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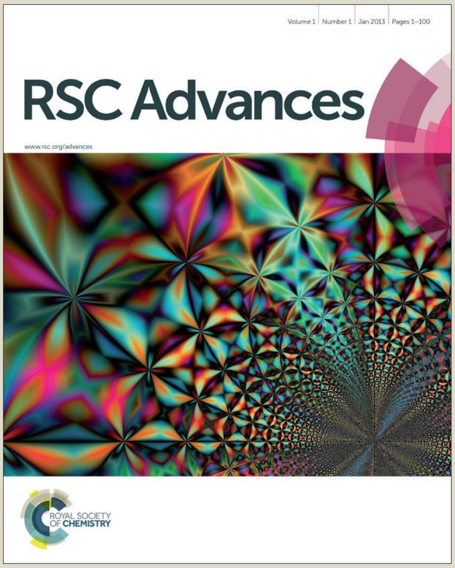

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Strained Surface Siloxanes as a Source of Synthetically Important Radicals

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The calcination of pure amorphous silica at temperatures of up to 850 °C results in the formation of strained siloxane rings which at room temperature, are capable of undergoing homolytic cleavage at room temperature to generate radicals when in the presence of an appropriate substrate. These surface radicals are shown act as radical initiators for the polymerisation of methyl acrylate (MA). Silica calcined at 600 °C ($SiO_{2(600)}$) was found to be the most active radical initiator. For example, in hexane at 70 °C, a yield of poly(methyl acrylate) (PMA) of 77% was obtained with a polydispersity index (PDI) of 1.4 after 24 h. In supercritical CO_2 (*sc*-CO_2) at 210 °C for 1 h, a yield of PMA of 85% with a PDI of 1.3 was obtained. The use of polyhedral oligo-silsesquioxanes (*a*6*b*0 and *a*7*b*3) as silica surface model compounds confirms the need for strained siloxane rings to induce radical polymerisation. Mass spectroscopic studies of silsesquioxane *a*6*b*0 in the presence of MA reveal the presence of numerous addition products resulting from the homolytic breaking of Si–O–Si bonds to form potential reaction intermediates.

Introduction

Silica is one of the most earth-abundant materials and distinguishes itself with remarkable structural and chemical flexibility.[1] Silica surfaces are composed of rings of siloxane bridges and silanol groups. The concentrations and types of these surface functionalities depend on a range of parameters, including the silica's synthesis method (sol-gel, flame pyrolysis) and the heating regimes to which the silica has been exposed in terms of temperature, duration and the presence or exclusion of water/water vapour.[2] So far, the surface of pure, amorphous untreated silica has been viewed as chemically reactive only in terms of the reversible hydrolysis of siloxanes to silanols and of silanols performing various types of acid catalysis. Although silica surface defects have been reported,[3] these have not been shown to have any synthetic utility. EPR and magnetic susceptibility have been used to study defects in quartz and silica for more than fifty years and the characterisation of such defects by EPR has been frequently reviewed.[4]

Surface silanol groups are either isolated, geminal or vicinal and can form strongly hydrogen-bonded, so-called silanol 'nests'.[5] When silica is exposed to high temperatures, some of the silanol groups condense to eliminate water and to produce siloxane rings, (*i.e.* four- (Si_2O_2), six- (Si_3O_3), eight- (Si_4O_4), *etc.* membered rings) with the proportion of strained (i.e., six membered) siloxane rings initially increasing with time and temperature.[1,6] At very high temperatures the siloxane rings can relax as the surface is close to melting, a process which decreases the number of strained surface species and, when occurring extensively, the surface area. Typically, silica heated above 250 °C has no adsorbed water, and the number of Si–OH groups decreases from 6 OH/100 $Å^2$ initially to 2 OH/100 $Å^2$ at 500 °C, then to 1 OH/100 $Å^2$ at 800 °C.[4a, 7]

Investigations published over the last four decades based on various electron paramagnetic resonance (EPR) experiments, involving silica-alumina and probe molecules, reveal that surface radicals can be present on calcined silica or silica-alumina and that spectroscopic evidence can be obtained of their existence on silica as well as silica-alumina oxide surfaces. For example, Rooney[8] used the EPR-silent perylene and anthracene and converted them to the corresponding EPR-active radical cations by exposure to freshly calcined (750 °C) silica-alumina in the absence of water. Hall showed that a range of polynuclear aromatic hydrocarbons and phenylated amines absorbed onto such supports (pre-treated in a variety of ways) also became EPR-active. This is consistent with the generation of the corresponding organic radicals upon surface interaction.[3, 9]

