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Structural investigation of polydimethylsiloxane–vanadate hybrid materials

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The structure of polydimethylsiloxane–vanadate (PDMSV) hybrid materials has been fully investigated. In particular, the use and interpretation of thermogravimetric analysis, IR, Raman and multinuclear NMR (^{1}H, ^{13}C, ^{17}O, ^{29}Si, ^{51}V) spectroscopies allowed an accurate description of their structure on a nanometric scale. The networks are composed of dimethylsiloxane segments with an average size of five to six units linked to monomeric vanadate units $VO(OSiMe_2..)_3$. Both units have been identified in cross-linked areas and in end groups. The dissolution and the degradation behaviour of the PDMSV materials are also described.

Introduction

Hybrid organic–inorganic nanocomposites can be obtained by mixing inorganic and organic components on the nanometric scale in virtually any ratio by use of soft chemical processing such as the sol–gel technique.[1] These hybrid materials are extremely versatile in their composition and properties.[2] Polydimethylsiloxanes (PDMS) have interesting intrinsic properties: elasticity of the siloxane backbone, low T_g, permeability, hydrophobicity, *etc.*[3] In order to improve and/or to conjugate these properties with those of inorganic species, several synthetic strategies have been developed to produce PDMS–metallate materials. Pre-formed PDMS chains have been filled by *in situ* formed silica or transition metal oxide.[4,5] Those chains have also been cross-linked to generate defined networks[6] that can subsequently be filled to improve their elastomeric properties.[7] In general, these routes allow control of the size distribution of the dimethylsiloxane (DMS) segments.[8,9] Other strategies are based on concomitant polycondensation of DMS and metallate units from their molecular precursors.[10,11] The connectivity between those two kinds of unit can be improved by this method. Although all these synthetic procedures are simple and versatile, the structural characterisation of the resulting materials, in particular of the interface between organic and inorganic moieties, is often complicated.

In this context, the presence of local probes, like NMR sensitive nuclei, is a valuable tool. This can be achieved in polydimethylsiloxane–vanadate materials. Vanadium 51 has one of the greatest NMR sensitivities and, if no strong paramagnetic centres are present, suitable structural information may be obtained. In addition, this information can contribute to a better knowledge on the dispersion of vanadate units in the siloxane matrix. The degree of sequestering and the coordination polyhedra of vanadium nuclei in silica based matrices has a paramount importance on their catalytic properties. The new polydimethylsiloxane–vanadate (PDMSV) materials have also been shown to have optical (luminescence) and mechanical (elastomeric) properties.[12] It has been suggested that the high degree of dispersion of the vanadate units and the copolymer effect between those units and the dimethylsiloxane units may account for the properties observed.

Following a complete characterisation (by thermogravimetry, EPR, IR, Raman, and multinuclear NMR) with an appropriate use of reference compounds, the structure of the PDMSV gels has been determined and is described. The dissolution and degradation behaviours of the gels have also been explored. These trends will bring complementary and pertinent information on the structure and stability of PDMS–metallate gels.

Experimental

Materials

Polydimethylsiloxane–vanadate gels (PDMSV). The standard procedure for the synthesis of the polydimethylsiloxane–vanadate (PDMSV) gels[12] consists first of a co-hydrolysis of 10^{-2} mol of diethoxydimethylsilane $Me_2Si(OEt)_2$ (DEDMS) and 10^{-3} mol of tri-*tert*-amyloxy vanadate $VO(OAm^t)_3$ with 10^{-2} mol of demineralised water under fast stirring (*ca.* 500 rpm) for 5 min. From the initial biphasic solution (alkoxide/water), the aqueous phase became yellow and gave rise to a red precipitate which dissolved upon stirring. Such coloration, characteristic of an increase of the coordination number of the vanadate units,[13] decreases during dissolution of the precipitate. The final colourless solution was then allowed to evolve in a closed sample vial for 24 h. Afterwards, the mixture is poured into an open Petri vessel. Evaporation of the alcohol and gelation take place within three weeks at room temperature without light exposure. Homogeneous, transparent and colourless gels are formed. These gels are used until no degradation occurs (phase separation, coloration). In a closed vessel, without light exposure and at 253 K, degradation is not observed for more than one year.

The standard procedure described above can be extended to other starting vanadium-to-silicon molar ratios in the range 0.05–0.15. Also, other routes have been found to produce PDMSV materials. The use of cyclo-hexamethyltrisiloxane $(Me_2SiO)_3$ as silicon precursor instead of the alkoxide $Me_2Si(OEt)_2$ *via* ring-opening reactions is one such alternative. In this case it is necessary to add an alcoholic solvent such as ethanol ($n_{ROH}/n_{Si} = 1$, with de-mineralised water) or *tert*-amyl alcohol [$n_{ROH}/n_{Si} = 10$, with an acidic aqueous solution (HCl, $pH = 2$)].[14] On examination by thermogravimetric and spectroscopic techniques, the resulting PDMSV gels exhibit a similar structure to those described above and were only used for qualitative comparison. In addition, $VO(OAm^t)_3$ can be replaced by the more usual alkoxide $VO(OPr^i)_3$ in the standard procedure. No further modifications are needed but the intermediate sols and gels are more sensitive to degradation.

Reference compounds. Some reference polydimethylsiloxane–vanadate solutions and gels [PDMS-OH/VO(OAm^t)$_3$] were synthesised by mixing pre-formed polydimethylsiloxane hydroxy terminated chains (PDMS-OH, 15 units in average) and VO(OAm^t)$_3$ at different vanadium-to-silicon molar ratios. The mixtures are simply stirred and poured into an open Petri vessel protected from light. The characteristic odour of Am^{t}OH was detected during the drying stage. No coloration was observed.

Tris(trimethylsiloxy)vanadate (VO(OSiMe$_3$)$_3$ was obtained from the addition of chlorotrimethylsilane to silver orthovanadate in toluene.[15] The product is conserved and analysed in an inert atmosphere. Silver orthovanadate[16] was precipitated in an aqueous solution of 0.4 M silver nitrate and 0.2 M sodium metavanadate adjusted to pH = 10 with 1 M NaOH. Chlorotrimethylsilane was used without further purification.

By mixing VO(OSiMe$_3$)$_3$ with Am^{t}OH, or VO(OAm^t)$_3$ with Me$_3$SiOEt and water, some solutions containing the siloxy-alkoxy vanadate species VO(OSiMe$_3$)$_{3-x}$(OAm^t)$_x$ have been prepared. The vanadium-to-silicon molar ratios can be varied in order to shift the equilibria between the vanadate species in a desired manner. These types of equilibria have already been described[17] and followed by ^{51}V NMR[18] in the case of trans-alcoholysis reactions undergone by vanadium oxo-alkoxides diluted in non-parent alcohols.

Reagents. Tri-*tert*-amyloxy vanadate VO(OAm^t)$_3$ was synthesised from ammonium metavanadate and *tert*-amyl alcohol as described elsewhere.[19–21] DEDMS, chlorotrimethylsilane, ethoxytrimethylsilane, hexamethyldisiloxane and hydroxy terminated PDMS were purchased from commercial companies (Fluka, Interchim) and used without further purification.^{17}O enriched water (10 atom%) was obtained from CEA-Saclay (France). All other reagents were purchased from Prolabo.

Characterisation techniques

Chemical elemental analyses were performed at Service d'Analyse (CNRS, Lyon). The thermogravimetric traces were obtained with a Netzsch STA 409 apparatus under a constant flow of argon (5 ml min^{-1}). A Bruker magnet operating at 9.24 GHz in the X-band was used for EPR experiments which were recorded at 293 and 77 K. FTIR spectra were recorded between 4000 and 400 cm^{-1} (2 cm^{-1} of resolution) on a Nicolet Spectrometer 550 fitted with an ATR equipment (ZnSe monocrystal). Raman analysis was carried out with a laser beam ($\lambda = 488$ nm, power = 150 mW) focused on part of a spinning sample. The spectral window was 200–1200 cm^{-1} with a step size of 1 cm^{-1}.

NMR experiments were performed on Bruker AM and MSL apparatus at 5.9, 7.0 and 9.4 T. All the spectra were referenced to conventional external standards: TMS for ^{1}H, ^{13}C and ^{29}Si, tap water for ^{17}O, and VOCl$_3$ for ^{51}V. ^{1}H broad band decoupling was systematically applied during the acquisition of the ^{29}Si signals independently of the pulse sequence used. Anisotropic ^{51}V spectra associated with the central transition were obtained with quadrupolar echo sequences with selective pulses ($\pi/8$). Longitudinal relaxation time (T_1) measurements were carried out using the standard inversion–recovery sequence. Magic angle spinning (MAS) is often necessary to achieve resolved spectra but introduces a physical compression of the gel. From our observations, such compression does not change the chemical structure of the PDMSV gel nor does it induce a glass transition,[22] but may modify the strength and the dynamics of some interactions. As an example, for the ^{17}O signal associated with the siloxane backbone the bandwidth measured in static conditions after MAS compression is twice that of a non-compressed PDMSV gel.[14]

When possible, the deconvolution of the NMR spectra was obtained with mixed Lorentzian–Gaussian functions (WinNMR and WinFit Bruker softwares). The parameters of the chemical shift anisotropy (CSA) have been quantified satisfactorily without the use of any supplementary interaction in the lineshape analysis of the anisotropic ^{51}V spectra (WinFit). This widely used procedure can induce some errors but those would not exceed 0.1 for η and 10 ppm for δ_{iso} and $\Delta\delta$, as deduced from previous work.[23,24] The definitions taken for each of the parameters were: $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$, $\Delta\delta = \delta_{33} - (\delta_{11} + \delta_{22})/2$ and $\eta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{iso})$ with $|\delta_{33} - \delta_{iso}| \geqslant |\delta_{11} - \delta_{iso}| \geqslant |\delta_{22} - \delta_{iso}|$.

