Hybrid organic-inorganic polydimethylsiloxane–vanadium–oxo materials crosslinked at the molecular level

Bruno Alonso, Jocelyne Maquet, Bruno Viana and Clément Sanchez*

Laboratoire de Chimie de la Matière Condensée (CNRS UMR 7574), Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris, France

L e t t e r

New hybrid materials made of dimethylsiloxane oligomers (linear and cyclic species) crosslinked at the molecular level by $O=V(O-)_3$ units with a very high degree of homogeneity and dispersion, even for a V : Si molar ratio of 10%, have been synthesized and characterized mainly by ^{29}Si and ^{51}V MAS NMR, DSC and DMA. The structure of these hybrids is very different from those proposed for other dimethylsiloxane–transition metal oxide systems. These dimethylsiloxane–vanadate copolymers exhibit higher glass transition temperatures than is usual for PDMS, as well as a very sharp variation of the loss factor tan δ. These hybrid materials exhibit, at low temperature, a strong phosphorescence usually associated with a ligand-to-metal charge transfer process.

It is a practical goal in the area of polymers to provide an easy adjustment of the mechanical properties. For elastomers, an internal mechanical reinforcement is usually obtained by incorporating high surface-to-volume interactive inorganic fillers. Conventional filler blending under high viscosity conditions usually leads to particle agglomeration, which diminishes polymer–filler interactions. The various characteristics of the sol-gel chemistry (metallo-organic precursors, organic solvents, low processing temperatures, mixing at a molecular level) can provide several opportunities to overcome these problems by reaching a nanometric homogeneity.[1] For many years metallo-organic precursors such as metal alkoxides have been used to produce, *via* hydrolysis-condensation reactions, oxo–metallic species that act as crosslinking reagents for many polymers and for polydimethylsiloxane (PDMS) in particular.[1]

Wilkes *et al.*[2a] as well as Sur and Mark[3a] developed simultaneously a new kind of composite material incorporating pre-formed polymeric materials with metal oxo polymers made by a sol-gel process. They reported that the condensation *via* sol-gel reactions between silanol or alkoxysilyl terminated telechelic polydimethylsiloxane polymers with tetraethoxysilane (TEOS) leads to materials with improved and modulable mechanical properties. When the hydrolysis-condensation rates of the precursor of the inorganic charge are controlled, the condensation between silanol terminated PDMS and silicate species leads to hybrid nanocomposites from which no micronic phase separation is detected.[2,3] These silica filled PDMS elastomers contain particles having an average diameter smaller than 100 Å, a relatively narrow size distribution and they present only little agglomeration. The silica network is more or less fuzzy depending on the pH used for hydrolysis. Moreover, HCl catalyzed PDMS–TEOS elastomers exhibit flexibility, gelation point and elongation at break properties that can be tuned with the acid content.[2b]

Another approach is to generate *in situ* both polydimethylsiloxane and metal oxo species from the hydrolysis and condensation of molecular precursors.[4] These siloxane-oxide hybrid compounds have been synthesized by the hydrolysis-condensation of diethoxydimethylsilane (DEDMS) and various metallic alkoxides, $M(OR)_n$ (M = Si, Ti, Zr, Al).[4a] This approach allows the mixing of inorganic and organic components in virtually any ratio to obtain the targeted properties, making these hybrid nanocomposites extremely versatile in their composition, in their processing and in their optical

and mechanical properties. Many of these polydimethylsiloxane–metal oxide materials have been described as copolymers made of D ($-O-SiMe_2-O-$) and Q ($SiO-_4$) species, which act as crosslinking agents,[4b] or as nanocomposites made of metal oxo polymers linked to polydimethylsiloxane chains, most likely through $M-O-Si$ bonds (M = Ti, Zr, Al).[1c,4]

The degree of phase dispersion of the transition metal in silica or organosilicon oxide based matrices depends strongly on the nature of the metal and on the M : Si ratio. When M = Ti or Zr, transparent polydimethylsiloxane–metal oxide materials can be easily processed in a M : S composition ratio ranging from 10% to 30%. The resulting polydimethylsiloxane–titanium oxide or polydimethylsiloxane–zirconium oxide hybrids can be schematically represented in Fig. 1(a).[4]