The results of the anthracene-silica experiments were interpreted in terms of the anthracene (A) being trapped as the cation radical ($A^{+\bullet}$) at a silica defect site. Such defect sites are known to act as deep electron traps, with one proposed mechanism involving the conversion of the paramagnetic non-bonding oxygen hole (NBOH) centre to a diamagnetic $Si–O^-$ site.[10] It has been suggested that the NBOH is generated by the homolysis of a Si–O–Si bond (Scheme 1), with the generation of a paramagnetic dangling bond (analogous to the *E′* centre in quartz[11]). The stoichiometry of the

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$$\equiv\mathrm{Si{-}O{-}Si}\equiv \;\rightarrow\; \equiv\mathrm{Si{-}O}\bullet \;+\; \bullet\mathrm{Si}\equiv$$

$$\equiv\mathrm{Si{-}O}\bullet \;+\; \mathrm{A} \rightarrow \;\equiv\mathrm{Si{-}O}^{-} \;+\; \mathrm{A}^{+}\bullet$$

Scheme 1. Homolysis of a Si–O–Si bond and reaction with anthracene (A).

presumed reaction of the NBOH with anthracene is illustrated in Scheme 1.

Classically, only Si–OH groups are thought to be synthetically reactive and it has been presumed that hydrolysis of a siloxane to generate two Si–OH groups was needed to activate siloxanes for synthetic purposes. However, in this contribution we contend that strained surface rings, including six-membered surface siloxanes, can also act as originators of surface radicals. We further show that these radicals can be synthetically active.

To illustrate this point further, we also exemplify the use of a strained silica surface by inducing well-behaved radical polymerisations, generating high quality poly(methyl acrylate) (PMA) with such a surface. We additionally prove the radical nature of the reaction by the addition of radical traps and demonstrate that these results are obtained using a variety of silica sources.

These findings are of significance as silica materials and silica-supported catalysts are ubiquitous,[12] but the synthetically meaningful radical chemistry that can be induced by their surfaces has been overlooked.

We underpin the interpretation of our findings not only by successfully testing a predictive mechanism, by replicating the observed surface behaviour with soluble silica surface model compounds (polyhedral oligo-silsesquioxanes), but also by being able to delineate distinct surface group reactivities through high resolution mass-spectroscopic investigations of substrate/silica surface model compound interactions.

Results and Discussion

The calcination of commercially available mesoporous silica (200–400 mesh, Ajax) at temperatures of 120, 300, 600 and 850 °C was performed under a stream of dry air for 20 h. This process removes the chemisorbed water from the surface and creates the desired siloxane species. The resulting materials, after cooling to room temperature, were characterised by N_2 sorption studies and the results are shown in Table 1. For ease of reference the calcined, then cooled, silcas are denoted as $SiO_{2(temp)}$ (where (temp) is the calcination temperature). Treatment of the silica at temperatures of 120, 300 and 600 °C resulted in a small decrease in surface area from the uncalcined material, with no change in the pore diameter or pore volume. However, in the case of $SiO_{2(850)}$ there is a dramatic decrease in surface area and pore volume due to annealing of the surface.

Since surface radicals can be detected following the interaction of anthracene with calcined silica using the same methods described by Hall[9] (see Figure S1), calcined silica should be able to initiate various radical reactions such as free-radical polymerisations. This type of polymerisation is commonly initiated/co-initiated by the decomposition of highly reactive and unstable species, such as azo-compounds (*e.g.* azobisisobutyronitrile, AIBN - Table 2, Entry 1), peroxides (*e.g.*, di-*tert*-butyl peroxide)[2b] or various metal complexes (Table 2, Entry 2)[14] or metallocenes, either as homogeneous (Table 2, Entry 3)[15-16]or immobilised species.[17] However, these catalysts are often expensive and frequently difficult to synthesise and/or handle. For those catalysts supported on silica and active in reactions where radicals can influence the reactivities and selectivities, there are possible significant implications if $SiO_{2(600)}$ were to be an active catalyst for such reactions.

Table 1. N_2 sorption data for the calcined commercial mesoporous silica.

Entry	Silica	Calcination Temp. (°C)	Surface Area (m^2/g)[a]	Pore Diameter (Å)	Pore volume (cm^3/g)
1	SiO_2	—	478	66.1	0.75
2	$SiO_{2(120)}$	120	446	66.3	0.71
3	$SiO_{2(300)}$	300	464	67.2	0.74
4	$SiO_{2(600)}$	600	462	66.7	0.73
5	$SiO_{2(850)}$	850	311	64.1	0.47

[a] BET surface area.

