Free-Radical Polymerisation in Supercritical Carbon Dioxide Using Activated Silica Initiators

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The art and science of polymerisation underpin many industrial processes, such as the production of plastics, paints and coatings as well as various electronic and biomedical devices. In this contribution we will show how radicals are generated on calcined silica (monitored by electron paramagnetic resonance) and employed as novel free-radical polymerisation initiators in supercritical CO_2 (scCO_2). Polymers have been analysed using gel permeation chromatography, ^1H nuclear magnetic resonance and scanning electron microscopy.

INTRODUCTION

Traditionally, free radical polymerisation is initiated by the decomposition of a highly reactive and unstable species, such as an azo-compound (e.g. azobisisobutyronitrile, AIBN) or a peroxide (e.g. di-t-butyl peroxide).[1] These molecules undergo homolytic cleavage to produce radicals that attack the monomer reactant, and thereby initiate polymerisation. Conventional radical initiators rely on the fact that they are highly reactive; however, as they are unstable, care must be taken in their handling and storage. Various metallocenes have also been used as radical initiators / co-initiators, either as homogeneous catalysts[2, 3] or anchored to silica as heterogeneous supports.[4, 5] When examining the immobilisation of traditional radical initiators on silica the question arises whether (a) the silica surface is, in fact, innocent during the reaction and (b) whether it is necessary at all to use these initiators, as silica may be sufficient. The coupling of our all-silica initiator with supercritical CO_2 represents a "green" approach to the production of polymers.

To date, silica is one of the most readily used heterogeneous supports. The silica surface is composed of cyclic siloxanes ($\equiv$Si-O-Si$\equiv$) and silanol groups ($\equiv$Si-OH). The concentrations and types of these functionalities depend on the temperatures of the surface pre-treatments.[6, 7] The siloxanes are generally constituent of four-, six-, eight-, etc. membered rings, while the silanol groups are either isolated, geminal, or vicinal. With an increase in the pre-treatment temperature, the mean size of the siloxane rings decreases, while the silanols condense to produce additional siloxane rings and water.[7] Siloxanes are generally strained and thus have the potential to be highly reactive. **Figure 1** shows one of the strained molecular rings, $(SiO_2)_n$, proposed by Bromley *et al.* where $n = 12$.[8]
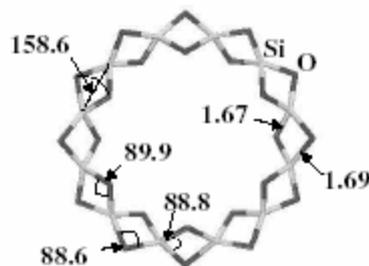
Figure 1. An example of the $(SiO_2)_n$ molecular ring proposed by Bromley *et al*., where $n = 12$. Bond lengths are given in Å and angles in degrees.[8]

Various groups have used electron paramagnetic resonance (EPR) to investigate the formation of radicals on the surface of calcined silica,[9-11] however to date, there has been no report of the use of silica-based-radicals as polymerisation initiators. For example, Rooney *et al*. investigated the EPR of naphthalene and anthracene on activated silica-alumina based catalysts, and confirmed the presence of radicals.[9] Similar work by Khulbe *et al*. reported phenothiazine radicals on the surface of silica, alumina and silica-alumina.[10] In each case the materials were calcined at 500°C for 20 h before being added to a solution of phenothiazine, and the system monitored *via* EPR. Hall also detected EPR signals generated from polynuclear aromatic hydrocarbons and phenylated amines absorbed onto silica-alumina supports, confirming the presence of hydrocarbon radicals on the surface of silica-alumina.[11]

Thus, although the notion of organic radicals being present on the surface of silica has been reported earlier, the mechanism of their formation has received little attention, and their exploitation, less. It is with this in mind that we aim to not only observe, but also utilise these silica-based-radicals as initiators for free-radical polymerisation. In the present contribution, radicals are generated on calcined silica and employed as novel polymerisation initiators.

MATERIALS AND METHODS
Methyl acrylate (Merck, 99 % stabilised with 100 ppm hydroquinone), chloroform (Merck), tetrahydrofuran (BDH) and carbon dioxide (BOC, industrial grade) were all used as received. Silica (Ajax, flash chromatography grade, 230-400 mesh) was calcined at 600 °C (ramp rate = 2 °C / min) for 10 h under a stream of air to remove any physisorbed or chemisorbed water. The pre-treated silica was then stored in a desicator until required to prevent any re-absorption of water.