Another interest of materials containing transition metal oxo species is due to the possibility of modifying the refractive index or of varying their oxidation state, leading to optical, electronic, magnetic or catalytic properties.[5] For catalytic purposes, transition metal atoms (Ti^{IV}, V^V) have been dispersed at the molecular level in silicon oxide based matrices but only when the M : Si composition remains lower than 1%.[6] Another possibility is to increase tremendously the surface area through templated growth processes. The resulting mesoporous oxide networks can accommodate a high degree of dispersion, even for higher levels of doping.[7] However, in the bulk it is a difficult task to reach an atomic dispersion level of a transition metal inside silicon oxide matrices for high M : Si concentrations.
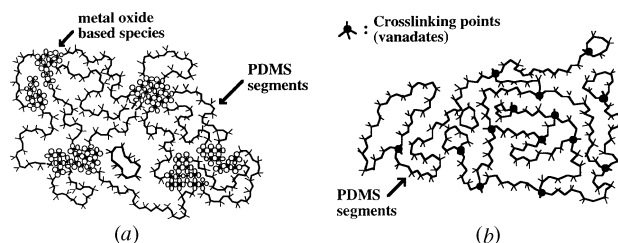

Fig. 1 Schematic representation of the structure of polydimethylsiloxane–metal–oxo hybrid materials (a) M = Ti, Zr, (b) M = V

Using a vanadium oxo–alkoxide precursor such as monomeric vanadium *tert*-amyloxide [VO(OAm^t)$_3$] as the inorganic crosslinking agent and DEDMS as the siloxane precursor, well-dispersed vanadate units in a perfectly defined siloxane environment can be obtained, even with a V:Si molar ratio up to 10%. This communication describes the synthesis and characterization of these new hybrids. Their interesting optical and mechanical properties are also discussed.

The hybrid gels were prepared through the hydrolysis and condensation of DEDMS and VO(OAm^t)$_3$. The two alkoxide precursors were mixed without any solvent dilution (in a molar ratio [V]/[Si] = 0.1) for a few minutes by magnetic stirring. Demineralized water (pH = 6.5) was then added with the hydrolysis ratio [H$_2$O]/[Si] = 1. After water addition the system is diphasic and upon stirring an orange–red fuzzy precipitate starts to appear. The orange–red color of the kinetically formed solid is characteristic of vanadium(v) oxo–alkoxo species in which vanadium is in a distorted square pyramidal environment.[8] This homocondensation of vanadium is confirmed by the 1D–2D ^{51}V NMR experiments performed immediately after water addition, which show the presence of many μ^2—O—V bridges between vanadium atoms.[9a]

After ten minutes of fast stirring, the precipitate is dissolved and the sol turns monophasic and colorless. At this stage, all vanadium atoms are in a four-fold coordination as shown by liquid ^{51}V NMR measurements.[9b] This return of vanadium(v) to the four-fold coordination points out a strong affinity of vanadates towards solvolysis reactions with dimethylsiloxane species.[9a,9c] This phenomenon is not observed when similar reactions are performed with titanates or zirconates and siloxane species.

The resulting sol is aged for 24 hours and then poured into an open petri vessel. Transparent and macroscopically homogeneous casted xerogels are obtained after two weeks of drying in the dark. The hydrolysis and condensation reactions are achieved during the drying step, which is performed in moist air. Chemical analysis performed on the hybrid xerogels indicates that the V:Si molar ratio is 0.1. Moreover, ^{1}H MAS (magic angle spinning) NMR experiments performed on the xerogel exhibit only the characteristic resonances (δ ^{1}H = 0.1 and 0.3) of methyl groups directly bonded to silicon nuclei, thus evidencing the removal of all alkoxy groups (ethoxy, *tert*-amyloxy).