Table 2. Polymerisation data for methyl acrylate using various initiators and silica initiators.[a]

Entry	Catalyst	Solvent	Yield (%)	M_n	PDI
1	CPDN/AIBN[g] [13]	benzene	90	16958	1.16
2	CuBr/TPEN[e]/EBiB[f] [14]	—	80	ND	1.15
3	$CpTiCl_3$/MAO[15]	toluene	51	7800	1.90
4	—	hexane	20	ND[c]	ND[c]
5	uncalcined SiO_2	hexane	22	ND[c]	ND[c]
6	$SiO_{2(600)}$	hexane	77	20000	1.4
7	$SiO_{2(600)}$/radical trap	hexane	13	ND[c]	ND[c]
8	*a*6*b*0	hexane	53	3600	3.9
9	*a*7*b*3	hexane	21	2700	4.1

[a] Reaction conditions: refluxing hexane (70 °C) for 24 h. [b] Yields were determined by integration of the ^{1}H NMR spectra of the reaction mixtures. [c] Not determined. [d] Number-average molecular weight. [e] TPEN = *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-ethylenediamine. [f] EBiB = ethyl 2-bromoisobutyrate. [g] CPDN = 2-cyanoprop-2-yl-1-dithionaphthalate.

Table 2 summarises the data of the relevant polymerisation experiments in refluxing hexane. Consistent with methyl acrylate polymerisation in general, there is a degree of thermally induced "background" polymerisation (Table 2, Entry 4). Addition of uncalcined silica (postulated to have no active radical surface species) does not lead to higher than background conversions (Table 2, Entry 5). However, the addition of the $SiO_{2(600)}$ (previously cooled to room temperature) as catalyst increases the yield to 77%, generating a high quality poly(methyl acrylate) with a polydispersity index (PDI) of 1.4 that is very close to the theoretically ideal value of 1.2 (Table 2, Entry 6).[18] As expected addition of the radical trap 2,6-di-*tert*-butylphenol, reduces the

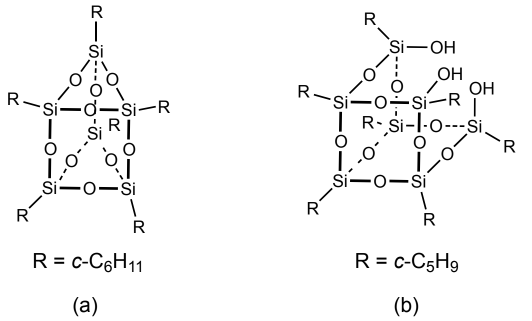


Figure 1. The silsesquioxanes (a) $a6b0$, and (b) $a7b3$.

yield to below background (Table 2, Entry 7), showing that the action of $SiO_{2(600)}$ is radical in nature. These results are also consistent with the absence of adventitious metal impurities as the origin of the catalytic effect, since the calcined reactive silica can be deactivated by air-exposure and re-activated by calcination at will (Table 3, Entries 3, 4 and 5) and because the effect is also observed in experiments using mesoporous silicas, such as TUD-1[19] and MCM-41,[20] generated from high purity tetraethoxysilane (i.e., generated in the absence of metals).

However, to further test whether the observed activity is, indeed, due to surface species and to absolutely rule out any metal contamination at ppm/ppb level being responsible, silsesquioxanes, molecular models of silanols (Si–OH), non-strained (eight-membered rings, Si_4O_4) and strained (six-membered rings, Si_3O_3) siloxanes (Figure 1), were reacted with methyl acrylate analogously to the polymerisations involving $SiO_{2(600)}$. For the silsesquioxane *a*6*b*0, the model containing the strained siloxanes, a distinct increase in yield over the background reaction could be observed (Table 2, Entry 8), whereas when using the silsesquioxane *a7b3*, containing silanol and non-strained siloxanes, no such additional activity resulted (Table 2, Entry 9). These results clearly and unequivocally prove that: (a) no metal contamination was responsible for the silica reactivity; (b) strained siloxanes are responsible for much of the observed radical chemistry; and (c) silanols have little or no effect on the polymerisation.

Based on the above, we propose the following mechanism (Figure 2). Two different radicals (which in this case can initiate polymerisation) are generated upon the homolytic opening of the siloxane ring, stabilised or induced by the presence of an organic species. Once the radicals have been generated they are free to react with suitable substrates, in this case the activated alkene in methyl acrylate.

