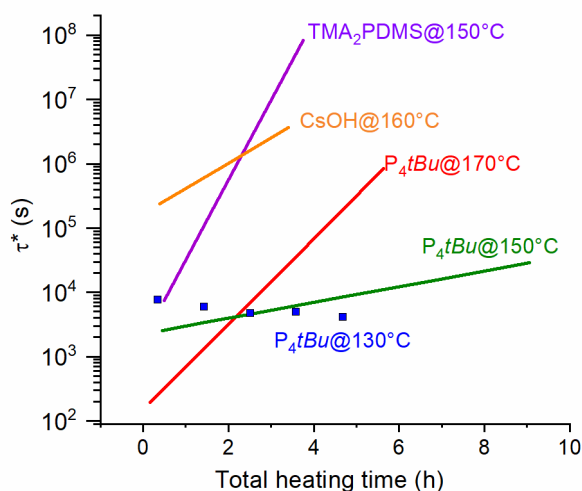
**Deactivation dynamics and modelling.** Further analysis of thermal deactivation in the 130-170°C range was carried out on networks containing 33 ppm of  $P_4tBu$ /Si using repeated stress relaxation cycles (Figure 5). While relaxations at 130°C are slow (ca. 4000 s) but relatively reproducible





**Figure 5.** Repeated stress relaxations (normalized) of model networks containing 33 ppm  $P_4tBu/Si$  at 130, 150 and 170°C. The total heating time for each series is represented by the color scale. Black lines are fits corresponding to a) individual stretched exponential decays, and b,c) general model (eq. 1) accounting for repeated deactivating relaxations.

over 5h, relaxations at 150 and 170°C are initially considerably faster, but slow down significantly over time. Delayed relaxations at 170°C are clearly not representative of classical mono- or stretched exponential decays encountered in dynamic networks,<sup>43</sup> but are likely indicative that the deactivation occurs over similar timescales as the stress relaxation.



**Figure 6.** Evolution of relaxation times at different temperatures in model silicone networks containing 33 ppm of additives. Dots correspond to individual fits while continuous lines correspond to first-order deactivation models (eq 1).

Thus, we derived a low-parameter model for stress relaxations that takes into consideration a first-order deactivation, i.e. that effective relaxation times are increasing exponentially with time:

$$G(t) = G_0 \cdot e^{-\left(\frac{\tau_d}{\tau_0} \left[ e^{-\frac{\Delta t}{\tau_d}} - e^{-\frac{t+\Delta t}{\tau_d}} \right] \right)^\beta} \quad (\text{eq. 1})$$

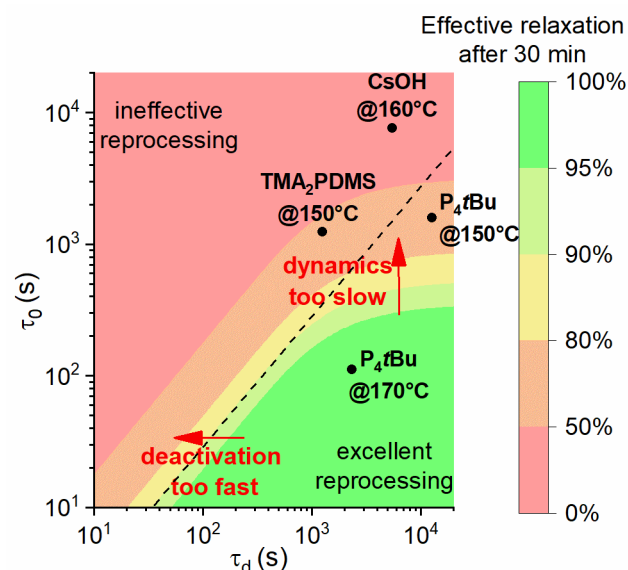
$G_0$  is the network modulus,  $\tau_0$  and  $\tau_d$  are the initial relaxation time and the characteristic deactivation time of the relaxation, respectively,  $\Delta t$  is the time-delay between the initial heating of the sample (start of the deactivation) and each successive stress relaxation experiment,  $\beta$  is the stretch parameter characteristic of the breadth of distribution of relaxation times. Details of derivation of eq 1 and simulations for different sets of values are represented in SI. For each temperature, fitting of all successive stress relaxation data is carried using a single set of  $\tau_0$ ,  $\tau_d$  and  $\beta$  values and fixed  $\Delta t$  parameters using the “Global fit” feature of Origin software (Figure 5). The  $G_0$  parameters are individualized during the fitting to account for small variations of initial moduli.