Results

Preliminary characterisation of PDMSV gels

Elemental chemical analysis. The vanadium-to-silicon molar ratio V/Si in non-degraded PDMSV gels was regularly checked by elemental chemical analysis and found to be 0.12. Otherwise, the determined amounts of hydrogen and carbon correlate with a removal of the alkoxy groups during the synthesis of the gels. More relevant data on this feature were obtained by spectroscopic techniques (*vide infra*).

Thermogravimetric analysis. The thermogravimetric traces of the PMDSV gels are quite simple [Fig. 1(a)]. From 293 to *ca.* 540 K, there is a pseudo-plateau with smooth weight loss (ranging from 0 to 10%). Continued heating leads to a sharp weight loss (80% within 30 K). Between 570 and 770 K, a second plateau can be observed. By bubbling the exhaust gas in toluene, the soluble part of the volatilised products can be recuperated and analysed by gas phase chromatography. This was done for a gel showing practically no weight loss before 540 K. Only a distribution of small dimethylsiloxane (DMS) rings (3–6 units) was identified by gas chromatography.

Interesting results were obtained with reference polydimethylsiloxane–vanadate compounds [PDMS-OH/VO-(OAm^t)$_3$]. Fig. 1(b) shows the thremogravimetric trace of the starting PDMS-OH. In this material, a significant distribution of small DMS rings has been observed by supercritical fluid chromatography.[14] The initial weight loss can therefore be associated with the evaporation of those rings. At higher temperatures ($T > 620$ K), degradation of the DMS chains occurs. When adding the vanadate alkoxide up to V/Si = 0.10, the trace of the resulting gel [Fig. 1(c)] is completely different from that of PDMS-OH and similar to that of the standard PDMSV gel. In this sense, the addition of VO(OAm^t)$_3$ to the PDMS-OH material seems to strongly affect the reorganisation process of the siloxane bonds and probably the size distribution of the DMS segments.

Taking all these results in account, the sharp weight loss

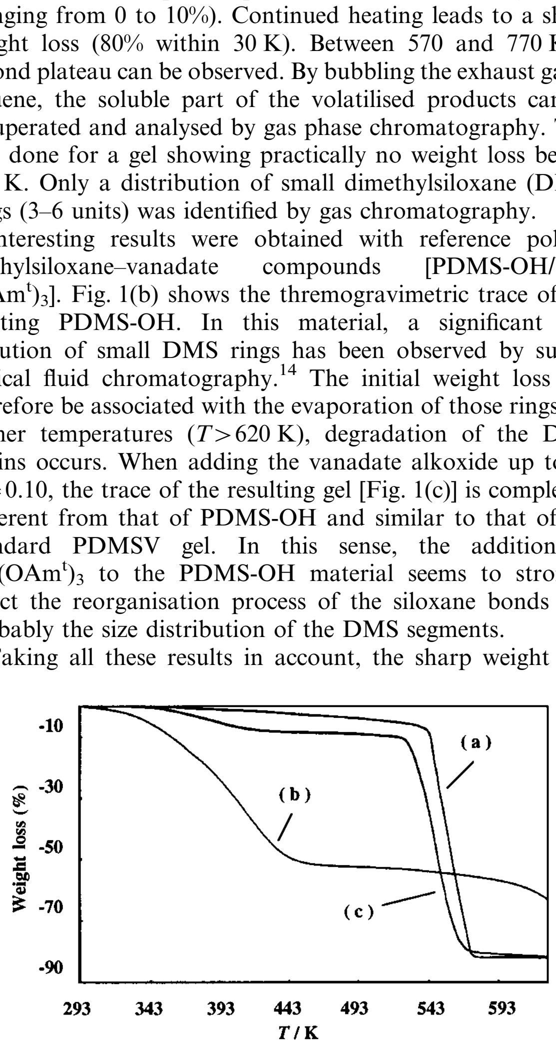

Fig. 1 Thermogravimetric traces: (a) PMDSV gel, (b) reference PDMS-OH and (c) reference PDMS-OH/VO(OAm^t)$_3$ (V/Si = 0.1).

between 540 and 570 K can only be associated to the evaporation of emergent siloxane rings. These are produced by the thermal degradation of the gels. Around 570 K, this kind of process is related to the reorganisation of the siloxane bonds in pure PDMS-OH[25] or in polysiloxane gels.[26] After the degradation of the PDMSV gels, the cumulative weight loss is $>80\%$. Comparing this value with the results of the elemental chemical analysis yields the conclusion that practically all the DMS units (87 wt%) have been evaporated and the resulting product mainly contains vanadium oxide. Finally, the smooth weight loss sometimes observed before 540 K corresponds to the evaporation of free volatile molecules (alcohol and, more probably, small DMS rings).

Glass transition. We only measured the values of the glass transition temperature T_g. According to DSC, T_g was found to be 177 K (heating at 20 K min^{-1}) while by DMA (dynamic mechanical analysis) a value of 180 K (frequency of 10 Hz) was found. These values are above those found for the DMS segments in pure rings or PDMS chains[27] or for DMS segments cross-linked by nano-sized objects.[28,29] Such behavior is explained by a copolymer effect between DMS and vanadate units.[12]

Electron paramagnetic resonance. Non-degraded PDMSV gels are EPR silent both at room temperature and at low temperature (77 K) indicating that no V(IV) centers are present. As discussed below, the presence of paramagnetic vanadium(IV) ions is related to degradation of the PDMSV gels.

Vibrational spectroscopies. FTIR and Raman results are summarised in Table 1. Bands of the stretching and bending vibrations of the hydroxy groups (at *ca.* 3500 and 1400 cm^{-1} respectively) are not observed in FTIR spectra of the non-degraded PDMSV gels. Considering the sensitivity of the technique towards those vibrations [ν(O–H) has a very high absorption coefficient], this suggests the absence of hydroxy groups in the PDMSV gels. Moreover, bands of the stretching vibration of Si–O–C bonds[30] as well as other bands associated with the vibrations of alcohol molecules or alkoxy groups[20] are absent in the FTIR spectra. The hydrolysis and condensation processes have thus gone to completion. In addition, the resulting materials show an intrinsically hydrophobic character.

All the characteristic bands of DMS segments[31,32] are observed in the FTIR and Raman spectra within the limits of the spectral window and spectra are compared between 600 and 1200 cm^{-1} in Fig. 2. The asymmetric stretching vibrations of the siloxane backbone give rise to intense bands in FTIR spectra between 1100 to 1000 cm^{-1}, but none in the corresponding Raman spectra.[32] However Raman spectroscopy does show a band at 1024 cm^{-1} probably hidden in the FTIR spectra. This band could correspond to the stretching vibration of the vanadyl bond in vanadate units of C_{3v} symmetry.[33,34] The absence of bands due to the stretching vibrations of V–O–V bonds around 200–300 and 500–800 cm^{-1}[35] indicates that those vanadate units are not connected to each other. The intense band at 895 cm^{-1}, only observed in FTIR spectra, does not correspond to specific vibrations of the DMS or vanadate units and may be related to the links between those two units. Considering the reported data for the stretching vibrations of Si–O bonds connected to vanadium atoms at 960 cm^{-1},[36] or Si–O–V bonds in vanadia–silica xerogels at 940 cm^{-1},[37] we tentatively assign the observed band at 895 cm^{-1} as the asymmetric stretching vibration of $(CH_3)_2$Si–O coupled to a vanadate unit.

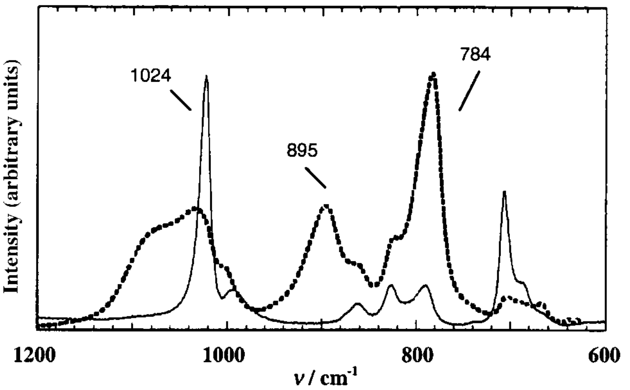

Fig. 2 FTIR (●) and Raman (- - -) spectra of PDMSV gel between 600 and 1200 cm^{-1}.

Table 1 Assignment of FTIR and Raman spectra for a PDMSV gel (V/Si = 0.12)

IR ($\tilde{\nu}$/cm^{-1})	Raman ($\tilde{\nu}$/cm^{-1})	Assignment
2964s		ν_a(C–H)
2920w		ν_s(C–H)
2850w		ν_s(C–H)
1410w		δ_a(C–H)
1258s		δ_s(C–H)
1080s	—[a]	ν_a(Si–O–Si)
1037s	—[a]	ν_a(Si–O–Si)
—[b]	1024s	ν(V=O)
1002m	996m	ν_a[V–O(–Si)]
895s	—[a]	ν_a[(V–)O–Si]
860w	863m	$\rho_s(CH_3)$
825w	827m	ν_s[V–O(–Si)]
784s	791m	$\rho_a(CH_3) + \nu_s$(C–Si–C)
704m	707s	ν_s(C–Si–C)
685w	688w	ρ_s(Si–CH_3)
665w	665w	ρ_s(Si–CH_3) or $\rho_a(CH_3)$
	486s	ν_a(Si–O–Si) or ring deformation

[a] Non-active. [b] Hidden.