^{51}V and ^{29}Si MAS NMR spectra of the xerogels are respectively reported in Fig. 2(a) and 2(b). The ^{51}V MAS NMR spectrum [Fig. 2(a)] exhibits three main resonances at -736 (85%), -727 (13%) and -705 (2%) ppm. Taking into account the well-documented literature concerning ^{51}V NMR data of vanadium oxo species, these three resonances can be assigned to different O=V(OSiMe$_2$...)$_3$ in which the vanadium atoms have a pseudo-tetrahedral environment.[9b,10] The two weaker signals are probably due to vanadium atoms located in heterocyclic structures, which generate a more strained environment.[10]

The ^{29}Si NMR spectrum [Fig. 2(b)] exhibits four main resonances. The first three resonances located at -21.9 (32%), -20.8 (30%), and -19.5 (3%) ppm can be assigned to D$_2$ units (SiMe$_2$—O—SiMe$_2$—O—SiMe$_2$) in PDMS species: these are linear or cyclic, with or without vanadium atoms as second metallic neighbors (V—O—SiMe$_2$—O—SiMe$_2$—O—SiMe$_2$). The fourth resonance is located at -11.0 ppm (35%). This kind of resonance in the D$_1$ region is generally observed upon hydrolysis of DEDMS in the presence of other transition metal alkoxides [M(OR)$_n$ M = Ti, Zr]. It was assigned to M—O—SiMe$_2$—O—SiMe$_2$ D$_1$ units.[4b] Moreover, the rectangular shape observed for this resonance in the present example is typical of a blurred octuplet resulting from a scalar coupling ^3J Si-V of about 11 Hz between ^{51}V ($I = 7/2$) and ^{29}Si ($I = 1/2$) nuclei. Such a broad octuplet is clearly observed
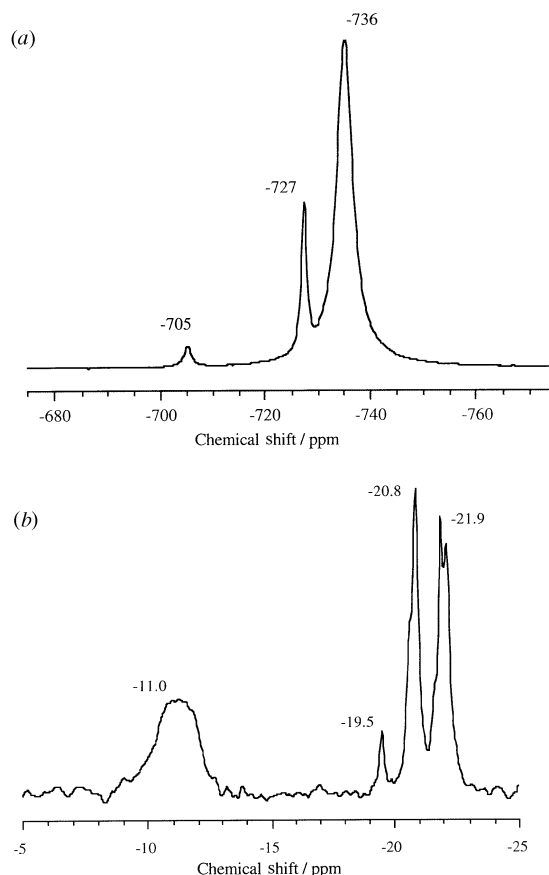

Fig. 2 MAS NMR spectra of the polydimethylsiloxane–vanadium–oxo materials. (a) ^{51}V, VOCl$_3$ reference, 78.9 MHz, spinning at 10 kHz, one-pulse sequence, 1500 scans, 0.5 s of recycling delay; (b) ^{29}Si, TMS reference, 59.6 MHz, spinning at 5 kHz, one-pulse sequence with proton decoupling during acquisition, 1536 scans, 15 s of recycling delay

in the ^{29}Si NMR spectra of reference compounds such as VO(OSiMe$_3$)$_3$.[11] Therefore, the fourth resonance can be assigned to D$_1$ units bonded to the vanadium oxo species V—O—Si(CH$_3$)$_2$—O—SiMe$_2$, confirming the linkage of vanadium and silicon atoms through oxo bridges.

No evidence of the presence of the oxo bridges V—O—V was found by either ^{51}V or ^{17}O NMR experiments, confirming that all vanadium atoms are sequestered at the molecular level by dimethylsiloxane species. Furthermore, in the gel state a ^{17}O NMR resonance located at 1160 ppm, characteristic of the oxygen of the vanadium—oxygen terminal double bonds V=O,[12] was also observed.[9a]

All this data confirm the sequestering of all vanadium(v) in a pseudotetrahedral O=V(O—)$_3$ coordination. The structure of these hybrids made from dimethylsiloxane oligomers (linear and cyclic species) crosslinked at the molecular level by O=V(OSiMe$_2$...)$_3$ units is schematically represented in Fig. 1(b). The whole polymeric structure is then quite different from those proposed for the other dimethylsiloxane–transition metal oxide systems [Fig. 1(a)].[1c,4] Both optical and mechanical properties of these new hybrids have been investigated.

