

# Synthesis of controlled-structure sulfate-based copolymers *via* atom transfer radical polymerisation and their use as crystal habit modifiers for BaSO<sub>4</sub>

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Received 9th January 2002, Accepted 19th February 2002  
First published as an Advance Article on the web 4th March 2002

Atom Transfer Radical Polymerisation (ATRP) has been used to polymerise ammonium 2-sulfatoethyl methacrylate (SEM) in aqueous media using various poly(ethylene glycol) (PEG) macro-initiators to give a range of controlled-structure, sulfate-based block copolymers. Such PEG–SEM diblock copolymers are effective crystal habit modifiers for the *in situ* precipitation of BaSO<sub>4</sub> in dilute aqueous solution. In the presence of the PEG–SEM copolymer, near-monodisperse, lozenge-shaped BaSO<sub>4</sub> particles were obtained, depending on the relative block lengths. X-Ray diffraction and thermogravimetric analysis of these particles demonstrated that they are polycrystalline in nature and contain around 8% copolymer by mass. This compares with the characteristic polydisperse rectangular platelets of single crystal BaSO<sub>4</sub> obtained in the absence of the copolymer. Control experiments suggest that, while only the SEM block interacts directly with the particle surface, the PEG block also plays an important role in controlling the crystal growth. Independent variation of the PEG and SEM block lengths therefore provides a subtle mechanism for controlling the morphology, size distribution and crystalline structure of the inorganic phase.

## Introduction

One of the key aspects in the development of new inorganic materials is the synthesis of particles with specific sizes and morphologies.<sup>1</sup> Many routes have been utilised to control crystal growth. Particles can be precipitated within a specific environment, which ultimately defines the final crystal size and shape. A wide range of systems has been investigated such as reverse micelles and microemulsions,<sup>2,3</sup> vesicles,<sup>4</sup> the cylindrical pores of track-etch membranes,<sup>5,6</sup> viruses,<sup>7</sup> and the spherical polypeptide shell of the protein ferritin.<sup>8</sup> More generally, crystals can be grown in the presence of naturally occurring soluble additives, which bind to the crystal surface and thus influence morphology.<sup>9</sup>

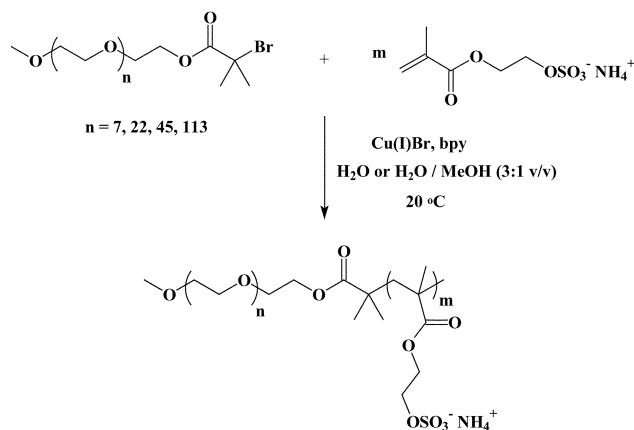
A number of recent reports have demonstrated that ‘double-hydrophilic’ block copolymers can be effective in controlling inorganic crystal morphologies.<sup>10–20</sup> Suitable copolymers have been used to produce calcium carbonate<sup>10,17</sup> calcium phosphate,<sup>12</sup> zinc oxide<sup>18</sup> and BaSO<sub>4</sub><sup>10,12,15</sup> particles with a wide range of morphologies. The copolymers used all have one (typically ionic) block that interacts strongly with the particle surface and a second non-ionic block that does not bind to the mineral, but indirectly affects crystal growth by acting as a steric stabiliser.<sup>21</sup> The morphology and polydispersity of particles produced can then be controlled by varying the structure and length of the two blocks, and by changing external conditions such as temperature, ionic strength and solution pH. Cölfen and co-workers have recently used double-hydrophilic diblock copolymers to modify the morphology of BaSO<sub>4</sub>.<sup>10,13,15</sup> Diblock copolymers based on poly(ethylene glycol) and either poly(ethylene imine) or poly(methacrylic acid) were derivatised by esterification, amidation or phosphonation chemistry in order to introduce carboxylic acid, sulfonic acid or phosphonic acid residues. A remarkable range of particle morphologies was obtained, including rods,

nanofibres, organised aggregates of nanofilaments, ‘peaches’, ‘peanuts’ and ‘flowers’. Some similar morphologies have been observed for BaSO<sub>4</sub> grown in reverse micelles<sup>2</sup> and in the presence of phosphonate-based inhibitor molecules.<sup>22,23</sup>

Since its discovery<sup>24,25</sup> in 1995, atom transfer radical polymerisation (ATRP) has proven to be a versatile technique for the controlled polymerisation of many monomer classes, including acrylates,<sup>26</sup> methacrylates<sup>27</sup> and styrenics.<sup>28</sup> Generally, ATRP syntheses are carried out at high temperatures, either in the bulk or in non-aqueous media. However, we have recently reported that ATRP is particularly effective for hydrophilic monomers under mild conditions. For example, sodium 4-vinylbenzoate can be polymerised in aqueous solution to over 95% conversion within 25 min at 20 °C, with final polydispersities of around 1.30.<sup>29</sup> A range of hydrophilic methacrylates have now been evaluated for ambient temperature ATRP in either aqueous or alcoholic media, including sodium methacrylate,<sup>30</sup> monomethoxy-capped oligo(ethylene glycol) methacrylate,<sup>31</sup> 2-(dimethylamino)ethyl methacrylate,<sup>32</sup> 2-hydroxyethyl methacrylate<sup>33</sup> and 2-methacryloyloxyethyl phosphorylcholine.<sup>34</sup>

