Syntheses and supramolecular associations of block and grafted phosphonated- and sulfoned-silicone copolymers†

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This paper presents some studies exploiting the ate-type addition of electron-withdrawing monomers to hydrogenosiloxane groups so as to generate original silicone materials. Two types of monomers were oligomerized onto silicone backbones, namely unsaturated phosphate and sulfone monomers. Phosphonated silicones are thermally more resistant than conventional silicones and can be transformed into amphiphilic polymers after selective ester hydrolysis. Sulfoned silicones generate solid supramolecular elastomers thanks to the strong pseudo-ionic interactions between multiple sulfone groups. Rheology and modulated DSC show a transition around 175 °C, corresponding to the disruption of strongly interacting stacked oligomers. Block copolymers can be reprocessed using a chaotropic salt, whereas grafted copolymers are not reprocessable after solvent removal. These results open new avenues in the generation of silicone block- and grafted-copolymers with unique functionality and properties.

Introduction

Silicones are important elastomeric materials for industry as they cover a large range of properties and application fields, from building, medical, and cosmetic to aeronautical domains. While most elastomers available on the market are filled and chemically crosslinked networks, more and more studies describe the generation of thermoplastic silicone elas-
Another way of doing this is to attach strongly interacting stickers onto the polymer chains by grafting reactions. Advanced materials based on hydrogen, ionic and dative interactions have for instance recently emerged, as reviewed here. In particular, the strong bonds generated by metal ions/cation pairs generally allow the development of interesting mechanical properties, while maintaining a very large elasticity, not attainable by conventional crosslinked elastomers. The main general drawbacks of all these elastomers nevertheless are their limited thermal stability and lack of solvent resistance.

The objective of the present work was to generate new silicone elastomers from simple PDMS functionalized with typically a few strongly interacting groups, using a new functionalization technology. This paper is a follow-up of a prior article, where we described the ate-complex-driven oligomerization of monomers with strong electron withdrawing groups on SiH moieties (Scheme 1A). We previously proposed a mechanism for this new reaction between model silane or siloxane molecules and electron-withdrawing monomers, namely phosphonated and sulfonated monomers (see structures in Scheme 1B).

In the present article, we describe the oligomerization of these functional monomers onto longer silicone polymer chains to generate triblock and comb-like grafted copolymers with original material properties. This is very different from, e.g., aza-Michael or thiol–ene additions, in which only one monomer is added per reactive function (see a brief state of the art on the single functionalization of silicones with phosphonate and sulfone groups below). We first summarize the different conditions of syntheses and chemical characterization of the phosphonated polymers prepared here. We also show briefly how these polymers exhibit interesting thermal properties and can lead to amphiphilic macromolecules. Then we describe the specific case of sulfonated polymers. Since strong and infusible elastomers are formed in most cases, we have characterized these thermoplastic elastomers mostly by physical techniques, namely rheology and electron microscopy. We finally discuss the strong interactions of sulfone moieties and their impact on the microstructuring of the elastomers.

### Rapid survey of phosphonate- and sulfone-modified silicone polymers

This part is not exhaustive but rather summarizes the different approaches and current interest in these functionalized copolymers.

#### Phosphonated silicone copolymers

It has long been known that phosphorus atoms and phosphorus-based groups impart strong thermal and fire resistance to materials. Since silicones are themselves fire-proofing elastomers, the combination of these two chemistries is particularly relevant and was patented in 1996. One simple approach to synthesizing phosphorus-containing silicones is to first prepare functional silanes and then polymerize them into silicones. Hydrosilylation does not proceed with a conventional platinum catalyst. Instead, the phosphorus-based groups can be introduced by different means: reaction between alkylphosphites and chloroalkylamines; a thiol–ene reaction of an allyl or vinyl phosphonate monomer onto a sulphide-based silane or silicone; or the Michael addition of diethyl vinyl phosphonate (DEVP, see Scheme 1B) on aminofunctional silanes. A less common approach is the radical copolymerization of vinyl phosphonate monomers with vinyl trialkoxysilane catalysed by peroxide initiators at high temperature.