Emission properties of vanadium oxo species in a distorted tetrahedral ligand field are strongly related to many of their interesting catalytic properties.[6a] A number of photochemically induced transformations such as the photooxidation of CO, the photoisomerisation of butene and the photopolymerization of acetylene are catalyzed by discrete oxovanadium centers in a pseudotetrahedral coordination environment that are bound to the substrate.[13] Many of the observed photochemical reactions are associated with particular excited state properties characterized by the presence of a

long-lived phosphorescence.[13] The emission spectra of the hybrid xerogel have been recorded under a 355 nm pulsed excitation coming from the third harmonic of a Nd:YAG laser in a temperature range of 45–300 K.

The emission spectra recorded at two different temperatures (45 and 77 K) are presented in Fig. 3. The position of the maximum of the emission band is located at 530 ± 5 nm, a value close to those reported for vanadium species in vanadates[14] or for pseudotetrahedral O=V(O—)$_3$ units grafted in different metal oxide based matrices.[15] The observed emission has been classified as phosphorescence since the excited state is a triplet and the fundamental state is a spin singlet.

Any variation in the position of this maximum is observed with a temperature decrease, but at low temperature it is possible to observe several transition bands, as emission only occurs from the zero phonon energy level of the triplet state. The resolution of these transitions is blurred, probably because of the presence of several vanadium centers in different VO(O—Si)$_3$ environments, as evidenced by the [51]V MAS NMR spectra (vide supra). From the derivative of the emission spectrum recorded for the hybrid xerogel, the splitting observed between the different vibrational bands was found to range between 900 and 1000 cm^{-1} with an accuracy of ±50 cm^{-1}. The separation between these bands has been associated with the energy gap between the different vibronic levels in the ground state.[13–16]

Based on the fact that the energy gap between the vibronic transitions is about 1000 ± 50 cm^{-1}, in agreement with the vibrational energy of the surface V=O bonds obtained from IR measurements, it was proposed in a first model that the photon energy associating the ground and the first excited state are both mainly localized on the short vanadyl V=O bonds.[13, 15] As a consequence, the emission was assigned to a reverse ligand-to-metal charge transfer (LMCT) process localized on the vanadyl groups. In these compounds, the LMCT process is usually explained as the transfer of one electron from the terminal oxygen orbitals to the vanadium(v) orbitals, leading to further reduction of the metal atom, although it has been theoretically described for tetrahedral vanadates as a rearrangement of the electron density both at the oxygen and vanadium with a small increase in the d orbital population.[17]

A recent study based on absorption-emission, Raman and polarization anisotropy measurements performed on O=V(O—SiO$_3$...)$_3$ species dispersed in a silica gel has demonstrated that, in fact, the long-lived vibronically structured emission of VO(O—)$_3$ species (phosphorescence) located at about 500–550 nm can be assigned to an $^3E \rightarrow {}^1A_1$ transition from the e antibonding orbital back to the a$_2$ nonbonding orbital $[(a_2)^1(e*)^1] \rightarrow [(a_2)^2(e*)]$.[16] Contrary to the conventionally accepted first model, the vibronic progression (of about 950 cm^{-1}) in the phosphorescence band was assigned

to a V—O stretch involving the basal plane oxygen atoms.[16]

As V—O bonding is affected by an electron transfer, the charge transfer mechanism is strongly temperature dependent. For instance, the area of the emission spectrum is divided by a factor six when the temperature of the hybrid sample is increased from 45 to 77 K. At 120 K, the emission vanishes, indicating that quenching mechanisms are important. The luminescence decay profiles have been recorded with an intensified optical multichannel analyser at 49 and 77 K. The decay profiles are always nonexponential at the short time values, probably due to concentration quenching processes. This observation could be related to slightly different vanadium environments in the siloxane matrix. Fitting the measured decays with a sum of two exponentials, long decay times of 178 μs and 1.36 ms were found at 77 and 49 K, respectively. These values are shorter than those reported for vanadium(v) oxo species dispersed in silica matrices,[13–16] suggesting also an important quenching mechanism.