Calcined silica (0.0975g) and methyl acrylate (18 mL) were placed in a Parr stainless steel reactor (fitted with a gas inlet valve and a bladed stirrer), the vessel pressurised with carbon dioxide (460 psi) and the system allowed to equilibrate for 10 min. The system was re-pressurised with carbon dioxide (460 psi) and left to equilibrate for a further 10 min. The system was finally re-pressurised with carbon dioxide (460 psi) and heated to achieve supercritical carbon dioxide conditions. After 1 h under supercritical conditions the system was cooled to room temperature and the carbon dioxide vented from the system. Opening the reactor revealed poly(methyl acrylate) as a pale yellow, highly tacky polymer. Unreacted monomer was removed by washing with methanol and the solvent removed to give poly(methyl acrylate) as an a rubbery translucent film. ^{1}H NMR (CDCl$_3$) ppm: 1.41 - 1.54

(~0.5 H, br m), 1.63 - 1.68 (1 H, br s), 1.91 - 1.98 (~0.5 H, br m), 2.31 - 2.33 (1 H, br d), 3.66 (3 H, br s).

RESULTS

Calcined silica and scCO$_2$ were successfully used to produce poly(methyl acrylate) *via* free radical polymerisation. It is proposed that calcination of the silica removes any chemisorbed and physisorbed water, generating strained and thus highly reactive siloxane based rings, such as those shown in **Figure 1**. In the presence of methyl acrylate, a highly reactive monomer, the strained SiO$_2$ based rings open, generating free radicals that react readily with the abundant methyl acrylate. **Scheme 1** outlines a proposed mechanism for the polymerisation of methyl acrylate. There are 2 types of radicals that are generated upon opening of the siloxane rings, and which can lead to the initiation of polymerisation. Following initiation the polymer chain continues to grow generating poly(methyl acrylate) (PMA) as a pale yellow, highly tacky polymer.
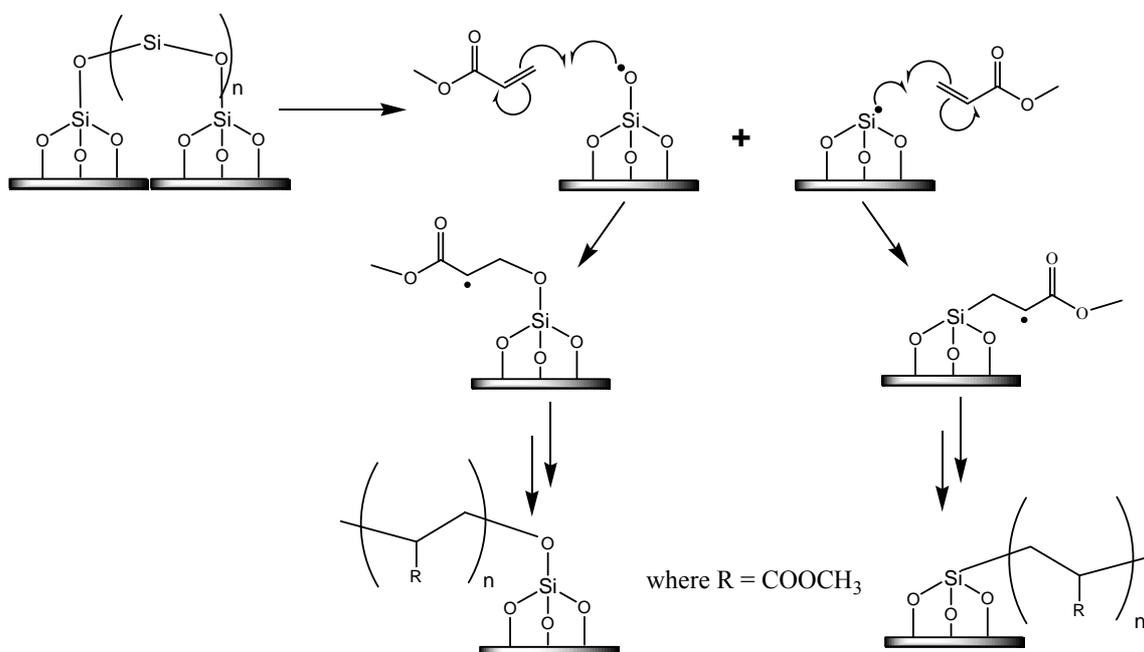
Scheme 1. Proposed polymerisation of methyl acrylate using radicals generated on the surface of calcined silica.