After partial or full hydrolysis of the ester groups of the phosphonate moiety, the functional silicones were blended with PEG for biomedical foamy implant applications or grafted to alumina particles as fire-resistant fillers in PMMA composites. In most cases, a strong shift of the TGA curve towards higher temperature was observed when alkylphosphonate groups were introduced, followed by a shift back of the onset temperature when the ester groups were hydrolysed.

#### Sulfoned silicone copolymers

The modification of silicone chains using sulfone groups has long been reported in a few patents, aiming to improve their...
resistance to polar solvents and high temperatures. Berger\textsuperscript{18} has for the first time proposed an exothermic Michael addition between aminopropyltriethoxysilane and divinylsulfone, intended for use as primers between plastic resins and glass sheets. Curtis\textsuperscript{19} and Kanner\textsuperscript{20} synthesized a series of cyclosiloxanes bearing sulfolanloyxalkyl groups, by hydrosilylation of methyl vinyl sulfone and other molecules using chloroplatinic acid as a catalyst at less than 120 °C. Kantor\textsuperscript{21} has made use of a thiol–ene reaction between 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclo-tetrasiloxane (D4) and an alkyl thiol, followed by an oxidation reaction; these have then been engaged in ring opening copolymerization between functional and non-functional cycles.\textsuperscript{22} The properties of the obtained polymers were not described, but it was noted that such polymers would not swell in solvents of interest to the aeronautical industry, such as kerosene.

In the open literature, reports of sulfone-functionalized silicones are scarce. One can notice the significant contribution of the group of Feng that published a series of papers on the synthesis of different types of polymers with sulfone- and siloxane-based backbones (see, e.g., ref. 23 and 24). These are prepared by thiol–ene addition, followed by oxone-based oxidation, then depolymerization into hybrid cycles and finally anionic polymerization. Both sulfone and silicone blocks are sensitive to mild acids and regenerate the starting cyclic monomer. The team of Opris\textsuperscript{25} functionalized some polyvinylmethylsiloxanes with different sulfone and sulfolane groups to prepare polymers that show low conductivity and high permittivity.

A more extensive body of literature has described the generation of grafted and block copolymers made of poly(olefin-sulfone) (POS) and PDMS. These date back to 1991 with the work of McGrath et al.\textsuperscript{26} on polybutylsulfone-\textsuperscript{g}-PDMS as prepared by anionic polymerization, then Bereaa et al.\textsuperscript{27} in 2004 through polycondensation of telechelic oligomers to generate multiple blocks, and Swager et al.\textsuperscript{28} in 2010 who performed click chemistry to produce crosslinked POS-co-PDMS networks. The group of Feng also prepared multiblock copolymers of mixed-sulfone-co-siloxane polymers with PDMS.\textsuperscript{29,30} In most of these studies, the nanostructuration of the copolymers through phase separation of the different blocks was systematically looked at, as well as their degradation by irradiation or using bases with lithographic applications as a systematic target.

**Why and how to study sulfoned silicone polymers**

This study takes its infancy from the useful remark of our colleague Prof. Boutevin concerning the role of sulfone groups as a structuring group in pendant alkyl or fluoroalkyl-functionalized polymers. Corpart et al.\textsuperscript{31} in 2001 showed that introducing a SO\textsubscript{2} rotula in the side groups of a perfluorinated homopolyacrylate allowed ordering and crystallizing C\textsubscript{6}F\textsubscript{13} groups; such structuration does not occur without this sulfone group. Later on, Lee et al.\textsuperscript{32} prepared long alkyl chain-functionalized polysiloxanes. Again, a sulfone rotula allowed the generation of perfectly defined smectic liquid-like crystalline phases in copolymers from C\textsubscript{10} to C\textsubscript{16} side chains; meanwhile, only the C\textsubscript{16} SO\textsubscript{2}-free equivalent polymer was able to partly crystallize into large spherulitic patterns. Clearly, the association of close-enough sulfone groups can induce interesting associative behaviour in silicone polymers.