Differential scanning calorimetry (DSC) measurements were performed on hybrid xerogels from 77 K up to room temperature. The heating rate was 20 °C min^{-1}. The DSC traces exhibit two thermal phenomena. The first one is a well-resolved glass transition associated with a variation of the heat capacity of 0.41 J °C^{-1} g^{-1}. The corresponding glass transition temperature is −96 °C. A quantitative argument about the degree of phase segregation of the PDMS soft segment is possible by measuring the heat capacity change, ΔC_p, at the glass transition. The highest reported value of the heat capacity change ΔC_p per gram of pure PDMS is 0.42 J °C^{-1} g^{-1},[18] a value very close to the one measured for these hybrids made with polydimethylsiloxane species crosslinked by VO(O—)$_3$ units. This result suggests that in these hybrids all the segments participate in the glass transition.

The second phenomenon is a weak endothermic peak located at −58 °C. This was assigned to the melting of one crystalline form of PDMS.[19] It was systematically observed in the range of −62 to −46 °C for many PDMS chains and cyclic polysiloxanes having average molecular weights M_w higher than about 1200 g mol^{-1}, with the intensity and the temperature corresponding to this transition increasing with M_w. The observations of these two phenomena corroborates the description of these hybrids as homogeneous copolymers made with substantially long hybrid moieties, inside of which all siloxane and vanadium units participate in the glass transition.

Dynamical mechanical analysis (DMA) was performed on hybrid materials with a specimen size of ca. 20 × 5 × 0.2 mm with a TA Instruments DMA 29–80 apparatus operating at 1 Hz from −150 to +150 °C. The results of dynamical mechanical testing for these PDMS based hybrids are displayed in Fig. 4. The storage modulus exhibited a plateau with a magnitude of 2 × 10^9 Pa below −100 °C, which is typical for glassy

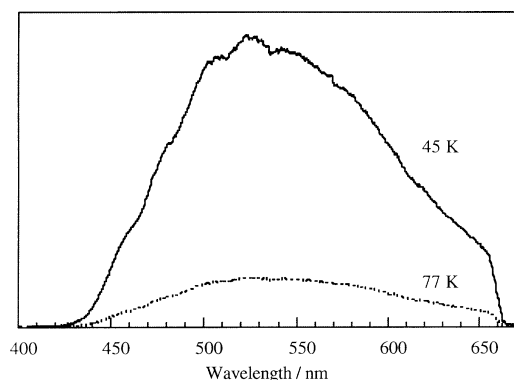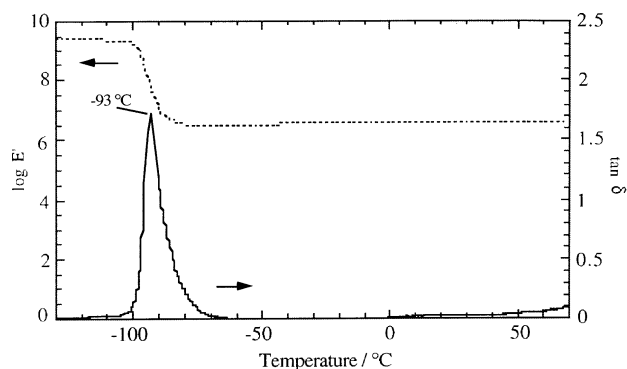**Fig. 3** Emission spectrum of the polydimethylsiloxane–vanadium-oxo materials

Fig. 4 Dynamical mechanical properties of the polydimethylsiloxane–vanadium–oxo materials (evolution of the modulus and tan δ versus temperature)

polymers. As the temperature rose, these hybrids exhibited a sharp transition associated with the observed decrease of the modulus. This transition is assigned to the backbone motion of the PDMS chains that accompanies its glass transition. After this transition, which occurs within a very narrow temperature domain the modulus reaches a second plateau, which extends over 150 °C. The storage modulus measured at the rubbery plateau is about 5 MPa, a value in agreement with those reported for stiff PDMS elastomers.[2,3]