Two medium bands in Raman spectra related to two shoulders in the FTIR spectra at *ca.* 1000 and 825 cm^{-1} also need to be assigned. Taking into account the literature data[33,38] and some of the results presented later, the most convincing assignment for the former band is the asymmetric vibration of the three V–O bonds coupled to silicon. In this case, the band at 825 cm^{-1} can be associated with the corresponding symmetrical vibration. Such an assignment is only hypothetical, but seems in qualitative agreement with the studies on the fundamental vibrations of the oxovanadium trihalides[39] and the semi-empirical correlation between Raman frequencies, bond order and interatomic distances.[40]

Multinuclear NMR study

^{1}H and ^{13}C NMR. From ^{1}H and CP ^{13}C{^{1}H} MAS spectra, the absence of alkoxy groups in the PDMSV gels is confirmed. The methyl groups of the DMS units give rise to four overlapping ^{1}H signals (two of them larger than the other two) and two ^{13}C signals (see Table 2). Their assignment is not trivial since the differences between the chemical shifts are small: 0.5 ppm for ^{1}H signals, 1 ppm for ^{13}C signals. Also, two different factors should affect the chemical shifts of the methyl group: the conformation of the siloxane backbone (length and geometry) and the nature of the chemical groups linked to the DMS unit. On the basis of reported data,[41] we propose possible assignments for the ^{1}H and ^{13}C signals in Table 2. More precise information on the DMS units distribution is obtained by means of ^{29}Si NMR analysis (*vide infra*).

^{17}O NMR. ^{17}O solution NMR data obtained from the reference compounds VO(OSiMe$_3$)$_3$ and VO(OAm^t)$_3$ are shown in Table 3. Each signal of the equivalent ^{17}O nuclei (terminal 'V=O' and bonding 'V–O–X') presents a hyperfine structure due to the scalar coupling with the ^{51}V nuclei. This

Table 2 NMR data for a PDMSV gel (V/Si = 0.12)

Nucleus	δ	Relative %[a]	Assignment[b]	Remarks
^{1}H[c]	0.3	<1	CH_3Si– (long segments)	
	0.2	≈ 30	CH_3Si– (short cyclic segments)	
	0.1	≈ 60	CH_3Si– (short linear segments)	
	−0.1	≈ 5	CH_3Si– (dimers)	
	—	≈ 5	Spinning side bands	
^{13}C[d]	1.5	40–35	CH_3SiOV	
	0.5	60–65	CH_3Si– (in short segments)	
^{17}O[e]	1165	7–14	V=O [in $VO(OSiMe_2..)_3$]	
	345	17–24	VOSi [in $VO(OSiMe_2..)_3$]	
	70	63–67	SiOSi	
	30	0–10	SiOEt	
	10	0–3	EtOH	
^{29}Si[f]	−11	36	D_1^V ($SiOMe_2\mathit{Si}OV$)	$T_1 = 11$ s
	−12/−14	<1	D_1^R ($SiOMe_2\mathit{Si}OR$, R = H, Et)	0–2 signals
	−19/−20	4	D_2 (short rings)	1–2 signals, $T_1 \approx 15$ s
	−20/−21	27	D_2 ($SiOMe_2\mathit{Si}OMe_2SiOV$)	2–3 signals, $T_1 \approx 27$ s
	−21/−23	33	D_2 (various)	3–4 signals, $T_1 \approx 19$ s
^{51}V[g]	−736	77	$VO(OSiMe_2..)_3$ (various)	A, $T_1 \approx 3.3$ ms
	−727	12	$VO(OSiMe_2..)_3$ (in a small ring)	B, $T_1 \approx 4.9$ ms, $T_2^* \approx 3$ ms[h]
	−705	2	$VO(OSiMe_2..)_3$ (in a small ring)	C, $T_1 \approx 2.7$ ms, $T_2^* \approx 2$ ms[h]
	—	9	Spinning side bands	

[a] Estimated from mixed Lorentzian–Gaussian deconvolutions. [b] Established from comparisons with literature data (see text). [c] $\nu_L = 300$ MHz, MAS 5 kHz. [d] $^{13}C\{^1H\}$ CP with variable contact times, $\nu_L = 75.5$ MHz, MAS 4 kHz. [e] $\nu_L = 54.2$ MHz, static and MAS 7 and 8 kHz. [f] From direct polarisation spectra with ^1H decoupling during acquisition, $\nu_L = 59.6$ and 79.5 MHz, MAS 4 and 5 kHz. [g] $\nu_L = 78.9$ MHz, MAS 9 kHz. [h] Values estimated assuming $\Delta\nu = (\pi T_2^*)^{-1}$. T_2^*: apparent transversal relaxation time.

feature is clearly observable for the spectrum of $VO(OSiMe_3)_3$ [Fig. 3(a)]. For the terminal oxygen, the resultant values $^1J(^{51}V^{17}O)$ are close to those reported for the aqueous vanadate species VO_4^{3-} and HVO_4^{2-} [42] and for the terminal oxygen of $V_2O_7^{4-}$.[43] As found for several aqueous vanadate species,[43,44] the higher order of the V–O bond involving the terminal oxygen implies the appearance of the ^{17}O resonance at higher frequencies than that corresponding to the μ-oxo bridges.

^{17}O solution NMR data obtained on $VO(OSiMe_3)_{3-x}(OAm^t)_x$ reference compounds are presented in Table 4. The signals were identified in solutions containing $VO(OAm^t)_3$, Me_3SiOEt and ^{17}O enriched water. ^{17}O nuclei were found in V=O and V–O–Si bonds owing to specific chemical processes, exchange and hydrolysis plus condensation, respectively. Both signals are rectangular shaped owing to $^1J(^{51}V^{17}O)$ coupling. Even if some overlapping exists, they can be unambiguously distinguished for each $VO(OSiMe_3)_{3-x}(OAm^t)_x$ compound. The assignments were made assuming a progressive evolution of chemical shift upon ligand substitution. A translation of this assignment to what is observed when replacing Me_3SiOEt by $Me_2Si(OEt)_2$ in the previous solutions allows identification of the $VO(OSiMe_2O..)_{3-x}(OAm^t)_x$ moieties. The corresponding assignments (Table 4) were found to be consistent with the expected variations in the $VO(OSiMe_2O..)_{3-x}(OAm^t)_x$ molar fractions when varying the relative molar ratios of the reagents.

The static NMR spectra of a ^{17}O natural abundance PDMSV gel is shown in Fig. 4. Three main signals are observed at δ 1165, 345 and 70(± 5 ppm) while residual bonds give rise to other resonances located at δ 30 and 10(± 5 ppm). The signal at δ 70 corresponds to ^{17}O nuclei in the siloxane backbone.[45,46] According to the assignment made for the reference compounds, the signals at δ 1165 and 350 can be associated solely with the ^{17}O nuclei in $VO(OSiMe_2..)_3$ centres. Also, their relative percentages (Table 2) are roughly in accordance with a descriptive formula such as $O{=}V(OSi..)_3$. When compared with that of the whole ^{17}O siloxane signal, these percentages lead to an approximate vanadium-to-silicon molar ratio of 0.1, close to the value obtained by elemental chemical analysis. The two signals are wide [$^1J(^{51}V^{17}O)$ coupling] and slightly broadened by site distribution and quadrupolar relaxation. No signal corresponding to oxo bridges between vanadate units[43,44] can be detected.

^{29}Si NMR. The ^{29}Si spectrum of the reference $VO(OSiMe_3)_3$ [Fig. 3(b)] was obtained using a refocused ^1H decoupled INEPT sequence based on the scalar coupling $^2J(^{29}Si^1H)$.[47] The scalar coupling $^2J(^{29}Si^{51}V)$ in $VO(OSiMe_3)_3$ can be determined by the measurement of the spacing between the outer lines and has a value of *ca.* 13 Hz. The ^{29}Si signal occurs at δ 24.5. Compared with the measured chemical shift of $(Me_3Si)_2O$ (δ 7.0), there is a substantial downfield shift when the trimethylsiloxyl group is replaced by a vanadate group.