Given the low amount of fitting parameters ( $\tau_0$ ,  $\tau_d$ ,  $\beta$ ) for such multiple datasets, the fit quality is remarkable and substantiates the validity of the model. As expected, the results indicate that initially, the relaxation times are significantly faster at 170°C than at 130°C. Yet, degradation occurs more significantly at higher temperatures and the situation becomes reversed after about 2h of heating (Figure 6).

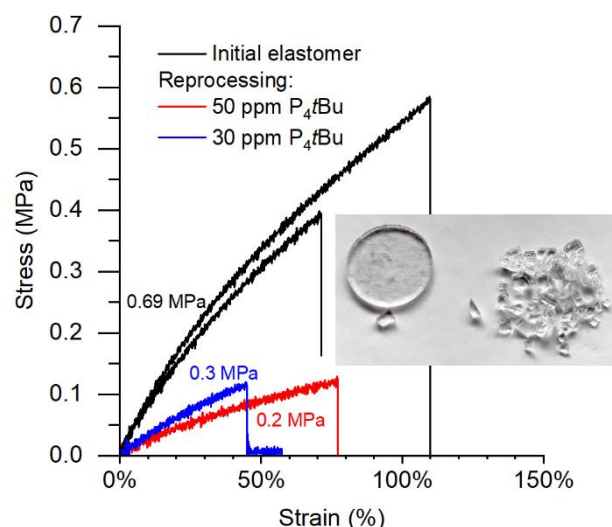
In line with initial studies on model compounds, the deactivation was also studied by rheology for PDMS networks containing 33 ppm/Si of  $TMA_2PDMS$  and  $CsOH$  additives. (See Figure 6 and corresponding sets of stress relaxation in Figure S8) It was found that the TMA additive was initially moderately efficient, but degraded very quickly at 150°C (deactivation time  $\tau_d$  about 20 min). In accordance with the above studies on model compounds,  $CsOH$  shows initially a much lower activity but also deactivates much more slowly ( $\tau_d$  about 1.5 h at 160°C).

**Reprocessability of PDMS elastomers.** The maximal stress relaxation expected during a single step before the deactivation completely transforms the dynamic network

into a permanent network can be determined from eq 1 using  $\Delta t = 0$  s and is strongly driven by the ratio  $\tau_d/\tau_0$ . Figure 7 gives in this way an estimation of the processability window after 30 min of deformation. The values obtained for the different additives at 33 ppm are reported, and indicate clearly that with such concentrations, proper reprocessing within 30 min could only be expected with  $P_4tBu$  at 170°C.



**Figure 7.** Diagram of processability window, displaying the expected amount of relaxed stress after deforming a sample for 30 min, depending on the corresponding initial relaxation time  $\tau_0$  and the deactivating time  $\tau_d$ . The calculation was made with  $\beta = 0.66$ . Experimental values obtained for PDMS samples loaded with 33 ppm of additives are reported.



**Figure 8.** Tensile testing of PDMS elastomers after reprocessing for 30 min at 170°C using 30 & 50 ppm  $P_4tBu$  /Si. Young moduli are reported next to each curve.

The effectiveness of the reprocessing was evaluated by impregnating shredded PDMS elastomer with 30 and 50 ppm  $P_4tBu$ /Si, and mold-pressing the fragments under 40 MPa, for 30 min at 170°C. In absence of additive, only non-cohesive powder is obtained. The sample containing 50 ppm

$P_4tBu$  recovers most of the elongation at break at the expense of a 70% decrease in modulus (Figure 8). In contrast, the sample containing 30 ppm  $P_4tBu$  suffers from a significant decrease of elongation at break and a lower decrease in modulus (~55%).

In view of the very low amount of additives used, such important changes are strongly driven by the topology of the model PDMS networks chosen that feature mainly long linear chains (99 wt%) anchored at extremities by poly-functional crosslinkers. It would be interesting in future developments of siloxane dynamic networks to either promote recoupling of cleaved chains in such topologies, or to focus on different topologies featuring permanent polymer backbones equipped with dynamic siloxane crosslinks.