The transition was determined from the maximum of the loss factor tan δ (Fig. 4). The DMA spectrum displays one sharp gaussian shaped (with a half-height linewidth of about 10 °C) and intense (tan δ = 1.8) relaxation, whose maximum located at −93 °C corresponds to the glass transition temperature of the hybrid polymer. This T_g value is in excellent agreement with those measured through DSC. Since the temperature of the glass transition T_g is estimated to be −123 °C for PDMS with an infinite molecular mass and reported experimental values of T_g recorded on pure PDMS are generally of about −120 °C, these PDMS crosslinked at the molecular level by $O=V(O-)_3$ sequestered species show an important shift to higher temperatures of the glass transition temperature.

It must be emphasized that the observed behavior for these hybrid polydimethylsiloxane–vanadium–oxo elastomers is quite original and different from that reported for weakly or highly charged crosslinked PDMS. Weakly charged PDMS,[3] presumably crosslinked at the molecular level by tetrafunctional silicate units in $SiO_2:SiMe_2O$ molar ratios of 1% or less, do not show any variation of the glass transition with the crosslink densities except for very short chains made of trimeric units.[20,21] In these compounds, crosslinking while introducing some constraints fails to reduce the overall mobility of the system by an appreciable degree. It was claimed that the lack of dependence of T_g on crosslink density was a result of the extreme flexibility of the PDMS chains. Therefore, the T_g of the network remains about the same, since main chain flexiblity overrides the constraining effect of the crosslink.[21] In addition, the loss factor peak is relatively sharp and intense for crosslinked networks made with siloxane short chains (tan δ = 0.95 for 9 units). The decrease of the maximum of tan δ with increasing chain length was assigned to an increase of crystallinity.

On the other hand, highly charged PDMS containing between 30 to 50 molar % of $Si(OR)_4$ or $Ti(OR)_4$ exhibits much broader variations of the loss factor. In some cases, the broad tan δ variation can spread between −110 and +50 °C and exhibit two main maxima, one at low temperature (−106 °C) and the other one at relatively higher temperature (−10 °C).[2] These observations result from phase segregation of a continuum of species ranging from PDMS rich phases (low transition temperatures), with generally undefined crosslinking interfaces, to better dispersed PDMS oligomers (higher transition temperatures) in the midst of network regions resulting from the hydrolysis and condensation of $Si(OR)_4$ or $Ti(OR)_4$.

In most polymers, crosslinking induces a severe constraint on the mobility of the chains, making it more difficult for the chains to participate in the cooperative chain movements associated with the glass–rubber transition. Consequently, as observed for the hybrid materials described in the present communication, the glass transition can be achieved only at temperatures greater than that for uncrosslinked polymers. For example, a linear decrease of T_g with the crosslink density is usually reported for model networks of polyglycols.[22] Also, increasing the crosslink density usually results in a progressively larger fraction of repeat units restrained and made unavailable for the loss process. Consequently, the values of the heat capacity change ΔC_p and the intensities of the tan δ peak, which are associated with the fraction of repeat units

available for the cooperative motion in the glass–rubber transition, decrease with increased crosslinking. However, this simple crosslinking mechanism can take into account the observed increase of T_g but cannot explain the large ΔC_p and the very intense value of the maximum of the loss factor measured for these hybrids.

The increase in T_g of a polymer because of crosslinking can also be due to a copolymer effect.[21] The crosslinking agent adds onto the main polymer system, modifying it into a copolymer made of difunctional units (the polymer) and isolated multifunctional units (the crosslinking agent) and thus changing its inherent T_g. This second mechanism can account for the observed thermal and mechanical behavior of these hybrids because the crosslink structure of the trifunctional vanadium oxo species appears to be quite compatible with the structure of the main dimethylsiloxane chains. Contrary to the tendency of PDMS crosslinked by silica or by transition metal oxides to phase separate, at least on the nanometer scale, into a PDMS rich and mobile domain and into an metal oxide rich and constrained domain,[2] the structural homogeneity of these hybrids results in the abscence of any phase separation. The crosslinking vanadate units appear to be as mobile as croslinked dimethylsiloxane oligomers with the whole hybrid polymeric network contributing to the glass transition.

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