EPR was employed in an attempt to detect any silica-based-radicals, thereby confirming that the process is free radical mediated, and to monitor radical formation throughout the course of a reaction. Samples investigated using EPR include; calcined silica, a reference sample of PMA and PMA produced using calcined silica and scCO$_2$. A suspension / saturated solution of each sample in chloroform were prepared, along with neat samples ready for EPR analysis.

Initially all samples were analysed at room temperature. The sample of PMA produced using calcined silica and scCO$_2$ displayed a very weak EPR signal at 3330 G (g ~ 2.0033), with no EPR signals observed for the other samples. Low temperature analysis at 150 K was attempted with the aim of improving the intensity of the EPR signal generated at room temperature. At low temperature, no EPR signal was detected for calcined silica alone (either in the dry state or as a suspension in chloroform), suggesting that the siloxane rings only open and thereby generate radicals, in the presence of methyl acrylate or another organic compound such as those previously mentioned in the literature.[9-11] The reference sample of PMA did also not produce any EPR signal at low temperature, confirming that PMA alone is insufficient to produce radicals.

The sample of PMA that was produced using freshly calcined silica in scCO$_2$ was analysed at low temperature, and the EPR spectrum shown in
Figure 2. Although still relatively weak, the sharp signal at 3340 G confirms the presence of at least one radical species, which is typical of a CH based radical that is part of an extensive hydrocarbon chain.[12] The PMA displayed an experimental *g* value of 2.0026, which was found to correlate well with corresponding literature values of 2.0032 obtained by Sugiyama.[12] Two other smaller broad EPR signals are also present at 3250G and 3290 G, and can be attributed to the radical being in a different part of the polymer. That is, the radical could be trapped in a branched part of the polymer or near an oxygen, thus giving rise to a different EPR signal. Different polymer lengths may also generate different EPR signals. G values for these two smaller signals can be calculated, however due to the fact that these signals are very broad, it is difficult to assign these g values.
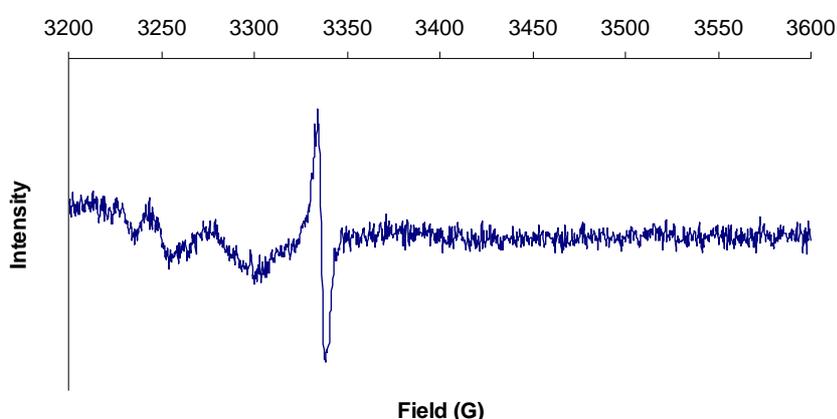
Figure 2. EPR spectrum of poly(methylacrylate) in CHCl$_3$ produced using calcined silica and scCO$_2$ confirms the presence of radicals.

The EPR results presented in this paper are consistent with those obtained in work performed by Khulbe *et al.*[10] When calcined silica, silica-alumina or alumina were added to a solution of phenothiazine, unusual spectra were obtained due to the formation of a phenothiazine cation radical on the surface of the support.[10] Without the phenothiazine no EPR signal was obtained. Earlier research conducted by Lagercrantz reported that it is difficult to obtain well-resolved EPR spectra involving silica or alumina based radicals, due to the dipole interaction arising between radicals in close proximity to one another.[13] Lagercrantz also suggested that the asymmetric shape of the EPR spectra may arise from varying *g* values caused by restricted rotation of surface-confined species in the magnetic field.