## CONCLUSIONS

We showed using model compounds that the dynamics of siloxane exchanges are extremely dependent on the environment of the silanolate living chain-ends, and that highly delocalized and hydrophobic cations such as the  $P_4tBu$  phosphazene derivative are extremely active even in low amounts (below 0.1 wt%). When implemented in crosslinked PDMS networks, such siloxane exchanges promote dynamic strand exchanges and stress relaxation. We also show that the silanolate active centers can be lost by two distinct phenomena: i) a partial deactivation around 90°C that we attribute to reactions with impurities and ii) a complete thermal deactivation that occurs above 120°C depending on the additive.

The understanding at the molecular level of such thermal deactivations remains unclear and challenging given the low concentrations of additives involved. We show however that simple rheological experiments (e.g. repeated stress relaxations) and a low-parameter model enables to quantify very easily both the initial dynamics of exchange and the corresponding deactivation time.

In the scope of CANs and more specifically vitrimers, such deactivating relaxations could constitute an interesting alternative against the problematic tradeoff between creep resistance at low temperatures and processability at high temperatures. Activation of the relaxations could for instance be triggered only when needed (e.g. during the recycling or reshaping of the materials by locally adding the additives) and further deactivated by annealing at high temperatures to yield permanent networks.

## ASSOCIATED CONTENT

**Supporting Information.** Experimental details on materials, instrumentation and synthetic procedures of model networks, Additional experimental results and derivation of deactivating stress relaxation models. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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## REFERENCES