The reference PDMS-OH/$VO(OAm^t)_3$ compounds exhibit a broad ^{29}Si NMR signal at δ *ca.* −11 which differs from the characteristic resonances of free PDMS-OH located at δ *ca.* −13 and −22. The main factors that would influence the ^{29}Si chemical shifts of the DMS units are the proximity of an end group and any conformational constraints. In the solution NMR analysis of reacted DEDMS mixtures,[48,49] the signal of the non-condensed DMS units D_0 are observed in the range

Table 3 Comparison of ^{17}O and ^{51}V NMR data for $VO(OSiMe_3)_3$, $VO(OAm^t)_3$ and the PDMSV gel

	^{17}O (295 K)									
	δ		^1J(VO)/Hz		^{51}V (295 K)		^{51}V (165 K)			
	V=O	V–O–X	V=O	V–O–X	δ	T_1/ms	δ_{iso}	$\Delta\delta$/ppm	η_σ	δ_{33}
$VO(OAm^t)_3$	1114	389	≈ 50	≈ 150	−685	88	-681 ± 5	-161 ± 5	0.15 ± 0.05	−788
$VO(OSiMe_3)_3$	1152	337	60	110	−711	45	-714 ± 5	-306 ± 5	0.05 ± 0.05	−918
Gel PDMSV	1165	345			−736 −727 −705	3.3 4.9 2.7	-735 ± 5	-345 ± 5	0.10 ± 0.05	−965

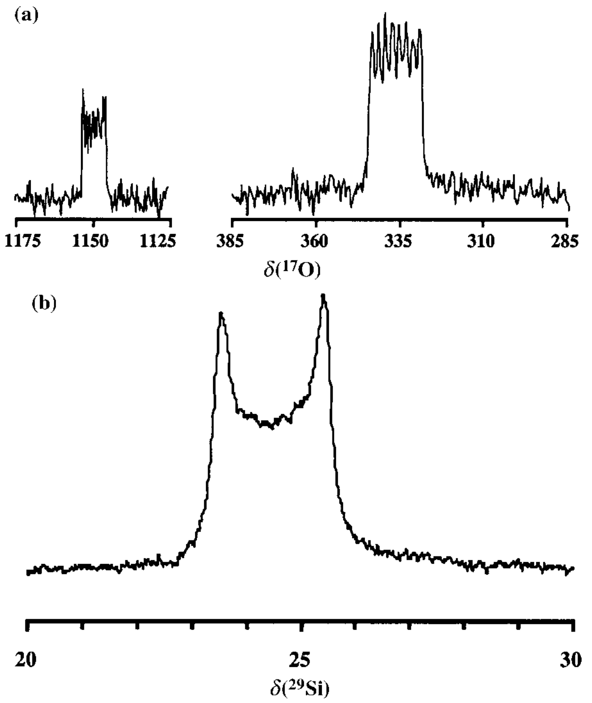

Fig. 3 ^{17}O and ^{29}Si NMR spectra of $VO(OSiMe_3)_3$: (a) direct polarisation ^{17}O spectrum, $\nu_L=54.2$ MHz and (b) $\{^1H\}^{29}Si$ refocused INEPT spectrum, $\nu_L=49.7$ MHz.

Table 4 ^{17}O and ^{51}V NMR chemical shifts of siloxy/alkoxy–vanadate species

		δ (^{17}O)		
		V=O	V–O–Si	δ (^{51}V)
$VO(OSiMe_3)_{3-x}(OAm^t)_x$	$x=0$	1152	337	−711
	$x=1$	1140	315	−701
	$x=2$	1127	290	−693
	$x=3$	1114	—	−685
$VO(OSiMe_2..)_{3-x}(OAm^t)_x$	$x=0$	1165	345	−736[a]
	$x=1$	1145	315	−716[a]
	$x=2$	1130	285	−698
	$x=3$	1114	—	−685

[a]PDMSV gel without strained rings.

δ −2 to −6. Those of terminal units linked to ethoxy or hydroxy groups D_1^{Et} and D_1^{H} are observed in the range δ −11 to −14, and those of fully condensed units D_2 belonging to small chains ($n \leqslant 6$) are observed in the range δ −21 to −22. Also, the three- and four-membered rings $(D_2)_3$ and $(D_2)_4$ give rise to signals located at δ −9 and −19, respectively, while the chemical shifts of five-membered and larger rings are in the range δ −21 to −22. Moreover, since the formation of Si–O–Am^t bonds seems unrealistic and Si–O–Et bonds are practically absent (FTIR, ^1H, ^{13}C and ^{17}O NMR), the new signal at δ −11 is associated with DMS units linked to vanadate units. This preliminary assignment is in accord with the downfield shift effect observed for $VO(OSiMe_3)_3$.

^{29}Si MAAS NMR spectra of the PDMSV gels obtained with three different pulse sequences are shown in Fig. 5. From the spectrum recorded with a direct polarisation sequence [Fig. 5(a)], two kinds of signal can be observed. A large quasi-rectangular shaped peak is located at δ −11 and represents 36% of the whole ^{29}Si signal, and a distribution of thinner lines are seen between δ −19 and −23 (Table 2). For the reference PDMS-OH/$VO(OAm^t)_3$ compounds, the signal at δ −11 is associated with DMS units linked to one vanadate unit and another DMS unit.[50] Using this assignment, the vanadium-to-silicon molar ratio is found to be 0.12, in accord with the elemental analysis. The scalar coupling between ^{29}Si and ^{51}V nuclei and a distribution of sites may be responsible for the quasi-rectangular shape of the signal [$^2J(^{29}Si^{51}V)$ *ca.* 17 Hz].

The other signals are related to D_2 units. The presence of such a distribution is explained by the existence of several short segments in which the DMS units are close to terminal units and/or in small rings [excluding $(D_2)_3$]. Although a complete and detailed assignment is not yet available, it should be noted that the signals located between δ −20 and −21 are not observed for pure DMS compounds and are probably related to DMS units in a second neighbouring position with respect to the vanadate units. In accordance with their assignment, the relative proportion of these signals (27%) is similar to those of DMS units directly linked to vanadium (36%).

The ^{29}Si spectra recorded with ^1H polarisation transfer sequences (INEPT or CP) give similar resolution with small variations in the relative intensities [Fig. 5(b) and (c)]. The disappearance of the resonance at δ −11 in the INEPT spectrum was unexpected and may be explained by a specific relaxation process of the ^{29}Si nuclei strongly coupled to the ^{51}V nuclei giving rise to smaller longitudinal relaxation rates T_1 (see Table 2). Without going into a theoretical interpretation of the ^{29}Si spectra obtained by each sequence, we wish to emphasise the predominant role of the scalar coupling interactions compared with the dipolar ones at moderate MAS rates (2–5 kHz). This feature must be linked to the lower restrictions in chain motions than those in other PMDS based hybrid materials for which CP MAS is required for a complete detection of the ^{29}Si signals.[8,11,51]

^{51}V NMR. In order to obtain information about the symmetry of the vanadate units from the width $\Delta\delta$ and the asymmetry η of the chemical shift anisotropy (CSA),[52] we have recorded low temperature static spectra on the reference

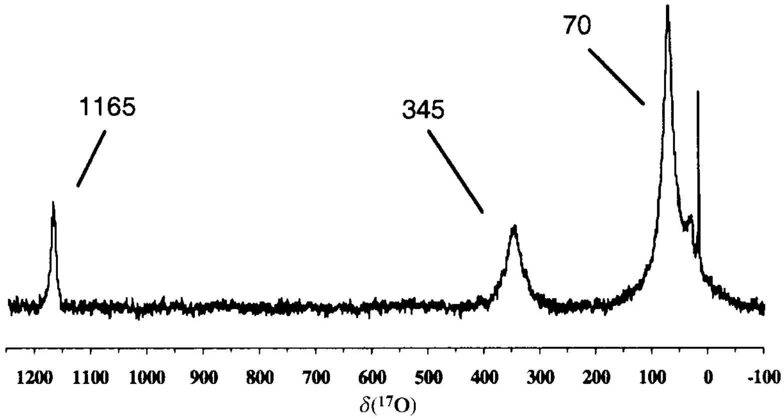

Fig. 4 ^{17}O NMR static spectrum of a PDMSV gel, direct polarisation, $\nu_L=40.7$ MHz.

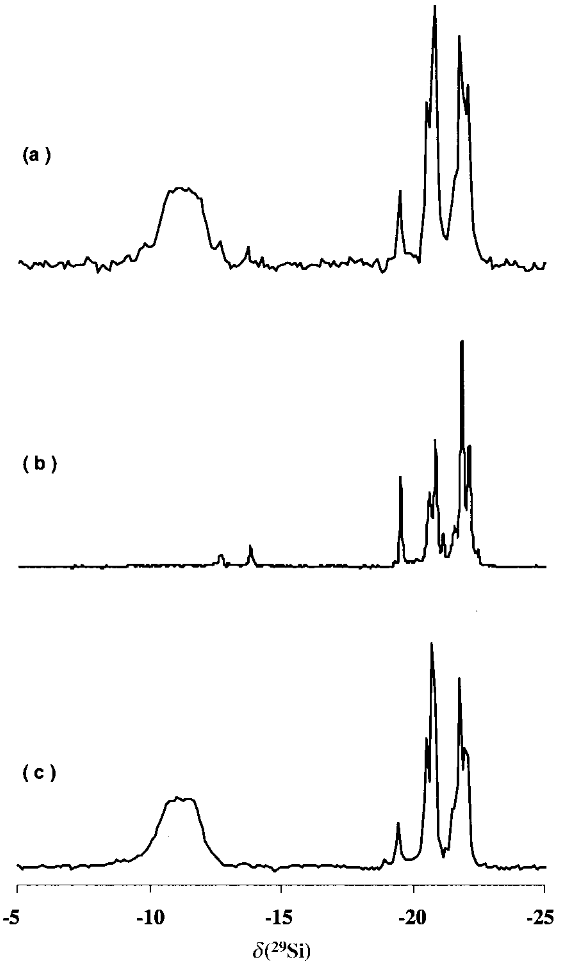

Fig. 5 ^{29}Si MAS NMR spectra of PDMSV gels: (a) direct polarisation, $\nu_L = 59.6$ MHz, spin rate = 5 kHz, (b) $\{^1H\}^{29}$Si refocused INEPT, $\nu_L = 59.6$ MHz, spin rate = 5 kHz and (c) $\{^1H\}^{29}$Si cross-polarisation, $\nu_L = 79.5$ MHz, spin rate = 2 kHz, contact time = 50 ms.

compounds VO(OSiMe$_3$)$_3$ and VO(OAm^t)$_3$, as well as on the PDMSV gel ($T = 165$ K). The results are reported in Table 3 and compared to those from the literature[23,52] in a plot of $\eta = f(|\Delta\delta|)$ (Fig. 6). The characteristic features (η,$|\Delta\delta|$) of solid VO(OAm^t)$_3$ are found to be close to those of vanadate units in near tetrahedral symmetry (monomeric and dimeric VO$_4$ structural units). The width of the CSA is small. Given the presence of a short vanadyl bond V=O and three V–O–C bonds, the local symmetry of the vanadium centre is considered here to be C_{3v} even if some configurations of the alkoxy groups could lead to C_3 or C_s symmetry.[53] For VO(OSiMe$_3$)$_3$, $|\Delta\delta|$ has a greater value. As also observed from the ^{17}O chemical shift values of V=O and V–O–X (Table 1), the siloxy groups have stronger effects than do alkoxy groups on the vanadate unit. Various factors (electronegativity differences and ionicity, orbital overlapping) may explain the increased electronic density around the vanadyl bond in VO(OSiMe$_3$)$_3$ in comparison to VO(OAm^t)$_3$. Nevertheless, a new area in the plot $\eta = f(|\Delta\delta|)$ has to be considered for vanadate units linked to three silyloxy groups in near C_{3v} symmetry.