Another important starting point that allowed the present study is the discovery and use of a chaotrophic salt first applied to carry out silanol polycondensation of PDMSs in bulk.\textsuperscript{33} We found out previously that this complex allows dissolving elastomers strongly crosslinked by physical interactions, e.g., non-soluble perfluorinated hybrid oligo-carboxysiloxanes.\textsuperscript{34} This salt is prepared as a 3/1 molar mixture between trifluoroacetic acid and tetramethylguanidine at 5% in THF. With this tool in hand, we can now manipulate some (but not all) elastomers after drying and/or purification by precipitation (vide infra).

**Experimental part**

**Materials**

B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (Alfa Aesar, 97%), dimethyl vinyl phosphate (DMVP, Aldrich, >95%), and methyl vinyl sulfone (MVS, Aldrich; 98%) were used as received. Diethyl vinyl phosphate (DEVP, Aldrich; 97%) was distilled from CaH\textsubscript{2} under reduced pressure (bp 47 °C/10\textsuperscript{−3} mbar). Toluene was refluxed with sodium for 6–8 h and then distilled under an inert atmosphere. CH\textsubscript{2}Cl\textsubscript{2}, cyclohexane, and tetrahydrofuran were dried and distilled from CaH\textsubscript{2} under an inert atmosphere. All polydimethylsiloxanes were purchased from Gelest and used as received, except for the thiol-functionalized polymer that was obtained from ABCR (see their description in the Table 1 footnote).

**Polymerization procedures**

Polymerization reactions were carried out under an inert atmosphere and at different temperatures, according to the monomer involved. The reactions were carried out in special glass reactors equipped with a Teflon\textsuperscript{®} coated magnetic stirrer bar. Before charging the reactants, the reactors were vacuumed three times and filled with argon. During the first vacuum step, they were heated up to 200 °C. A required amount of B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} was first poured into the glass reactor that was vacuumed without heating for 15–20 min and filled with argon; then, toluene and the monomer were poured into the reactor. The reaction mixture was stirred for a few minutes and then the polysiloxane was added through a syringe at room temperature. After that, the reactor was immediately placed into a temperature-controlled bath (T = 25 °C or 85 °C for sulfone or phosphonated monomers, respectively) and reactions started to occur. After a given time (30 minutes or 5 h for sulfone or phosphonated monomers, respectively), the reaction mixture was poured into a balloon and dried first using a rotary evaporator and then under vacuum until reaching a constant weight.

**Re-precipitation procedure**

Telechelic siloxanes functionalized with oligoDEVP (0.2 g) were dissolved in CH\textsubscript{2}Cl\textsubscript{2} (0.5 ml) and precipitated using
excess ethanol (6–8 mL). A solid product was recovered by centri-
figuregation followed by careful decantation. Finally, the repri-
pitated polymer was dried to a constant weight under vacuum.
A similar procedure was performed for sulfone-modified
copolymers.

**Polymer characterization**

Size exclusion chromatography (SEC) was performed on a
Spectra Physics apparatus with two columns (PL gel, 5, 300
and 500 mm, 100 Å) and one pre-column (PL gel 5 mm guard)
thermostated at 30 °C. The detection was achieved using an
SP8430 differential refractometer and tetrahydrofuran (THF)
was eluted at a flow rate of 1.0 mL min⁻¹. The calculation of
molar mass and polydispersity was based on polystyrene stan-
dards (Polymer Labs, Germany).

¹H NMR spectra were recorded in CDCl₃ at 25 °C on a
Bruker AC-400 spectrometer calibrated relative to the solvent
peak in reference to a tetramethylsilane standard.

Thermogravimetric (TG) measurements were performed on a
TGA51 TA Instrument apparatus operating between 25 and
580 °C (using aluminium pans) under nitrogen at a heating rate
of 20 °C min⁻¹.