- Shit, S. C.; Shah, P. A Review on Silicone Rubber. *Natl. Acad. Sci. Lett.* **2013**, *36* (4), 355–365. DOI 10.1007/s40009-013-0150-2.
- Mazurek, P.; Vudayagiri, S.; Skov, A. L. How to Tailor Flexible Silicone Elastomers with Mechanical Integrity: A Tutorial Review. *Chem. Soc. Rev.* **2019**, *48* (6), 1448–1464. DOI 10.1039/c8cs00963e.
- Yilgör, I.; Riffle, J. S.; Wilkes, G. L.; McGrath, J. E. Siloxane-Urea Segmented Copolymers - 1. Synthesis and Characterization of Model Polymers from MDI and  $\alpha$ ,  $\omega$ -Bis(Aminopropyl)Polydimethylsiloxane. *Polym. Bull.* **1982**, *8* (11–12), 535–542. DOI 10.1007/BF00262932.
- Falco, G.; Simonin, L.; Pensec, S.; Dalmas, F.; Chenal, J. M.; Bouteiller, L.; Chazeau, L. Linear and Nonlinear Viscoelastic Properties of Segmented Silicone-Urea Copolymers: Influence of the Hard Segment Structure. *Polymer* **2020**, *186* (December 2019). DOI 10.1016/j.polymer.2019.122041.
- Zhu, B.; Grassman, M. Silicone Urethane Urea Copolymer and Preparation and Use Thereof. WO2018151780, 2017.
- Mani, S.; Cassagnau, P.; Bousmina, M.; Chaumont, P. Morphology Development in Novel Composition of Thermoplastic Vulcanizates Based on PA12/PDMS Reactive Blends. *Macromol. Mater. Eng.* **2011**, *296* (10), 909–920. DOI 10.1002/mame.201000406.
- Gornowicz, G.; Zhang, H. THERMOPLASTIC SILICONE VULCANIZATES PREPARED BY CONDENSATION CURE. 6,153,691, 2000.
- Stark, F. O.; Falender, J. R.; Wright, A. P. Silicones. *Compr. Organomet. Chem.* **1982**, *2*, 305–363. DOI 10.1016/B978-008046518-0.00016-7.
- Rupasinghe, B.; Furgal, J. C. Full Circle Recycling of Polysiloxanes via Room-Temperature Fluoride-Catalyzed Depolymerization to Repolymerizable Cyclics. *ACS Appl. Polym. Mater.* **2021**, *3* (4), 1828–1839. DOI 10.1021/acsapm.0c01406.
- Okamoto, M.; Suzuki, S.; Suzuki, E. Polysiloxane Depolymerization with Dimethyl Carbonate Using Alkali Metal Halide Catalysts. *Appl. Catal. A Gen.* **2004**, *261* (2), 239–245. DOI 10.1016/j.apcata.2003.11.005.
- Chang, C. L.; Lee, H. S. J.; Chen, C. K. Nucleophilic Cleavage of Crosslinked Polysiloxanes to Cyclic Siloxane Monomers: Mild Catalysis by a Designed Polar Solvent System. *J. Polym. Res.* **2005**, *12* (6), 433–438. DOI 10.1007/s10965-004-1871-1.
- Julian, D. J.; Katsoulis, D.; Link, B. A.; Peitz, T. A.; Zhu, B. METHOD OF RECYCLING SILICONE WASTE WITH THE USE OF ORGANIC POLYMER AND DEPOLYMERIZATION CATALYST. WO 2014/130948, 2014.
- Fouquet, T.; Bour, J.; Toniazio, V.; Ruch, D.; Charles, L. Characterization of Ethanolysis Products of Poly(Dimethylsiloxane) Species by Electrospray Ionization Tandem Mass Spectrometry. *Rapid Commun. Mass Spectrom.* **2012**, *26* (17), 2057–2067. DOI 10.1002/rcm.6317.
- Chakma, P.; Konkolewicz, D. Dynamic Covalent Bonds in Polymeric Materials. *Angew. Chemie - Int. Ed.* **2019**, *58* (29), 9682–9695. DOI 10.1002/anie.201813525.
- Elling, B. R.; Dichtel, W. R. Reprocessable Cross-Linked Polymer Networks: Are Associative Exchange Mechanisms Desirable? *ACS Cent. Sci.* **2020**, *6* (9), 1488–1496. DOI 10.1021/acscentsci.0c00567.
- Zheng, N.; Xu, Y.; Zhao, Q.; Xie, T. Dynamic Covalent Polymer Networks: A Molecular Platform for Designing Functions beyond Chemical Recycling and Self-Healing. *Chem. Rev.* **2021**, *121* (3), 1716–1745. DOI 10.1021/acs.chemrev.0c00938.