Gel Permeation Chromatography (GPC) results are summarised in **Table 1** with M_n, M_w and the polydispersity index (PDI) reported for each sample. From Table 1 it is evident that when methyl acrylate alone is dissolved in supercritical CO_2 for 1 h, only very small molecular weight products are obtained, giving rise to a very broad PDI of 5.16. Conversely, when freshly calcined silica is used larger molecular weights are achievable after only 15 min. By extending the reaction time to 1 h it is possible to produce PMA that displays a narrow PDI of 1.25. Silica that had been calcined and then exposed to air at room temperature for 3 months prior to use was also tested, and when used as a initiator, low molecular weight PMA was obtained with a broad PDI indicative of a range of molecular weights.

These experiments indicate that when freshly calcined silica is exposed to the atmosphere for 3 months prior to use, a significant loss in polymerisation activity and selectivity is observed. Conversely, if the air-exposed, previously-calcined silica is re-calcined before use in a reaction, its original activity and selectivity returns. This observation is consistent with the hydrolysis of the strained and highly reactive siloxane rings on standing, thus decreasing polymerisation performance.

Table 1. GPC data for polymerisation of MA in $scCO_2$ using different silica based initiators.

Initiator	Time (h)	M_n	M_w	PDI
n/a	1	798	4 117	5.16
Calcined SiO_2	0.25	2 668	15 257	5.72
Calcined SiO_2	1	12 230	15 324	1.25
Calcined SiO_2*	1	1 741	10 114	5.81

* Denotes SiO2 that was calcined and then exposed to air at room temperature for 3 months prior to use.

Polymer morphology was also investigated using scanning electron microscopy (SEM). **Figure 3** shows a typical image of PMA obtained by polymerising methyl acrylate with freshly calcined silica in $scCO_2$. Inspection of the image reveals a film-like material that features a network of pores. It is likely that the cavities in the film were caused by the loss of CO_2 from the system during the depressurisation of the reaction vessel, and are routinely observed in other similar polymer systems that use $scCO_2$.[14] Energy Dispersive X-ray Spectroscopy was also conducted on the polymeric film, with carbon, oxygen and gold (used to coat all samples) detected in reasonable quantities, with trace amounts of silicon scattered throughout. This observation of the silicon being scattered throughout the polymer, is consistent with experimental observations whereby the silica is neither identifiable, nor easily recovered after polymerisation. Instead the silica is presumed to be intimately dispersed throughout the polymeric material.
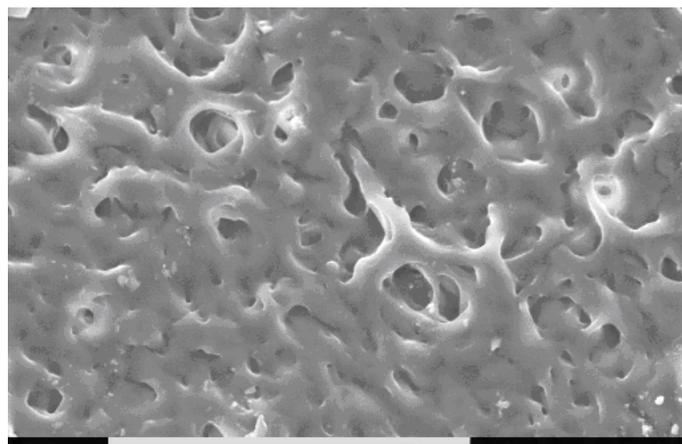
0.1 mm; 20.0 kV; 7.10E2

Figure 3. SEM of PMA produced using calcined SiO_2 and $scCO_2$.

CONCLUSION

Silica was calcined generating a series of strained and thus highly reactive siloxane rings, which in the presence of methyl acrylate appear to open, producing free radicals that can then initiate polymerisation. EPR has been used to confirm the presence of CH-based radicals with g values that are indicative of those found in extensive hydrocarbon chains. Unfortunately no silica based radicals could be directly detected, however EPR was able to demonstrate that in the presence of methyl acrylate, radicals do form. GPC indicates that the combination of freshly calcined SiO_2 and $scCO_2$ produces the best quality PMA with a narrow polydispersity index. Polymer morphology has also been investigated using SEM. When freshly calcined SiO_2 and $scCO_2$ are employed in the polymerisation of methyl acrylate, a porous film-like polymer is produced, presenting both a novel and a green approach for the production of PMA.

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