PerkinElmer Pyris Diamond equipment was used to
perform differential scanning calorimetry (DSC) measure-
ments. Samples with masses of 12.0 ± 0.5 mg were heated from
25 °C to 275 °C at a rate of 10 °C min⁻¹ under a nitrogen flow (20 mL min⁻¹), followed by an isotherm at 275 °C for
2 min before a cooling ramp at 10 °C min⁻¹ from 275 to 25 °C.
This full procedure was repeated a second time for one sample.

Environmental scanning electron microscopy was performed on an FEI Quanta 200 SEM. The samples were cryo-
factured before analyses. All images were obtained under low vacuum at a voltage of 15.0 kV with a spot size of 2.8 mm and
a working distance of 8.2 mm. Energy-dispersive X-ray (EDX)
measurements were conducted as an integrated tool to deter-
mine the elemental composition of the residue on micro-

**Results and discussion**

Table 1 summarizes all relevant experiments that were chosen
to illustrate the polymerization process and materials associ-
ation. More data are available on the two patents quoted in
this manuscript.
Phosphonated silicone copolymers

As seen in Scheme 1B, syntheses were carried out with dimethyl- and diethyl-vinyl phosphonate monomers (DMVP and DEVP, respectively). Experiments were performed with different Si–H functional polymers, one telechelic (PDMS A: $M_n = 23.5$ kg mol$^{-1}$) and two others with SiH side groups (PDMS B: 5 SiH/chain, $M_n = 5.1$ kg mol$^{-1}$; PDMS C: 12 SiH/chain, $M_n = 10.3$ kg mol$^{-1}$). All experiments were performed in toluene, whereas the solvent of NMR and SEC analyses varied according to the solubility of the final polymers.

The case of dimethyl vinyl phosphonate (DMVP)

Several preliminary experiments on the grafting of DMVP onto the polysiloxane backbone were performed. As shown in Table 1, the grafting reaction of DMVP onto different kinds of polysiloxanes proceeded smoothly. However, the obtained polymers (especially when using polydimethylsiloxanes with 5 and 12 Si–H groups per chain, respectively) were found insoluble in most solvents after precipitation and drying. We did not further characterize these new polymers to focus on DEVP-functionalized polymers.

The case of diethyl vinyl phosphonate (DEVP)

The reaction of DEVP with different PDMSs is characterized by a slower rate and starts at higher temperatures (typically between 75 and 85 °C) than previously shown with model hydrido-siloxane components (PMDS and MD’M). Consequently, it proceeded in a controlled manner, giving modified silicones with a high conversion of DEVP (see Table 1). The products were typically recovered as a very viscous liquid or a gel (the latter when PDMS C with a larger number of Si–H groups was used). The final polymers prepared with DEVP were characterized by NMR (Fig. 1) and SEC (see traces in Fig. S1†).

Organophosphoric fragments introduced in polymer chains are known to considerably increase the flame resistance and thermal stability of the resulting material. Indeed, we checked that the PDMS functionalized with oligoDEVP shows considerably higher thermal stability in comparison with the original PDMS with larger residues at high temperature. Typically, the main peak of degradation shifts from basically 280 °C to 410 °C while adding phosphorus units to the silicone (Fig. 2). The thermal resistance of the present polymers is higher than those of the previously reported phosphonated silicone copolymers (10 wt% loss at about 400 °C against 450 °C in this study), obviously thanks to the oligomeric nature of grafted chains here.

Phosphonic acid-based polymers are known for their interesting applications such as in antiscaling, anticorrosion or ignifugation, as well as their proton-conducting capability. For this last purpose, we studied the hydrolysis of the DEVP-grafted polysiloxane (see Scheme 2 for conditions and reaction). Fig. 1B shows a zoomed-in view of the $^1$H NMR spectrum of pristine and hydrolysed products around the peak corresponding to the phosphate groups of the oligoDEVP fragment centred around 4.1 ppm. The peak of the protons of ethyl groups fully disappears, confirming that the ester hydrolysis procedure is complete. Note that the thermogravimetric analysis of hydrolyzed samples showed a noticeable drop in thermal stability with the onset of decomposition at 200 °C (not shown). This agrees with what was observed previously for monomolecular phosphonated side groups. In a patent, we have described the use of DEVP-grafted copolymers as a surface modifier of silica to prepare composite materials.