- Scheutz, G. M.; Lessard, J. J.; Sims, M. B.; Sumerlin, B. S. Adaptable Crosslinks in Polymeric Materials: Resolving the Intersection of Thermoplastics and Thermosets. *J. Am. Chem. Soc.* **2019**, *141* (41), 16181–16196. DOI 10.1021/jacs.9b07922.
- Cuminet, F.; Caillol, S.; Dantras, E.; Leclerc, E.; Ladmiral, V. Neighboring Group Participation and Internal Catalysis Effects on Exchangeable Covalent Bonds: Application to the Thriving Field of Vitrimers Chemistry. *Macromolecules* **2021**. DOI 10.1021/acs.macromol.0c02706.
- Van Zee, N. J.; Nicolaÿ, R. Vitrimers: Permanently Crosslinked Polymers with Dynamic Network Topology. *Prog. Polym. Sci.* **2020**, *104*, 101233. DOI 10.1016/j.progpolymsci.2020.101233.
- Guerre, M.; Taplan, C.; Winne, J. M.; Du Prez, F. E. Vitrimers: Directing Chemical Reactivity to Control Material Properties. *Chem. Sci.* **2020**, *11* (19), 4855–4870. DOI 10.1039/d0sc01069c.
- Winne, J. M.; Leibler, L.; Du Prez, F. E. Dynamic Covalent Chemistry in Polymer Networks: A Mechanistic Perspective. *Polym. Chem.* **2019**, *10* (45), 6091–6108. DOI 10.1039/c9py01260e.
- Gou, Z.; Zuo, Y.; Feng, S. Thermally Self-Healing Silicone-Based Networks with Potential Application in Recycling Adhesives. *RSC Adv.* **2016**, *6* (77), 73140–73147. DOI 10.1039/c6ra14659g.
- McGregor, R. R.; Warrick, E. L. Treating Dimethyl Silicone Polymer with Boric Oxide, US Patent 2,431,878. 2431878, 1947.
- Xiang, H. P.; Rong, M. Z.; Zhang, M. Q. A Facile Method for Imparting Sunlight Driven Catalyst-Free Self-Healability and Recyclability to Commercial Silicone Elastomer. *Polymer* **2017**, *108*, 339–347. DOI 10.1016/j.polymer.2016.12.006.
- Zhang, H.; Cai, C.; Liu, W.; Li, D.; Zhang, J.; Zhao, N.; Xu, J. Recyclable Polydimethylsiloxane Network Crosslinked by Dynamic Transesterification Reaction. *Sci. Rep.* **2017**, *7* (1), 1–9. DOI 10.1038/s41598-017-11485-6.
- Tran, T. N.; Rawstron, E.; Bourgeat-Lami, E.; Montarnal, D. Formation of Cross-Linked Films from Immiscible Precursors through Sintering of Vitrimer Nanoparticles. *ACS Macro Lett.* **2018**, *7* (3), 376–380. DOI 10.1021/acsmacrolett.8b00173.
- Feng, Z.; Yu, B.; Hu, J.; Zuo, H.; Li, J.; Sun, H.; Ning, N.; Tian, M.; Zhang, L. Multifunctional Vitrimer-Like Polydimethylsiloxane (PDMS): Recyclable, Self-Healable, and Water-Driven Malleable Covalent Networks Based on Dynamic Imine Bond. *Ind. Eng. Chem. Res.* **2019**, *58* (3), 1212–1221. DOI 10.1021/acs.iecr.8b05309.
- Stukenbroeker, T.; Wang, W.; Winne, J. M.; Du Prez, F. E.; Nicolaÿ, R.; Leibler, L. Polydimethylsiloxane Quenchable Vitrimers. *Polym. Chem.* **2017**, *8* (43), 6590–6593. DOI 10.1039/c7py01488k.
- Ishibashi, J. S. A.; Kalow, J. A. Vitrimers: Silicone Elastomers Enabled by Dynamic Meldrum's Acid-Derived Cross-Links. *ACS Macro Lett.* **2018**, *7* (4), 482–486. DOI 10.1021/acsmacrolett.8b00166.
- Hurd, D. T.; Osthoff, R. C.; Corrin, M. L. The Mechanism of the Base-Catalyzed Rearrangement of Organopolysiloxanes. *J. Am. Chem. Soc.* **1954**, *76* (1), 249–252. DOI 10.1021/ja01630a064.
- Osthoff, R. C.; Bueche, A. M.; Grubb, W. T. Chemical Stress-