To test the mechanism postulated, we varied the reaction conditions, changing temperature regime, solvent and catalyst pre-treatment. Supercritical carbon dioxide (*sc*-CO_2) has similar powers of solvation to hexane. However, due to the supercritical state of the solvent, it can be expected that heat and mass transfer (especially at high conversions) are improved. In addition, any background activity that might distort the results should be significantly enhanced at the much higher temperatures, providing a further check. The relevant experiments are summarised in Table 3.

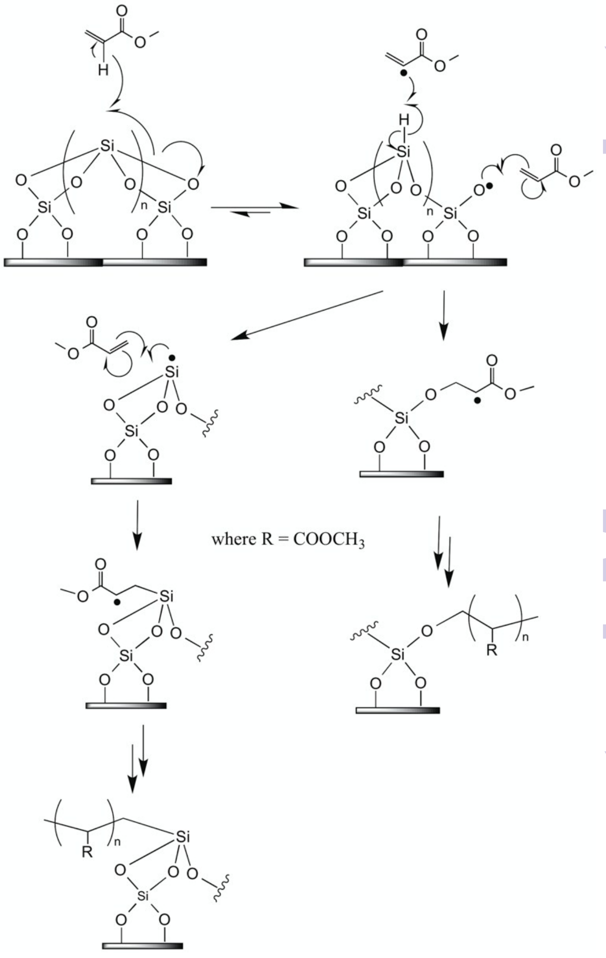


Figure 2. Proposed polymerisation of methyl acrylate using radicals generated on the surface of $SiO_{2(600)}$.

In the high-temperature *sc*-CO_2 reaction systems the reaction time was reduced to 1 h, in order to achieve similar levels of background polymerisation activity to those observed with hexane as solvent. A comparable yield was observed (Entry 1, Table 3). Use of the catalyst for 15 min (Entry 2, Table 3) results a higher than background conversion, but the resulting polymer has low molecular weight and high PDI. When using the catalyst for 1 h in *sc*-CO_2 (Entry 3, Table 3), higher conversions (up to 85%) than those obtained after 24 h in hexane were obtained, whilst again yielding a polymer with high molecular weights and a near-ideal PDI.

Our model of the active site would predict that calcined silica with more than brief exposure to the atmosphere should lead to a poor catalytic performance. Equally, we would predict a full recovery of the activity and selectivity after re-calcination and this is exactly what we observe (Table 3, Entries 4 and 5). A further prediction of the model is that using catalysts that have been subjected to a lower calcination temperature (300 °C, giving a lesser extent of silanol condensation, yielding fewer strained siloxane groups) or a much higher calcination temperature (850 °C, giving

Table 3. Polymerisation data for methyl acrylate using various initiators and silica initiators.[a]

Entry	Catalyst	Time (h)	Yield (%)[b]	M_n[e]	PDI
1	—	1	22	800	5.1
2	$SiO_{2(600)}$	0.25	39	2700	5.6
3	$SiO_{2(600)}$	1	85	12000	1.3
4	$SiO_{2(600)}$[c]	1	35	1700	5.9
5	$SiO_{2(600)}$[d]	1	81	11000	1.5
6	$SiO_{2(300)}$	1	63	10000	4.3
7	$SiO_{2(850)}$	1	59	5400	5.2

[a] Reaction conditions: *sc*-CO_2 at 76 bar and 210 °C. [b] Yields were determined by integration of the ^1H NMR spectra of the reaction mixtures. [c] Silica that was calcined at 600 °C then exposed to the atmosphere at room temperature for 3 months. [d] Silica used in entry 4, but re-calcined at 600 °C prior to use. [e] Number-average molecular weight.