![Fig. 1](image)

(A) Full $^1$H NMR spectrum of PDMS-co-DEVP (run 4, Table 1); peaks assigned to toluene (solvent of synthesis) and ethanol (reprecipitation solvent) are marked with an asterisk; the monomer is not present here. (B) Zoomed-in view between 3.4 and 4.5 ppm of spectra before (bottom) and after (top) ester hydrolysis, showing the disappearance of the ethylene group of the ester moieties.
membranes by simple casting. The films were hydrolysed in concentrated HCl solution (12 M) to be later used in fuel cell applications.36

Sulfoned silicone copolymers

We performed a large variety of experiments with different silicone polymers and methyl vinyl sulfone (MVS) or allyl phenyl sulfone (APS) (see structures in Scheme 1B). We report here only the experiments that led to characterization (other examples are available in a patent that we published on the topic).37

Here, we used mainly three silicones: the same telechelic polymer as described before with a molecular weight of about 23.5 kg mol\(^{-1}\) and a polydispersity index of 1.5 (PDMS A); a copolymer of a much larger molar mass, 55 kg mol\(^{-1}\), with an average of 2.3 pending Si–H groups per chain (PDMS D) and a copolymer of 103 kg mol\(^{-1}\) with an average number of 16 SiH groups per chain (PDMS E). The reason for those two last choices lies in the necessity to use large molar mass polymers to generate mechanically interesting materials (\textit{vide infra}).

Synthesis and visual aspects of the copolymers

All the conditions for the synthesis of copolymers presented here are summarized in Table 1. Experiments were performed in a solvent, toluene, in sealed tubes, typically with an excess of monomer and a substantial amount of catalyst (see the footnotes of Table 1). After a short inhibition period, polymerization took place rapidly with no gas released. In contrast to phosphonated monomers, the oligomerization of sulfone monomers proceeded readily at room temperature, generating a slight exotherm. With PDMS A, the medium became viscous with time, whereas with PDMS D, we observed a clear gelling of the medium, for both MVS and APS monomers.

Fig. 3 shows some samples obtained in this study after precipitating the polymers and removing the solvent. From the original oily PDMS A (Fig. 3A), one generates gums (Fig. 3B) that are visually highly elastic (Fig. 3C). Gums obtained from MVS and PDMS A are easily hand-processable (Fig. 3D-left), whereas grafted copolymers do not redissolve with the chaotropic salt.33 APS-based polymers, whether from telechelic PDMS A (Fig. 3D right) or from PDMS-co-PHMS D (Fig. 3E), are non-deformable elastomers that cannot be redissolved once dried, even after adding large contents of chaotropic salt solution in THF.

We did not succeed in carrying out NMR measurements throughout this study, because the chaotropic salt is not efficient in deuterated solvents. HR-MAS analysis of the copolymers was not conclusive either (see an example extracted from our patent in Fig. S2†). We could thus neither determine the conversions in monomers nor analyse the grafted oligomers’ DP. We infer from the previous model study\(^9\) that oligomers of typically 3 to 4 units are attached to the SiH groups of MVS and APS, respectively (see Scheme 1).