- Relaxation of Polydimethylsiloxane Elastomers. *J. Am. Chem. Soc.* **1954**, 76 (18), 4659–4663. DOI 10.1021/ja01647a052.
- (32) Kantor, S. W.; Grubb, W. T.; Osthoff, R. C. The Mechanism of the Acid- and Base-Catalyzed Equilibration of Siloxanes. *J. Am. Chem. Soc.* **1954**, 76 (20), 5190–5197. DOI 10.1021/ja01649a076.
- (33) Wright, P. V. Cyclization Equilibrium Constants and the Conformations of Polydimethylsiloxane Chains. *J. Polym. Sci. Part A-2 Polym. Phys.* **1973**, 11 (1), 51–64. DOI 10.1002/pol.1973.180110106.
- (34) Wright, P. ; Semlyen, J. . Equilibrium Ring Concentrations and the Statistical Conformations of Polymer Chains: Part 3. Substituent Effects in Polysiloxane Systems. *Polymer* **1970**, 11 (9), 462–471. DOI 10.1016/0032-3861(70)90051-0.
- (35) Zheng, P.; McCarthy, T. J. A Surprise from 1954: Siloxane Equilibration Is a Simple, Robust, and Obvious Polymer Self-Healing Mechanism. *J. Am. Chem. Soc.* **2012**, 134 (4), 2024–2027. DOI 10.1021/ja2113257.
- (36) Schmolke, W.; Perner, N.; Seiffert, S. Dynamically Cross-Linked Polydimethylsiloxane Networks with Ambient-temperature Self-Healing. *Macromolecules* **2015**, 48 (24), 8781–8788. DOI 10.1021/acs.macromol.5b01666.
- (37) Zheng, N.; Hou, J.; Zhao, H.; Wu, J.; Luo, Y.; Bai, H.; Rogers, J. A.; Zhao, Q.; Xie, T. Mechano-Plastic Pyrolysis of Dynamic Covalent Polymer Network toward Hierarchical 3D Ceramics. *Adv. Mater.* **2019**, 31 (11), 1–6. DOI 10.1002/adma.201807326.
- (38) Saed, M. O.; Terentjev, E. M. Catalytic Control of Plastic Flow in Siloxane-Based Liquid Crystalline Elastomer Networks. *ACS Macro Lett.* **2020**, 9 (5), 749–755. DOI 10.1021/acsmacrolett.0c00265.
- (39) Fuchise, K.; Igarashi, M.; Sato, K.; Shimada, S. Organocatalytic Controlled/Living Ring-Opening Polymerization of Cyclotrisiloxanes Initiated by Water with Strong Organic Base Catalysts. *Chem. Sci.* **2018**, 9 (11), 2879–2891. DOI 10.1039/c7sc04234e.
- (40) Jehanno, C.; Flores, I.; Dove, A. P.; Müller, A. J.; Ruipérez, F.; Sardon, H. Organocatalysed Depolymerisation of PET in a Fully Sustainable Cycle Using Thermally Stable Protic Ionic Salt. *Green Chem.* **2018**, 20 (6), 1205–1212. DOI 10.1039/c7gc03396f.
- (41) Van Herck, N.; Maes, D.; Unal, K.; Guerre, M.; Winne, J. M.; Du Prez, F. E. Covalent Adaptable Networks with Tunable Exchange Rates Based on Reversible Thiol–Yne Cross-Linking. *Angew. Chemie - Int. Ed.* **2020**, 59 (9), 3609–3617. DOI 10.1002/anie.201912902.
- (42) Debsharma, T.; Am, V.; Alicja, A.; Baere, I. De; Paepegem, W. Van; Prez, F. E. Du. Fast Dynamic Siloxane Exchange Mechanism for Reshapable Vitriimer Composites. **2022**. DOI 10.1021/jacs.2c03518.
- (43) Jourdain, A.; Asbai, R.; Anaya, O.; Chehimi, M. M.; Drockenmüller, E.; Montarnal, D. Rheological Properties of Covalent Adaptable Networks with 1,2,3-Triazolium Cross-Links: The Missing Link between Vitrimers and Dissociative Networks. *ACS Appl. Mater. Interfaces* **2020**, 53, 1884–1900. DOI 10.1021/acs.macromol.9b02204.
- (44) Boileau, S.; Illy, N. Activation in Anionic Polymerization: Why Phosphazene Bases Are Very Exciting Promoters. *Prog. Polym. Sci.* **2011**, 36 (9), 1132–1151. DOI 10.1016/j.progpolymsci.2011.05.005.
- (45) Köhler, T.; Gutacker, A.; Mejía, E. Industrial Synthesis of Reactive Silicones: Reaction Mechanisms and Processes. *Org. Chem. Front.* **2020**. DOI 10.1039/d0qo001075h.
- (46) Hupfield, P. C.; Taylor, R. G. Ring-Opening Polymerization of Siloxanes Using Phosphazene Base Catalysts. *J. Inorg. Organomet. Polym.* **1999**, 9 (1), 17–34. DOI 10.1023/A:1021429320083.
- (47) Markó, I. E.; Stérin, S.; Buisine, O.; Berthon, G.; Michaud, G.; Tinant, B.; Declercq, J. P. Highly Active and Selective Platinum(o)-Carbene Complexes. Efficient, Catalytic Hydrosilylation of Functionalised Olefins. *Adv. Synth. Catal.* **2004**, 346 (12), 1429–1434. DOI 10.1002/adsc.200404048.
- (48) Khedaoui, D.; Boisson, C.; D'Agosto, F.; Montarnal, D. Polyethylene Aerogels with Combined Physical and Chemical Crosslinking: Improved Mechanical Resilience and Shape-Memory Properties. *Angew. Chemie - Int. Ed.* **2019**, 58 (44), 15883–15889. DOI 10.1002/anie.201908257.
- (49) Cazacu, M.; Marcu, M. Silicone Rubbers. IX. Contributions to Polydimethylsiloxane- $\alpha,\omega$ -Diols Synthesis by Heterogeneous Catalysis. *J. Macromol. Sci. Part A* **1995**, 32 (7), 1019–1029. DOI 10.1080/10601329508019142.