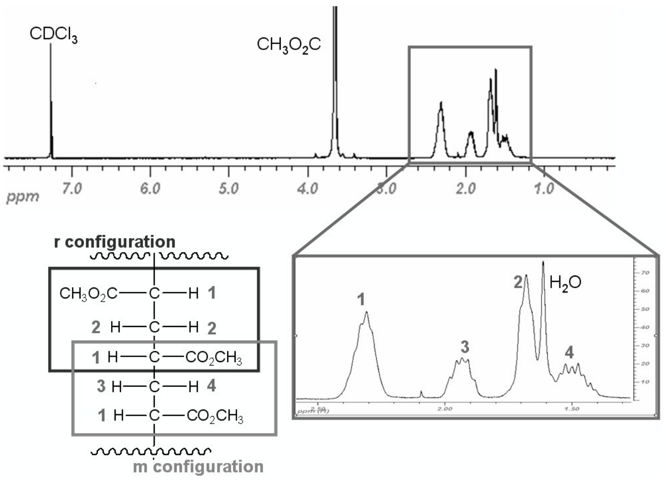


Figure 3. ^1H NMR spectra (in $CDCl_3$) and assignments of poly(methyl acrylate) produced using calcined silica in $scCO_2$ (1 h).

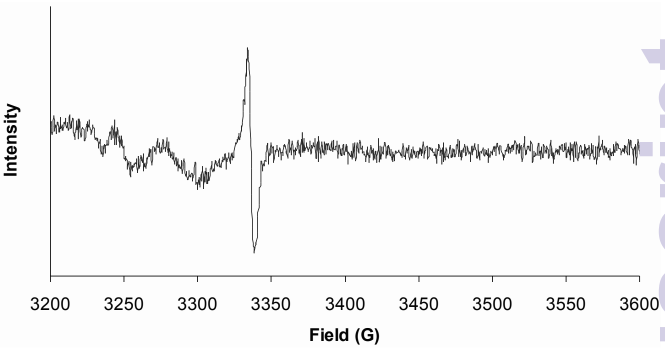


Figure 4. EPR spectrum of PMA produced using $SiO_{2(600)}$. EPR sample prepared as a saturated solution in $CHCl_3$ The EPR spectrum was recorded at 77 K.

more relaxed surface siloxanes, fewer strained ones) will result in a lower activity silica as compared to $SiO_{2(600)}$. Again, this is exactly what is observed (Table 3, Entries 6 and 7).

All polymers obtained were analysed by ^1H NMR spectroscopy. A representative spectrum is shown in Figure 3. In all cases the polymers have both *r* and *m* configurations,[15] and are also atactic.[21] ^1H NMR can also give information regarding the end-groups on the polymer chain. [22,23] However, from Figure 1 it is evident that no end-group information is available, as there are no additional proton environments within the ^1H NMR spectrum other than those already assigned as PMA, as expected if the initiator is not an organic material. In contrast, Energy Dispersive X-ray spectroscopy (EDX) was conducted on a sample of PMA produced using *sc*-CO_2 and low concentrations of silicon were detected throughout the polymer sample, which is consistent with the experimental observations that the silica was neither identifiable nor recoverable after polymerisation. This result may be indicative that some of the polymer chains contain SiO_2 groups at the initiating terminus of the polymer chain, although this has not been confirmed experimentally.

When a saturated solution of PMA (freshly synthesised using $SiO_{2(600)}$ and $scCO_2$) was prepared in $CHCl_3$, frozen and irradiated at 77 K a relatively weak EPR signal was obtained, confirming the presence of at least one radical species (Figure 4). The narrow, intense signal at 3336 G (*g* = 2.0026) is typical of a CH-based radical that is part of an extensive hydrocarbon chain,[24] with the two smaller, broad signals at 3245 G (*g* = 2.0569) and 3278 G (*g* = 2.0329), attributable to the presence of low concentrations of silyl peroxy and organo peroxy radicals, respectively, in the PMA.[25] The EPR spectrum displays no distinct hyperfine structure, suggesting the radical is delocalised throughout the polymer, while the experimental *g*-value of 2.0026 correlates well with other low-temperature results for PMA. Reports in the literature also indicate that the EPR spectra of PMA samples vary dramatically depending on instrument temperature and irradiation time.[26] The position of the propagating radical also has a significant impact on the shape of the resulting EPR spectrum, with end- and mid-chain radicals both producing different spectra.[24, 27]

The effect of silica concentration on the yield of polymer was also probed (Figure 5). Increasing the amount of silica used resulted in a gradual increase in PMA production up to a maximum yield of 80% for 100 mg of silica. As the amount of silica is increased further, the PMA yield decreased slightly, which may be associated with increased viscosity of the reaction mixtures as a consequence of a greater number of polymer chains, leading over time to decreased propagation due to lower diffusional rates of the monomers.[28] When larger amounts of calcined silica were used (460 or 600 mg), silica was identified at the bottom of the reaction vessel. This result was not observed in the reactions using a lesser amount of silica and is likely to be a consequence of more silica surface and, by implication radical surface sites, being available than necessary or even usable for radical induction. That is, once organic radicals are formed, they will be tethered to the silica surface, and can be expected to react more easily with the incoming monomer species than with additional silica surface sites.