SEC analyses of the PDMS-co-o(MVS) triblock copolymer

We confirmed by SEC the behaviour of the telechelic polymer functionalized with oligo(MVS), which is soluble in THF (run 9, Table 1). The results are given in Fig. 4. Clearly, the way the polymer is processed has a strong influence on the supramolecular associations and thus the molar mass, as given by SEC. The polymer solubilized in THF in the presence of a chaotropic salt\(^33\) gives a molar mass very close to that of the starting PDMS-co-PHMS, as expected from the few sulfone molecules attached to the backbone. Meanwhile, after precipitation in methanol, the apparent molar mass doubled. By gently evaporating the sample and re-dissolving it in THF, even larger molar masses are obtained (about 5 times the actual value). This demonstrates that the supramolecular associations of sulfones

![Scheme 2](image-url)  

**Scheme 2** Hydrolysis conditions of DEVP-grafted PDMS to obtain oligo(phosphonic acid)-based copolymers.
work even in the presence of solvent and depend strongly on the way polymers are isolated.

**Thermal analyses**

To remove any trace of monomers, we first solubilized the polymers, treated them with a chaotropic salt and reprecipitated them a few times to achieve complete purification. Thermal analyses were performed using a modulated DSC operating at 20 °C per minute, making 4 ramps of temperature, two rising and two decreasing ramps between 25 and 275 °C. Fig. 5 shows two thermograms of functional polymers, namely one with PDMS A and APS (run 12, Table 1), for which the full analysis is reported (Fig. 5A), and polymer D functionalized with MVS and APS (runs 10 and 12, Table 1, Fig. 5B). All copolymers show a clear transition at 170 °C. This transition appears only during the first ramp, a signature of physical interactions; indeed, these do not have time to form back to show up on the second rising ramp and further ramps. It is thus tentatively assigned to the debonding of the sulfone complexes (*vide infra*). Note that we did not perform low-temperature ramps to highlight other thermal transitions of the copolymers (*T_g*, *T_f* and *T_c*). From the literature, it is known that in block copolymers, these appear at similar temperature values than for conventional (see, e.g., ref. 24).

We also examined the TGA of the raw sulfoned silicone (PDMS A with MVS and APS, Fig. 6). The sulfone polymers are less sensitive to temperature degradation than the original PDMS, with no residue at 600 °C. This is relevant given the fact that, on one hand, Si–H groups can accelerate polymer degradation by backbiting and, on the other hand, sulfone moieties provide some thermal resistance to the materials, as noticed in the literature survey presented before.

**Microscopy observations**

We wanted to confirm here that a phase separation in the copolymer was responsible for the solidification of the materials. We analyzed both MVS- (run 8, Table 1) and APS- (run 12, Table 1) comb-like grafted copolymers first on an environmental SEM/EDX apparatus (ESEM), which allows working under low vacuum and does not require that the
sample be metallized. The APS-based sample was also characterized by a more conventional but very powerful SEM, which requires metallization with platinum and operates under very low vacuum (then removing any traces of solvents from the sample). A compilation of these different photographs is given in Fig. 7.

The ESEM gives similar photographs for MVS- and APS-functionalized materials, namely a silicone matrix on which small water droplets are regularly distributed on the surface of the material. These are located on the polar phase of the copolymer, i.e., most likely on clusters of oligosulfones. Droplets on the APS-based copolymer seem to be smoother, but are basically of similar sizes (from 1 to 10 μm) and distribution (droplets are separated by spaces of about 20 to 50 μm). By EDX analysis on the matrix and the location of the droplets, we observed that the clusters topped with water effectively contain the sulfone oligomers with some fluorine inside (provided by the catalyst, see Scheme 1), whereas the rest of the matrix is only made of silicone (Fig. 7, insets D and F). It is remarkable that so many clusters appear in the ESEM image with such a regular distribution when considering the low contents of sulfone moieties that are grafted on the silicones (less than 1% in most cases).

To confirm the fact that water aggregates on the polar clusters, we performed a conventional SEM analysis (Fig. 7G and H). In this case, the vacuum is so high that all traces of volatile molecules, including solvents, are removed. We observed quite different pictures in this case, with smooth surfaces. Finally, note that the MVS triblock copolymer only gave neat films in ESEM without any particular structuration (Fig. S3†).