The PDMSV gels contain vanadium only in oxidation state +V (no EPR signal or colour) and thus ^{51}V NMR analysis can give a precise description for all the vanadate units. The spectrum of a PDMSV gel in its glassy state ($T < 177$ K) is shown in Fig. 7(a). The shape is characteristic of an axially symmetric CSA. The position of the resulting point (η, $|\Delta\delta|$) is very close to that of VO(OSiMe$_3$)$_3$. Owing to the chemical similarity of the silyloxy groups, it is possible to consider the vanadium centres in the PDMSV gel as being linked to three dimethylsiloxyl moieties in near C_{3v} symmetry. With this preliminary result, the ^{51}V NMR data at room temperature allow a more acurate characterisation of this system.

Solution ^{51}V NMR of VO(OSiMe$_3$)$_3$ and VO(OAm^t)$_3$ (295 K) are given in Table 3. Substitution of the *tert*-amyloxy groups by trimethylsiloxyl groups leads to a decrease in the ^{51}V chemical shift which could be due, to a first approximation, to the electronegativity difference between the two groups.[54] The signals of the intermediate VO(OSiMe$_3$)$_{3-x}$(OAm^t)$_x$ species ($0 < x < 3$) have been assigned from the evolution of the intensities as a function of the alkoxyl-to-siloxyl ratio in solutions containing VO(OSiMe$_3$)$_3$ and Am^{t}OH; the signals have intermediate chemical shift values (Table 4). A similar but more pronounced trend in the chemical shifts is observed when replacing a *tert*-amyloxyl group by a dimethylsiloxyl terminal group as observed for PDMS-OH/VO(OAm^t)$_3$ solutions with

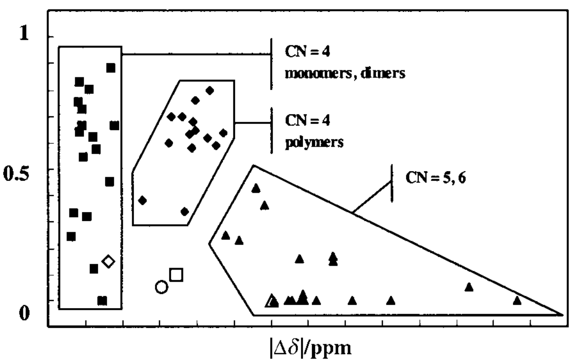

Fig. 6 Plot $\eta = f(|\Delta\delta|)$ based on the CSA parameters of vanadate compounds. Open diamond: VO(OAm^t)$_3$; open circle: VO(OSiMe$_3$)$_3$; open square: PDMSV gel; open triangle: degraded PDMSV gel.

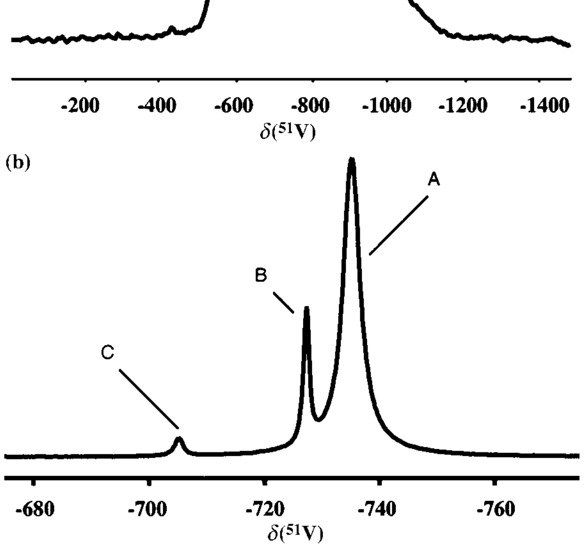

Fig. 7 ^{51}V NMR spectra of the PDMSV gel: (a) $T = 165$ K, quadrupolar echo, $\nu_L = 78.9$ MHz and (b) $T = 295$ K, direct polarisation, $\nu_L = 78.9$ MHz, spin rate = 9 kHz.

variable vanadium-to-silicon molar ratios.[55] In those solutions, the ^{51}V signal corresponding to the vanadate units linked to three dimethylsiloxane units is found to be at δ −736.

The ^{51}V static and MAS spectra of the PDMSV gel at ambient temperature are well resolved and always exhibit three signals A, B and C located at δ −736, −727 and −705 respectively [Fig. 7(b)]. These represent around 85, 13 and 2% of the total area of the MAS spectrum (excluding the spinning side bands). Signal A has been already identified using reference compounds. The less abundant signals B and C were assigned taking into account several observations. Both signals were found for gels obtained with $VO(OAm^t)_3$ or $VO(OPr^i)_3$ as the vanadate precursor. This suggests that they can not be associated with vanadate units linked to specific alkyl groups. From the results of FTIR, Raman and ^{17}O NMR analysis, links with hydroxy groups or other vanadate units are also excluded. As concluded from low-temperature ^{51}V NMR results, the three signals are related to vanadium centres linked to three siloxyl groups. This attribution is also supported by other facts. The values of the ^{51}V isotropic chemical shifts are in the range expected for vanadate units with a coordination number of four[20,54,56] and, more precisely, in the region of known siloxy vanadate compounds: $VO(OSiMe_3)_3$ (δ −711) (Table 3), $VO(OSiPh_3)_3$ (δ −728).[57]

The existence of three different chemical shifts for vanadium sites denoted as $VO(OSiMe_2O..)_3$ can be explained by the presence of moieties with different O–V–O angles. This effect, previously observed for vanadate silsesquioxane compounds, can lead to differences in ^{51}V chemical shifts as great as 34 ppm.[57] While signal A (δ −736) may correspond to a large variety of vanadate sites, signals B and C (δ −727 and −705) are associated with vanadate units in defined strained geometry. Small DMS segments (3–5 units) linked to one vanadate unit will create rings with such a strained geometry. Results which support this latter attribution were obtained from study of diluted PDMSV gels.

Dissolution of the PDMSV gels

In contrast to other cross-linked PDMS materials, the non-degraded PDMSV gels can be completely dissolved in nonpolar hydrophobic solvents such as toluene, cyclohexane and *n*-hexane. As the solutions remain colourless and no precipitate is formed (when light exposure is avoided), the chemical nature of the vanadate units in the gels appears to be conserved. Moreover, when the solvents are evaporated a PMDSV gel is reformed. This behaviour allowed to characterise the PDMSV gels by usual solution techniques, and to take into account dilution effects upon the distribution of different species.

The analysis of the solutions by spectroscopic techniques (FTIR, NMR) does not show any new signals related to the formation of new chemical bonds. V–O–Si bonds are preserved to the same extent as in the PDMSV gel. As expected, the three kinds of signals A, B and C do not correlate in any of the attempted ^{51}V NMR 2D COSY experiments. Also, no increase was noted for ^{29}Si signals corresponding to small pure DMS rings. As for the gel, $(D_2)_3$ and $(D_2)_4$ signals are only found in solution at a low level. For all these reasons, we can conclude that the DMS segments are still linked to one or two vanadate units and that no phase separation is operating.

Dilution effects have been studied mainly by ^{51}V solution NMR of PDMSV gels dissolved in toluene. First, the complete dissolution of a PDMSV gel (0.1342 g) in toluene (0.7 ml) was followed closely. The three signals A (δ −736), B (δ −727) and C (δ −705) characteristic of the gel are progressively converted to several narrower signals in the same chemical shift range. While B and C give rise to less than five signals located around δ −705 and −726(±1 ppm), signal A is transformed to a wider distribution of signals with chemical shifts in the range δ −732 to −739. At the end of the dissolution process, the relative proportion of signals B and C has increased to 26 and 13%, respectively, the whole ^{51}V signal. The observation of narrower signals can be explained only in terms of increased mobility of the DMS segments when the gel is swollen, with the variation in the proportion of each type of signal suggesting a radical change in the distribution of the vanadate units.

Table 5 Simulation of the variation of the relative proportion of each type of vanadate unit *vs.* the weight concentration of gel using the formula $\alpha+\beta C_{gel}$; C_{gel} in g ml^{-1}

	α	β	R^a
A total	0.43	+0.5	0.91
A (δ −739 to −736)	0.09	−0.1	0.91
A (δ −736 to −735)	0.14	+0.8	0.98
A (δ −734 to −732)	0.19	−0.0	0.98
B total	0.34	−0.2	0.99
C total	0.23	−0.4	0.96

[a] Regression coefficient.