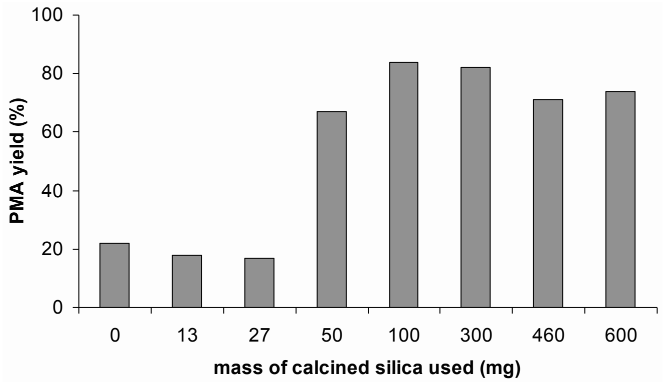


Figure 5. The effect of $SiO_{2(600)}$ concentration on the amount of PMA produced in *sc*-CO_2 at 210 ˚C for 1 h (18 mL of MA used).

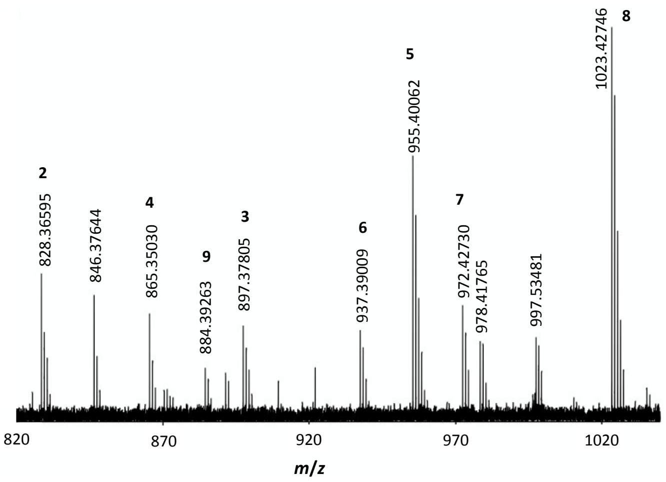


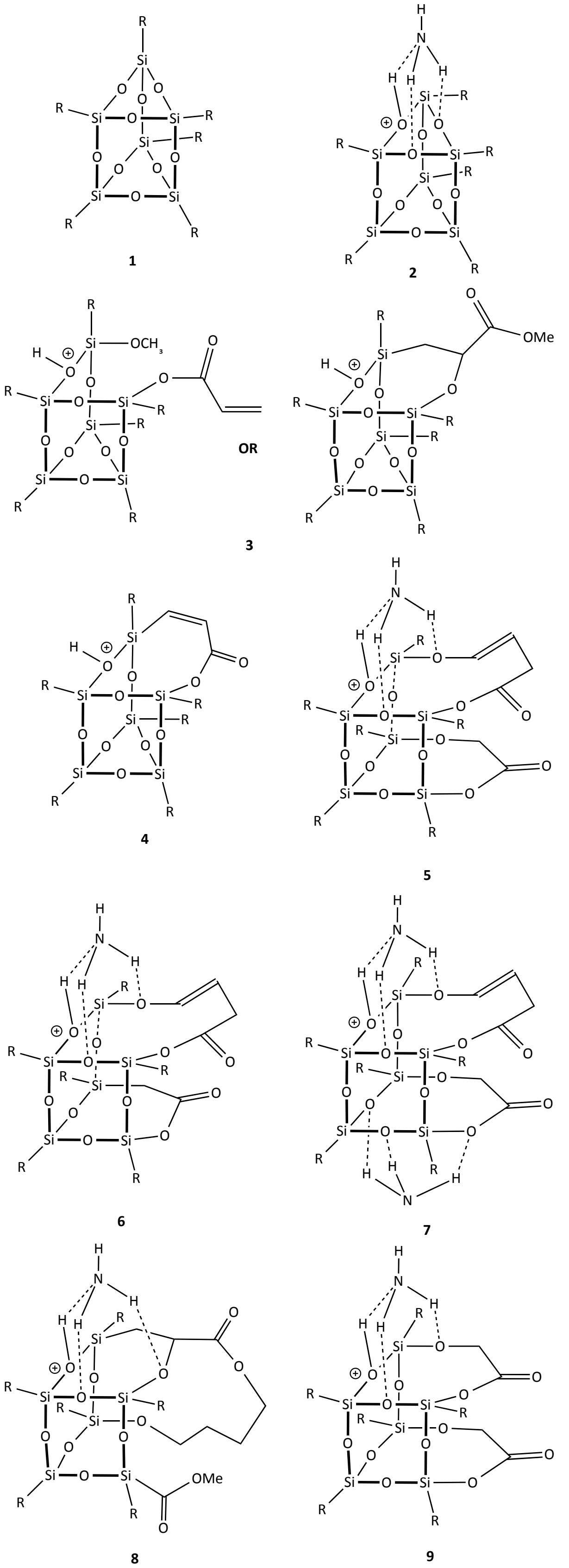
Figure 6. APCI mass spectrum of *a*6*b*0 (R = C_6H_{11}) with methyl acrylate.