**Rheology of copolymers**

Samples of gums functionalized with MVS were placed into two plates on a rheometer to measure the different moduli of the samples at different temperatures. Fig. 8A shows the resulting curves for the triblock copolymer (PDMS A, run 8, Table 1) and the comb-like grafted copolymer (PDMS E, run 11, Table 1) functionalized with MVS. Both copolymers are solid, with $G'$ systematically above $G''$ over a wide range of temperatures.

On the other hand, the content of functional groups and the location of the oligomer moieties have a strong effect both on the intrinsic values of the moduli and their variation with frequency. The triblock copolymer ‘melts’ at high temperature, typically above 175 °C (Fig. 8B). Note that this relaxation is not accompanied by the homogenisation of the material, because even when sulfones do not interact physically anymore, the corresponding grafted oligomers are still not compatible with
Fig. 7 SEM analyses of PDMS D silicone oil functionalized with MVS (top line) and APS (bottom line). (A, B, C and E) photographs from ESEM apparatus; (D and F) EDX analyses of the spots in the photographs (C) and (E); (G and H) photographs obtained with a conventional SEM after metallization. Scales are given in the photographs.

Fig. 8 (A) Elastic moduli (in red) and viscous moduli (in blue) for the MVS-functionalized copolymers generated from PDMS A (squares, at RT) and PDMS E (stars, measurement done in this case at 200 °C); variation of tan δ (at 4 different frequencies) versus temperature of measurement for the copolymer from PDMS A (B) and from PDMS E (C). The dashed–dotted line on graph (B) represents the 175 °C isoline. (D) Evolution of tan δ = f(ω) at different temperatures (from 150 to 220 °C, top to bottom curves) for the comb-like grafted copolymer. (E) Evolution of the frequency at the maximum of tan δ as a function of the temperature of analysis for the comb-like grafted copolymer.
PDMS and remain clustered. However, above this temperature, it is easy to process the material by extrusion (not shown).

The situation is different for the comb-like grafted copolymer that strengthens with temperature (Fig. 8C). However, when plotting tan δ as a function of frequency for increasing temperatures, a bell curve is obtained (Fig. 8D); the frequency at which the maximum tan δ is picked shifts above 175 °C (Fig. 8E). This is an indication that the strongly functionalized material also phase-separates and restructures at high temperature.

### Insight into the specific interactions of sulfones

Strong dipole–dipole interactions between the sulfone groups are known and ascribed to their high dipole moment (4.49 D). Evans et al. have also shown that the strong planar dipole moment (1.69 D) and the spatial arrangement of sulfone groups (O=S=O angle of ≈109°) induce a preferred orientation on neighboring molecules with pseudo-ionic interactions (Scheme 3A).

As we have shown in our previous study, the ate-complex reaction of sulfone monomers on Si–H moieties proceeds through typically 3 to 4 additions. Among other popular techniques of functionalization, namely Michael addition of methylvinylsulfone and divinylsulfone, as well as thiol–ene reaction and oxidation, none of these were reported to give methylvinylsulfone and divinylsulfone, as well as thiol–ene polyaddition (Scheme 3B). When precipitating and drying the polymer, the polar phase demixes and forms clusters in the material that are hardly broken without the help of the chaotropic salt in THF, coming back to block copolymer ‘unimers’ (Scheme 3C).

By DSC and rheology, the temperature at which sulfone pairs show debonding has been estimated to be 175 °C. Such a value is in line with the literature values of closely related studies, where sulfone groups associate. For instance, Du Prez et al. have prepared polysulfide polymers using an AB monomer thiol–ene polyaddition. After oxidation to sulfone, the new polymer shows a transition at 175 °C ascribed to its melting point. In previously related sulfone-rotula work, in addition to the crystallisation of perfluorinated groups, a second transition was observed at 179 °C. We have also shown that telechelic PEG polymers terminated by sulfone-co-phosphonic acid groups exhibit a transition as determined by DSC at 169 °C.