In order to understand this phenomenon, dissolved PDMSV gels in toluene at 15 different concentrations ranging from 0.01 to 0.25 g ml^{-1} were analysed in a second experiment. The relative proportion of ^{51}V signals over a short chemical shift range (2–3 ppm) corresponds to the relative proportion of the associated vanadate units and has been plotted against the weight concentration of the gel C_{gel}. The experimental points can be fitted by lines of general expression $\alpha+\beta C_{gel}$. In this expression, α is the relative proportion of each vanadate unit at infinite dilution, and β is a factor of proportionality that quantifies the effect of the dilution. Obtained data are summarised in Table 5. It is possible to distinguish two classes of vanadate units as a function of the value of β. On the one hand, units that are less favoured by dilution ($\beta > 0$) are of type A with chemical shifts in the range δ −735 to −736 and their relative proportion at infinite dilution is small (0.14). On the other hand, many vanadate units are slightly or strongly favoured by dilution ($\beta \leqslant 0$). This is the case for the units associated with signals B and C but also for some units associated with signal A.

It has been shown that pure PDMS materials consist of a distribution of linear polymers plus a distribution of cyclic oligomers. The dilution of PDMS favours this latter distribution which becomes centred for lower molecular weights.[58] Previous assignments for the signals B and C based on their ^{51}V chemical shifts thus appear to remain valid. Upon dilution, their relative proportions increase strongly to become predominant. In addition, signals B and C can be observed at long retention times after separation by preparative gel permeation chromatography (GPC). This behaviour is expected for vanadate units inserted in small DMS rings. Similar but weaker effects have been observed for the signals in the range δ −732 to −734 and their associated vanadate units may be those inserted in larger DMS rings. Finally, the signals located between δ −735 and −736 are shown to decrease with dilution and to correspond to the bulkiest oligomers (GPC) and are related to vanadate units linked to three different DMS segments. It should be reiterated here that those signals were also the only ones observed for the $VO(OSiMe_2..)_3$ units in the reference PDMS-OH/$VO(OAm^t)_3$ compounds.

By contrast, the dissolution of the PDMSV gels in polar and protic solvents such as ethanol produces intermediate yellow–red solutions which yield red–green precipitates upon ageing. As observed by ^{51}V and ^{29}Si NMR, the V–O–Si bonds are transformed into V–O–Et and Si–OH bonds. Thus, the coordination number of the vanadium is increased from four to five or six *via* ethoxy multibridging, and phase separation is favoured.

Degradation of the PDMSV gels

Up to now we have considered the PDMSV gels without consideration of their stability. Ageing of the gels always produces an irreversible degradation depending mainly upon the storage conditions. This degradation is observable by coloration of the gels: first yellow, then red and dark green. An increasing opacity and a change in rheological properties follows. At this stage the vanadium-to-silicon molar rato is *ca.* 40 as found by elemental analysis. The T_g measured by DSC can have a value of 150 K, close to the values found for long-chain PDMS.[27] At the end of the process, the gel is converted in a green powder with a vanadium-to-silicon molar ratio of >150. Once it has started in part of the gel degradation spreads to the whole sample.

Thermogravimetric traces are changed upon degradation. From 293 to 470 K, they often present a continuous decrease of weight ranging between 75 and 85% and are very similar to those of pure $(D_2)_5$ rings (not shown). The FTIR spectra of degraded PDMSV gels show no band associated with hydroxy groups around 3500 cm^{-1}. However, the bands of the asymmetric stretching vibration of the siloxane bonds are now located at 1015 and 1080 cm^{-1} close to those of PDMS compounds.[32] Finally, no band related V–O–Si bridges are detected.

The evolution of the degradation process can be followed qualitatively by ^{51}V solid-state NMR. The spectra recorded at three stages of the degradation process are shown in Fig. 8. The three signals A, B and C are present in all cases but an increasingly broad signal is observed as the degradation progresses. The presence of a signal showing an axially symmetric CSA rather than a Lorentzian function indicates a decrease in the mobility of the vanadate units. Simulation of Fig. 8c yields the following CSA values: $\delta_{iso} = -575 \pm 5$; $\Delta\delta = -600 \pm 5$ ppm and $\eta = 0.0 \pm 0.1$. These values clearly do not correspond to the values obtained for a PDMSV gel at low temperature but are similar to those of highly coordinated vanadate units (Fig. 6).

During degradation, EPR signals become visible and a spectrum obtained on a red–green gel is shown in Fig. 9. Two signals are observed at 77 K: a resolved hyperfine signal ($g_{\parallel} = 1.93$, $A_{\parallel} = 195$ G, $g_{\perp} = 1.99$, $A_{\perp} = 75$ G, magnetic parameters obtained by simulation) and a broad signal ($g_{iso} = 1.96$, $\Delta B_{1/2} = 200$ G). The former is characteristic of non-interacting vanadyl(V) and (IV) ions in axial symmetry and with a coordination number above four,[20,59] while the latter is related to spin–spin interacting vanadium(IV) ions. As the degradation develops, the broad signal becomes increasingly significant. In order to simulate the influence of light exposure on degradation, we performed UV irradiation ($\lambda = 365$ nm, power $= 24$ W) on the PDMSV gels at room temperature for a variety of times and EPR spectra at 77 K were subsequently recorded. For an irradiation of 15 s or more, degradation becomes visible after a few hours (red coloration). Moreover, the intensity of the detected EPR signal is proportional to the irradiation time. In addition, the broad signal of the interacting vanadium(IV) ions increases ten times faster than the hyperfine signal during the first minute of irradiation. Finally, this type of experiment allows us to estimate the initial content of vanadium(IV) sites with respect to the total concentration of vanadium in the non-degraded PMDSV gel under study as $\leqslant 0.003\%$.

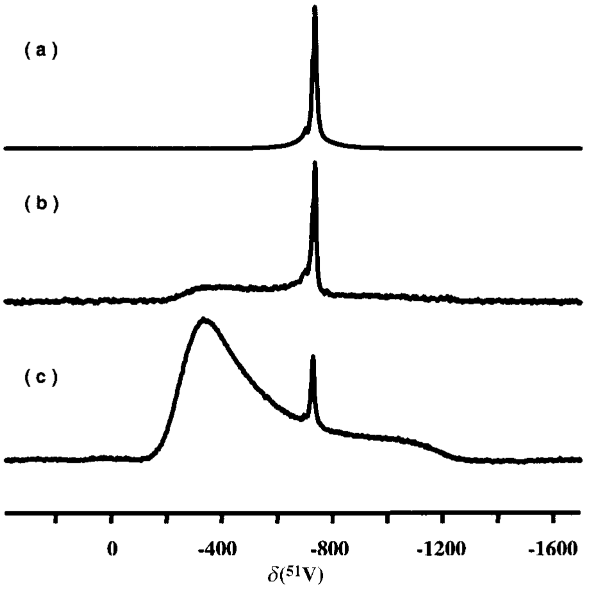

Fig. 8 ^{51}V solid-state spectra recorded at 295 K on three gels showing an increase in their degradation level: (a) non-degraded gel, (b) slightly degraded gel (orange coloration) and (c) degraded gel (dark red coloration).

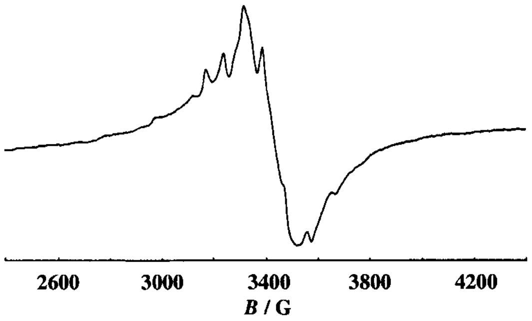

Fig. 9 Derivative EPR spectrum of a degraded PDMSV gel (9.24 GHz, 77 K).

Taking into account all these observations, the degradation is believed to involve a phase separation in the PDMSV gel. On one hand, a rigid phase is formed containing vanadium ions in oxide clusters with a coordination number above four. On the other hand, a silicon rich phase contains large PDMS species as well as small DMS rings. When the ageing of the PDMSV gels is not controlled, degradation could be promoted by an increase in V/Si due to continuous volatilisation of small DMS rings and/or by the reduction of vanadium(V) to vanadium(IV) upon UV exposure.

Discussion

Structure of the PDMSV gels

Considering the results from all the techniques employed, the chemical formula for the non-degraded PDMSV gels is $(Me_2SiO)_1(VO_{5/2})_x$ ($x = 0.12$ for an initial V/Si $= 0.10$). It has been established that on the nanometric scale the vanadium atoms are in monomeric vanadate units which are completely dispersed in the DMS network. Those units can be described by the chemical formula $VO(OSiMe_2..)_3$ and their symmetry is close to C_{3v}. However, two classes of units can be distinguished. The first class corresponds to units inserted in DMS rings in which the link with the network can only be *via* one DMS segment; these vanadate units thus act as end groups. Their relative proportion should be significant and for those inserted in the smallest rings (^{51}V NMR signals B and C) this is around 15%. The second class of vanadate units corresponds to units linked to three different DMS segments. These units are inserted in the network and act as efficient cross-links (Fig. 10).