As seen in Table 2, the silsesquioxane *a*6*b*0 is capable of catalysing the polymerisation of methyl acrylate in hexane at 70 °C. Attempts to isolate a reaction intermediate from this reaction proved unsuccessful, thus, it was decided to interrogate the reaction system using mass spectrometry as previously undertaken for simple reactive molecules.[29] The high resolution APCI mass spectrum of the silsesquioxane *a*6*b*0 (R = C_6H_{11}, **1**) obtained with the co-injection of methyl acrylate/CH_3CN is shown in Figure 6. In addition to the molecular ion at *m/z* = 811.33900 (not shown),[29] the spectrum suggests that methyl acrylate reacts with this molecular ion, generating several products (see Table 4 and Figure 7).

The ion at *m/z* = 828.36595 corresponds to the previously reported species generated from the addition of NH_3 to the molecular ion $[MH]^+$ to afford $[Si_6cy_6O_9NH_4]^+$ (**2,** $[C_{36}H_{70}NO_9Si_6]^+$; calculated *m/z* = 828.36607). The NH_3 is formed in the mass spectrometer as a result of the reaction of the N_2 carrier gas passing through the discharge in a proton rich environment.[29] An ion at *m/z* = 897.37805 corresponds to $[MH^+ + H_3COC(O)CH{=}CH_2]$ (**3**, $[C_{40}H_{73}O_{11}Si_6]^+$; calculated *m/z* = 897.37685) and is assigned as arising from the addition of one molecule of methyl acrylate across a Si–O–Si fragment. Loss of methanol from this ion gives the ion at *m/z* = 865.35030 (**4**, $[C_{39}H_{69}O_{10}Si_6]^+$; calculated *m/z* = 865.35064). The ion at *m/z* = 955.40062 (**5**, $[C_{42}H_{77}NO_{12}Si_6]^+$; calculated *m/z* = 955.40559) could be generated by addition of NH_3 and loss of a C_2H_4 fragment from reaction of two molecules of methyl acrylate with the protonated molecular ion. The resultant species with *m/z* = 955 can then lose H_2O to generate the species with *m/z* = 937.39009 (**6**, $[C_{42}H_{75}NO_{11}Si_6]^+$; calculated *m/z* = 937.39502) or react with another NH_3 to form the species with *m/z* = 972.42730 (**7**, $[C_{42}H_{80}N_2O_{12}Si_6]^+$; calculated *m/z* = 972.43214). The species observed at *m/z* = 1023.42746 (**8**, $[C_{46}H_{80}NO_{13}Si_6]^+$; calculated *m/z* = 1023.43180) results from addition of two molecules of methyl acrylate to the species with *m/z* = 897 followed by loss of CO_2, CH_4 and H_2. The species with *m/z* = 884.39263 (**9**, $[C_{39}H_{73}NO_{10}Si_6]^+$, calculated *m/z* = 884.39228) is the result of addition of two methyl acrylate molecules to form the unobserved species with *m/z* = 959 followed by loss two C_2H_4 units and CO_2. The proposed structures of the species identified are shown in Figure 7 and summarised in Table 4 with mass errors for the assignments up to 5 ppm due to space charge effects from the dominant *a6b0* present in the spectrum.[30] Notably, such addition products are completely absent when the same experiment is performed using the incompletely condensed silsesquioxane *a*7*b*3 (R = C_5H_9) in the presence of methyl acrylate, with only the expected elimination products for the silsesquioxane observed.[29]

Table 4. Summary of species observed in the high resolution APCI mass spectrum of the silsesquioxane *a*6*b*0 (R = C_6H_{11}) and methyl acrylate.