### How many aligned sulfone groups are needed for polymer structuration?

In the course of this study, we employed a different chemistry to prepare a comb-like grafted silicone copolymer with bis-sulfone groups (see Scheme 4). We first performed the radical

Some authors have proposed that sulfone complexes would crystallize after pairing [e.g. ref. 41]. We have performed SAXS experiments on the MVS-grafted copolymer and did not observe any transitions, before and after rheological analysis at high temperature (see Fig. S4†).

### Impact of the microstructuration of copolymers on materials properties

In our experiments, we can distinguish different categories of materials, according to the location of the sulfone oligomers (at chain ends or grafted to the chains) and the nature of the monomers (MVS and APS). Telechelic Si–H silicones lead to triblock copolymers after modification with short oligosulfone external moieties that can be further characterized. Copolymers with pendant side chains were found to be neither soluble nor manipulatable, even under heat, so we do not consider these in the following discussion.

Block copolymers made from MVS are soluble in THF. Their measured molar masses are directly related to the way they were recovered. The polymer chains elongate through the pairing of oligo(MVS)s that however do not clusterize (Scheme 3B). When precipitating and drying the polymer, the polar phase demixes and forms clusters in the material that are hardly broken without the help of the chaotropic salt in THF, coming back to block copolymer ‘unimers’ (Scheme 3C).

In the course of this study, we employed a different chemistry to prepare a comb-like grafted silicone copolymer with bis-sulfone groups (see Scheme 4). We first performed the radical...
monoaddition of MVS to a PDMS grafted with thiol moieties, i.e., 4–6% mercaptopropylmethyl siloxane-dimethylsiloxane copolymer with $M_n = 11$ kg mol$^{-1}$ ($D = 1.81$). The use of an equimolar ratio of MVS to –SH groups produced the expected initial monoadduct, with some low molecular weight by-products, which are attributed to low molecular weight oligomers (see SEC traces in Fig. S5A†). After extraction of the oligomers by reprecipitation, the $^1$H NMR spectrum shows that the thiol groups were all functionalized (see Fig. S5B†).

The oxidation of the sulfide group using bis(monoperoxypthalate) magnesium hexahydrate (MMPP) as an oxidizing agent was then carried out to produce the bis-sulfone polymer.41 After drying the solvent, the obtained material was solid, very close to those prepared using the ate-complex-mediated process, which we could not characterise anymore by NMR. This 2-step molecular reaction thus allows the gene-

The ate-complex reaction allows the preparation of new types of functional triblock or comb-like grafted silicone copolymers with enhanced thermoplastic properties brought about by multiple functional groups. The described materials are thermally stable, which is generally an initial requirement for silicone materials for their further applications. Supramolecular materials grafted with oligosulfones are solids in a full temperature range up to 220 °C. Finally, the possibility to structure the chains simply by introducing bis-sulfone groups opens new areas for physically crosslinking other conventional polymers.

Conclusions

The ate-complex reaction allows the preparation of new types of functional triblock or comb-like grafted silicone copolymers with enhanced thermoplastic properties brought about by multiple functional groups. The described materials are thermally stable, which is generally an initial requirement for silicone materials for their further applications. Supramolecular materials grafted with oligosulfones are solids in a full temperature range up to 220 °C. Finally, the possibility to structure the chains simply by introducing bis-sulfone groups opens new areas for physically crosslinking other conventional polymers.

Author contributions

Conceptualization, F. G.; methodology, E. P., E. H. G., and S. V. K.; validation, C. L., P. L., I. V. V., and C. J. D.; formal analysis, E. P., S. V. K. and F. G.; writing – original draft preparation, E. P. and S. V. K.; writing – review and editing, F. G.; supervision, F. G.; project administration, F. G.; funding acquisition, F. G. All authors have read and agreed to the published version of the manuscript.

Data availability

The data that support the findings of this study are available from F. Ganachaud but restrictions apply to the availability of these data, which were used under the license for the current study, and so are not publicly available. Data are however available from the authors upon reasonable request and with the permission of CNRS.

Conflicts of interest

There are no conflicts to declare.

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References

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