Most of the DMS segments should be linked to vanadate units as no hydroxy and ethoxy groups are present, and as the existence of pure DMS rings at a significant level in the non-degraded PDMSV gels can be excluded. Large DMS rings as well as large DMS segments are only formed at a residual level (1–2% of the whole ^{29}Si signal) and there is no clear evidence for the presence of small rings from ^{29}Si NMR analysis.

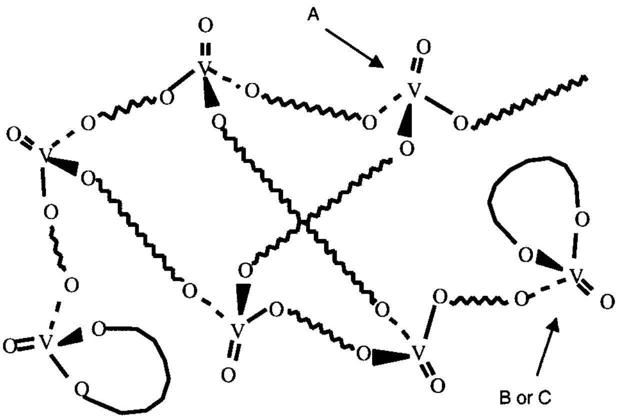

Fig. 10 Schematic representation of the PDMSV gel structure: end groups containing DMS rings (loops) and vanadate units (^{51}V signals B or C for small rings), cross-linked areas containing DMS segments (springs) linked to two different vanadate units (^{51}V signals A).

Moreover, no significant weight loss is observed in thermogravimetric traces before 540 K, although rings with three, four, five or six units would already be evaporated at this temperature.[60] Some rings could be formed during the synthesis but may have been evaporated afterwards, this can be an explanation for the small increase in the vanadium-to-silicon molar ratio V/Si from the beginning (0.10) to the end of the synthesis (0.12).

Like the vanadate units, two classes of DMS segments can be postulated: those linked to the same vanadate unit and those linked to two different units (Fig. 10). An equilibrium may exist between those two classes in a similar way to the equilibrium observed between rings and chains in pure PDMS materials.[58] Each class of DMS segments has a corresponding size distribution. From the value of $V/Si = 0.12$, the average number of units in the DMS segments can be estimated as *ca.* five to six. This low value implies that the size distributions of each class of DMS segments may be centred on closer values.

The resulting structure of the gel can be considered to arise from two complementary driving forces: the 'building up of the network' and the 'closure of the end segments'. Study of these phenomena during synthesis has been undertaken in a parallel study.[61] Our purpose here is to verify the existence of characteristic signs for this structure, as suggested from thermogravimetric traces (Fig. 1) as well as from DSC and DMA measurements.[12] The thermal degradation and glass transition processes both concern the whole material and occur over a short defined temperature range. By inspecting the thermal behaviour of the gel, it is possible to verify the absence of phase separation. In this sense, the PDMSV gel is more like a copolymer than a nanocomposite material. The ^{51}V and ^{29}Si NMR spectra are also characteristic of this structure. The same distribution of signals was observed for some gels synthesised from different silicon and vanadium alkoxide precursors and with different synthetic procedures. This suggests that the structure of the gel has to be a preferential state under particular chemical conditions.

A metastable state

At temperatures above T_g, a high level of mobility in the whole gel was evidenced by DSC and DMA measurements.[12] This feature, which is quite surprising for vanadate units, is confirmed when inspecting the relaxation behaviour of the ^{51}V nuclei (Tables 2 and 3) and a more detailed study of this phenomenon will be reported soon.[61] One of the consequences of the high mobility within the gel is the fast evolution towards other states under perturbations such as dissolution or UV irradiation. In this sense, the non-degraded PDMSV gel is in a metastable state. In particular, this state has only been attained for vanadium-to-silicon molar ratios of between 0.05 and 0.15; for higher ratios, the resultant gels are phase separated.

The structure of the non-degraded PDMSV gel can be defined by at least two chemical parameters. The first is the vanadium-to-silicon molar ratio, which increases to very high values under continuous volatilisation of small DMS rings during the degradation process. The second parameter is the functionality of the vanadate units, which is related to the coordination number and the degree of oxidation of the vanadium. In particular, vanadium(IV), with a higher ionic radius (0.63 Å) than vanadium(V) (0.59 Å), prefers a higher coordination number than four. Therefore, the formation of vanadium(IV) sites will promote homocondensation and thus nanophase separation, as observed when reduction is induced by UV irradiation.

These two parameters, the vanadium-to-silicon molar ratio and the functionality of the vanadate units, are linked. Generally, the higher the functionality of the cross-links, the lower the degree of dispersion of vanadium.[62] This view of the PDMSV gels can be extended to other PDMS–metallate materials. For many, the functionality of the metallate units is $\geqslant 4$ and the metal-to-silicon ratio is >0.1. Therefore, a molecular dispersion of the metal units is difficult to achieve and these materials always show phase separation with DMS rich domains and metal–oxo based species interpenetrated at the nanometer scale.[4,51]

Conclusions

1. The chemical homogeneity of polydimethylsiloxane–vanadate (PDMSV) hybrid materials has been confirmed by the use of complementary characterisation techniques. Monomeric vanadate units are linked to three dimethylsiloxane (DMS) units maintaining a C_{3v} like symmetry, and the DMS segments have an average size of five to six units.

2. Two equilibria for DMS segments and vanadate units have been identified corresponding to cross-linked areas and end groups as revealed by thermogravimetry and ^{29}Si and ^{51}V NMR spectra.

3. The PDMSV materials are a metastable state. The intrinsic mobility of the structural units accounts for their rapid evolution towards other states. When dissolved in apolar solvents, the gels are converted into stable dimethylsiloxane–vanadate oligomers, while if aged in an open atmosphere and/or under light, the gel is degraded. UV irradiation causes reduction of vanadium(V) to vanadium(IV). In turn, this promotes an increase in the coordination number of the vanadate units and leads to phase separation between the DMS and inorganic vanadium–oxo species. Volatilisation of small DMS rings also favours phase separation by increasing the vanadium-to-silicon molar ratio.

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References

1 A. Morikawa, Y. Iyoku, M. Kakimoto and Y. Imai, *J. Mater. Chem.*, 1992, **2**, 679; Y. Chujo and T. Saegusa, *Adv. Polym. Sci.*, 1992, **100**, 11; B. M. Novak, *Adv. Mater.*, 1993, **5**, 422; C. Sanchez and F. Ribot, *New J. Chem.*, 1994, **18**, 1007; U. Schubert, N. Hüsing and A. Lorenz, *Chem. Mater.*, 1995, **7**, 2010; D. A. Loy and K. J. Shea, *Chem. Rev.*, 1995, **95**, 1431; U. Schubert, *J. Chem. Soc., Dalton Trans.*, 1996, 3343; P. Judenstein and C. Sanchez, *J. Mater. Chem.*, 1996, **6**, 511; J. Y. Wen and G. L. Wilkes, *Chem. Mater.*, 1996, **8**, 1667.

2 *Better Ceramics Through Chemistry VI*, ed. A. Cheetham, C. J. Brinker, M. MacCartney, C. Sanchez, D. W. Schaefer and G. L. Wilkes, *Mater. Res. Soc. Symp. Proc.*, Materials Research Society, Pittsburgh, PA, 1994, vol. 346; *Better Ceramics Through Chemistry VII: Organic/inorganic Hybrid Materials*, ed. B. K. Coltrain, C. Sanchez, D. W. Schaefer and G. L. Wilkes, *Mater. Res. Soc. Symp. Proc.*, Materials Research Society, Pittsburgh, PA, 1996, vol. 435; *Sol–Gel Optics I*, ed. J. D. Mackenzie and D. R. Ulrich, *Proc. SPIE*, Washington, DC, 1990, vol. 1328; *Sol–Gel Optics II*, ed. J. D. Mackenzie, *Proc. SPIE*, Washington, DC, 1992, vol. 1758; *Sol–Gel Optics III*, ed. J. D. Mackenzie, *Proc. SPIE*, Washington, DC, 1994, vol. 2288.

3 W. Noll, *Chemistry and Technology of Silicones*, Academic Press, London, 1960; J. E. Mark and B. Erman, *Rubberlike Elasticity. A Molecular Primer*, Wiley, New York, 1988; J. E. Mark, in *Silicon-based Polymer Science*, ed. J. M. Zeigler and F. W. G. Fearon, Am. Chem. Soc., Washington, DC, 1990, p. 47.

4 G. L. Wilkes, B. Orler and H. H. Huang, *Polym. Prep.*, 1985, **26**, 300; H. H. Huang, B. Orler and G. L. Wilkes, *Macromolecules*, 1987, **20**, 1322; R. H. Glasser and G. L. Wilkes, *Polym. Bull.*, 1988, **19**, 51.

4 R. H. Glasser and H. H. Huang, *Polym. Bull.*, 1988, **19**, 51.

5 N. Yamada, I. Yoshinaga and S. Katayama, *J. Mater. Chem.*, 1997, **7**, 1491.

6 J. E. Mark and J. L. Sullivan, *J. Chem. Phys.*, 1977, **66**, 1006; A. L. Andrady, M. A. Llorente and J. E. Mark, *J. Chem. Phys.*, 1980, **72**, 2282.

7 J. E. Mark and S.-J. Pan, *Makromol. Chem., Rapid Commun.*, 1982, **3**, 681; J. Wen and J. E. Mark, *Polym. J.*, 1995, **27**, 492.