Species	Exp. mass (amu)	Calc. mass (amu)	Difference (amu (ppm))	Formula
1	828.36595	828.36607	0.00012 (0.1)	$[C_{36}H_{70}NO_9Si_6]^+$
2	897.37805	897.37629	0.00176 (2.0)	$[C_{40}H_{73}O_{11}Si_6]^+$
3	865.35030	865.35064	0.00340 (3.9)	$[C_{39}H_{69}O_{10}Si_6]^+$
4	955.40062	955.40559	0.00497 (5.2)	$[C_{42}H_{77}NO_{12}Si_6]$
5	937.39009	937.39502	0.00493 (5.3)	$[C_{42}H_{75}NO_{11}Si_6]$
6	972.42730	972.43214	0.00484 (5.0)	$[C_{42}H_{80}N_2O_{12}Si_6]^+$
7	1023.42746	1023.43180	0.00434 (4.2)	$[C_{46}H_{80}NO_{13}Si_6]$
8	884.39263	884.39228	0.00035 (0.4)	$[C_{39}H_{73}NO_{10}Si_6]^+$
9	828.36595	828.36607	0.00012 (0.1)	$[C_{36}H_{70}NO_9Si_6]^+$



1 2 3 4 5 6 7 8 9

Figure 7. Proposed structures of the species observed in the high resolution APCI mass spectrum. In all structures R = C_6H_{11}.

Conclusions

When pure silica, irrespective of its meso- or macrostructural features and its origin (*i.e.*, whether sol-gel, flame pyrolysis molecular or oxidic precursors), is heated to 600 °C then cooled to ambient temperatures, active radical surface species are induced when strained siloxane rings come into contact with organic reactants, as shown by spectroscopic (Figure S1) and reactivity studies. At least some of these surface sites are strained Si_3O_3 rings, as successfully modelled by such rings present in molecular analogues, *i.e.*, the polyhedral silsesquioxane *a*6*b*0. The related molecular species *a*7*b*3 that contains no such rings, but only Si_4O_4 rings and silanols, is able to quench radicals (see Figure S2) and therefore displays no polymerization activity.

A detailed mass spectroscopic study[29] shows that Si_3O_3 rings, indeed, react with the organic substrate, whereas Si_4O_4 rings do not. Therefore, in the case of strained Si_3O_3 there is now good evidence of the organic substrate either inducing radical formation or arresting extremely fast radical interconversions within the strained ring structure. From these insights, we were able to predict which surface pre-treatment would yield the more active catalyst type, based on the relative abundance of strained-surface species – directly confirming our postulate that strained surface siloxanes can yield synthetically active radicals. These results necessitate careful assessment of the potential influence of such calcined silica surfaces in catalytic reactions that are susceptible to influence by radical chemistry, given the abundance of such support surfaces that are exposed to heating during pre-treatment.

Experimental

For full details see supplementary information.

Polymerisation reactions involving *sc*-CO_2 were conducted in a Parr stainless steel batch-type reactor that was fitted with a gas inlet valve and a bladed stirrer. Temperature and stirring speed was varied with a Parr controller unit (Model #4842).

Preparation of PMA in hexane: The selected silica source (0.0400 g) and methyl acrylate (8 mL) were heated under reflux in hexane (30 mL) for 24 h. The reaction mixture was cooled to room temperature and the hexane removed *in vacuo* to afford poly(methyl acrylate) as a highly viscous gel.

Preparation of PMA in sc-CO_2: In a typical example, pre-treated silica (0.0975g) and methyl acrylate (18 mL) were placed in a Parr reactor. The reactor was pressurised with CO_2 (32 bar) and the system equilibrated for 10 min. The system was re-pressurised with CO_2 (32 bar) and left to equilibrate for a further 10 min. The system was then finally re-pressurised with CO_2 (32 bar) and heated (ramp rate 5 °C/min.) in order to achieve sc-CO_2 conditions (76 bar, 210 ^{o}C). After 1 h under sc-conditions the reactor was cooled to room temperature and the CO_2 vented. Poly(methyl acrylate) was obtained as a pale yellow, highly tacky polymer. The polymers were analysed by ^{1}H NMR ($CDCl_3$) to determine conversion, tacticity[15, 21] and end-group information.[22-23]

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