8 C. L. Schutte, J. R. Fox, R. D. Boyer and D. R. Uhlman, in *Ultrastructure Processing of Advanced Materials*, ed. D. R. Uhlmann and D. R. Ulrich, Wiley, New York, 1992, p. 95.

9 B. Erman and J. E. Mark, *Macromolecules*, 1998, **31**, 3099.

10 S. Diré, F. Babonneau, C. Sanchez and J. Livage, *J. Mater. Chem.*, 1992, **2**, 239.

11 F. Babonneau, *Polyhedron*, 1994, **13**, 1123.

12 B. Alonso, J. Maquet, B. Viana and C. Sanchez, *New J. Chem.*, 1998, **22**, 935.

13 M. Nabavi, C. Sanchez and J. Livage, *Eur. J. Solid State Inorg. Chem.*, 1991, **28**, 1173.

14 B. Alonso, Ph.D. Thesis, Université Pierre et Marie Curie, Paris, 1998.

15 F. Schindler and H. Schmidbaur, *Angew. Chem. Int. Ed. Engl.*, 1967, **6**, 683.

16 B. Raveau, *Rev. Chim. Miner.*, 1967, **4**, 729; P. Fleury, *Rev. Chim. Miner.*, 1969, **6**, 819.

17 R. K. Mittal and R. C. Mehrotra, *Z. Anorg. Allg. Chem.*, 1964, **327**, 311.

18 M. Nabavi, S. Dœuff, C. Sanchez and J. Livage, *J. Non-Cryst. Solids*, 1990, **121**, 31.

19 F. Cartan and C. N. Caughlan, *J. Phys. Chem.*, 1960, **64**, 1756.

20 M. Nabavi, Ph.D. Thesis, Université Pierre et Marie Curie, Paris, 1989.

21 J. Livage, *Chem. Mater.*, 1991, **3**, 578.

22 J. E. Roots, K. T. Ma, J. S. Higgins and V. Arrighi, *Chem. Phys.*, 1999, **1**, 137.

23 H. Eckert and I. E. Wachs, *J. Phys. Chem.*, 1989, **93**, 6796; O. B. Lapina, V. M. Mastikhin, A. A. Shubin, V. N. Krasilnikov and K. I. Zamarev, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1992, **24**, 457; J. Skibsted, N. C. Nielsen, H. Bildsøe and H. J. Jakobsen, *J. Am. Chem. Soc.*, 1993, **115**, 7351.

24 J. Skibsted, C. J. H. Jacobsen and H. J. Jakobsen, *Inorg. Chem.*, 1998, **37**, 3083.

25 N. Grassie and I. G. MacFarlane, *Eur. Polym. J.*, 1978, **14**, 875.

26 V. Belot, R. J. P. Corriu, D. Leclerq, P. H. Mutin and A. Vioux, *J. Polym. Sci. A*, 1992, **30**, 613.

27 S. J. Clarson, K. Dogson and J. A. Semlyen, *Polymer*, 1985, **26**, 930.

28 S. J. Clarson, J. E. Mark and K. Dogson, *Polym. Commun.*, 1988, **29**, 208.

29 A. L. Andrady, M. A. Llorente and J. E. Mark, *Polym. Bull.*, 1991, **26**, 357.

30 R. Okawara, *Bull. Chem. Soc. Jpn.*, 1958, **31**, 154; K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A: Theory and Applications in Inorganic Chemistry*, Wiley-Interscience, New York, 1997; J. Gnado, P. Dhamelincourt, C. Pélégris, M. Traisnel and A. LeMaguer-Mayot, *J. Non-Cryst. Solids*, 1996, **208**, 247.

31 L. Bois, Ph.D. Thesis, Université Pierre et Marie Curie, Paris, 1993.

32 A. L. Smith and D. R. Anderson, *Appl. Spectrosc.*, 1984, **38**, 822.

33 C. Cristiani, P. Forzatti and G. Busca, *J. Catal.*, 1989, **116**, 586; K. Tran, M. A. Hanning-Lee, A. Biswas, A. E. Stiegman and G. W. Scott, *J. Am. Chem. Soc.*, 1995, **117**, 2618; D. C. M. Dutoit, M. Schneider, P. Fabrizioli and A. Baiker, *J. Mater. Chem.*, 1997, **7**, 271.

34 D. C. M. Dutoit, M. Schneider, P. Fabrizioli and A. Baiker, *Chem. Mater.*, 1996, **8**, 734.

35 N. Das, H. Eckert, H. C. Hu, I. E. Wachs, J. F. Walzer and F. J. Feher, *J. Phys. Chem.*, 1993, **97**, 8240.

36 P. R. H. P. Rao, *Zeolites*, 1993, **13**, 663; A. Tuel and Y. B. Taârit, *Appl. Catal. A*, 1993, **102**, 201.

37 R. Neumann, M. Chava and M. Levin, *J. Chem. Soc., Chem. Commun.*, 1993, 1685.

38 L. R. Lecoustumer, B. Taouk, M. Lemeur, E. Payen, M. Guelton and J. Grimblot, *J. Phys. Chem.*, 1988, **92**, 1230.

39 F. A. Miller and L. R. Cousins, *J. Chem. Phys.*, 1957, **26**, 329; F. A. Miller and W. K. Baer, *Spectrochim. Acta*, 1961, **17**, 112; H. Selig and H. H. Claasen, *J. Chem. Phys.*, 1966, **44**, 1404.

40 F. D. Hardcastle and I. E. Wachs, *J. Phys. Chem.*, 1991, **95**, 5031.

41 G. Engelhardt, H. Hjancke, M. Mägi, T. Pehk and E. Lippmaa, *J. Organomet. Chem.*, 1971, **28**, 293; Q. T. Pham, R. Pétiaud, H. Waton and M. F. Llauro-Darricades, *Proton and Carbon NMR Spectra of Polymers*, Penton Press, London, 1991; A. R. Bassindale and K. H. Pannell, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1801; L. Garrido, J. E. Mark, C. C. Sun, J. L. Ackerman and C. Chang, *Macromolecules*, 1991, **24**, 4067; F. C. Schilling, M. A. Gomez and A. E. Tonelli, *Macromolecules*, 1991, **24**, 6552.

42 O. Lutz, W. Nepple and A. Z. Nolle, *Z. Naturforsch., Teil A*, 1976, **31**, 1046.

43 E. Heath and O. W. Howarth, *J. Chem. Soc., Dalton Trans.*, 1981, 1105.

44 A. T. Harrison and O. W. Howarth, *J. Chem. Soc., Dalton Trans.*, 1985, 1953; G. A. Pozarnsky and A. V. McCormick, *J. Mater. Chem.*, 1994, **4**, 1749.

45 U. Scheim, K. Rühlmann, J. W. Kelly and S. A. Evans, *J. Organomet. Chem.*, 1989, **375**, 33.

46 E. Liepins, I. Zicmane and E. Lukevics, *J. Organomet. Chem.*, 1986, **306**, 167.

47 P. Lux, F. Brunet, J. Virlet and B. Cabane, *Magn. Reson. Chem.*, 1996, **34**, 100.

48 Y. Sugahara, S. Okada, K. Kuroda and C. Kato, *J. Non-Cryst. Solids*, 1992, **139**, 25.

49 P. Lux, F. Brunet, J. Virlet and B. Cabane, *Magn. Reson. Chem.*, 1996, **34**, 173.

50 Note that the other possible assignments for the resonance at δ −11 are not convincing. The ^{29}Si resonances of D_1 units linked to one ethoxy or hydroxy group are expected to give residual thin signals. Another possibility could be a DMS unit linked to two vanadate units. The corresponding signal would have a different chemical shift from that of DMS units linked to one vanadate unit. This assignment seems to be unlikely as it would imply a vanadium-to-silicon molar ratio of >0.3.

51 C. Guermeur, J. Lambard, J.-F. Gerard and C. Sanchez, *J. Mater. Chem.*, 1999, **9**, 769.

52 S. Hayakawa, T. Yoko and S. Sakka, *J. Solid State Chem.*, 1994, **112**, 329.

53 W. Priebsch and D. Rehder, *Inorg. Chem.*, 1990, **29**, 3013.

54 W. Priebsch and D. Rehder, *Inorg. Chem.*, 1985, **24**, 3058.

55 From additional experiments with MeSi(O-)$_3$ and Si(O-)$_4$ units, we observe that the replacement of the methyl groups attached to the silicon by 'oxy' groups leads effectively to an increase in the ^{51}V chemical shift differences.

56 D. Rehder, C. Weidemann, A. Duch and W. Priebsch, *Inorg. Chem.*, 1988, **27**, 584.

57 F. J. Feher and J. F. Walzer, *Inorg. Chem.*, 1991, **30**, 1689.

58 H. Jacobson and W. H. Stockmayer, *J. Chem. Phys.*, 1950, **18**, 1600; J. F. Brown and G. M. J. Slusrczuck, *J. Am. Chem. Soc.*, 1965, **87**, 931.

59 C. J. Balhausen and H. B. Gray, *Inorg. Chem.*, 1962, **1**, 111; F. Babonneau, P. Barboux, F. A. Josien and J. Livage, *J. Chim. Phys.*, 1985, **82**, 761.

60 M. J. Hunter, J. F. Hyde, E. L. Warrick and H. J. Fletcher, *J. Am. Chem. Soc.*, 1946, **68**, 667.

61 B. Alonso and C. Sanchez, manuscript in preparation.

62 In a homogeneous gel, the average number 'n' of DMS units in a segment linked to metallate units is related to the functionality 'f' of these units and their relative ratio to silicon 'r' by the simple formula $n = 2/fr$.

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