In the present study we demonstrate for the first time that ATRP can be used to prepare a range of controlled-structure, sulfate-based copolymers based on a commercially available monomer, ammonium 2-sulfatoethyl methacrylate† (SEM, see Fig. 1). SEM monomer is synthesised on an industrial scale by reacting chlorosulfonic acid with 2-hydroxyethyl methacrylate, followed by neutralisation with ammonia. It is somewhat unusual in that it is a sulfate-based (rather than sulfonate-based) monomer. There are rather few literature reports concerning the polymerisation of SEM. Recently Hay and co-workers homopolymerised SEM using conventional free

†This is the name given by the supplier Laporte Performance Chemicals; however, the IUPAC name is 2-sulfonatoxyethyl methacrylate.



**Fig. 1** General reaction scheme for the homopolymerisation of SEM by atom transfer radical polymerisation (ATRP) in aqueous or aqueous methanolic solution at 20 °C using various PEG-based macro-initiators.

radical chemistry and it was suggested that the resulting anionic polymers had some potential as low toxicity inhibitors of tumour cell growth.<sup>35</sup>

Herein, we investigate the influence of a series of SEM-based diblock copolymers on the precipitation of BaSO<sub>4</sub> (barite). This is an important mineral since it is widely used in many pharmaceutical formulations and also as a pigment; in some circumstances its presence can also be undesirable, *e.g.* scale formation in offshore oil wells. We postulated that the SEM-based copolymers should be effective growth modifiers for BaSO<sub>4</sub> given that the sulfate groups on the SEM copolymers can partially substitute for the sulfate di-anions in expressed crystal faces of the mineral, leading to changes in particle morphology. Indeed, Langmuir monolayers of sulfate-terminated surfactants have been shown to select a specific crystal nucleation face of BaSO<sub>4</sub>.<sup>36</sup> A particular advantage of these SEM-based copolymers for an application such as crystal growth additives is their relative ease of synthesis by ATRP (high yields, mild conditions, no protecting group chemistry, no post-polymerisation derivatisation steps required), at least compared to the multi-step syntheses required for many similar crystal habit modifiers reported to date.<sup>37,38</sup>

As far as we are aware, there have been no literature reports describing the use of sulfate-based copolymers as crystal habit modifiers for BaSO<sub>4</sub>, or, indeed, for any other inorganic materials. Accordingly, in this study, the formation of BaSO<sub>4</sub> was investigated in the presence and absence of sulfate-based (co)polymers. A series of AB diblock copolymers were employed in which the two block lengths were systematically varied and their respective influence on particle morphology and particle size distribution was determined.

## Experimental

### Materials

SEM monomer was kindly donated as a 25 w/v% aqueous solution by Laporte Performance Chemicals, Hythe, UK. The following reagents were purchased from Aldrich: Cu(I)Cl, 2,2'-bipyridine (bpy), 4-(bromomethyl)benzoic acid (BMBA), 4-(2-hydroxyethyl)morpholine, sodium sulfate (ACS reagent) and barium chloride dihydrate (ACS reagent) and were used as supplied. The water used in the BaSO<sub>4</sub> synthesis was obtained from an Elgastat Prima reverse osmosis water system and was further purified using a Milli-Q Plus water system (resistivity, 18.2 MΩ cm).

### Initiator syntheses

The ATRP (macro)initiators were synthesised by reacting either the poly(ethylene glycol) PEG ( $D_p = 7, 22, 45, 113$ ); the

$M_w/M_n$  in each case was less than 1.10, as judged by aqueous GPC studies using PEG calibration standards) or 4-(2-hydroxyethyl)morpholine (ME) with 2-bromoisobutyryl bromide and triethylamine at room temperature in dry toluene for at least 3 h. The resulting reaction solution was filtered to remove the amine salt, stirred with activated carbon, dried with MgSO<sub>4</sub>, filtered and the solvent was removed under vacuum. <sup>1</sup>H NMR was used to calculate the degree of esterification in each case.

### ATRP syntheses

In a typical experiment, a PEG<sub>45</sub>-Br macro-initiator (361 mg; 0.18 mmol) was dissolved in the 25 w/v% aqueous solution of SEM monomer (thus 6.54 g, or 7.2 mmol, was required for a SEM block with a  $D_p$  of 40). This solution was degassed using a nitrogen purge and then degassed methanol (1.64 mL; overall solvent composition was 3 : 1 v/v water–methanol) was added. To this reaction solution was added the bpy ligand (70.5 mg; 0.45 mmol) and the Cu(I)Cl catalyst (17.9 mg; 0.18 mmol). The dark brown solution was stirred at 20 °C. Polymerization occurred immediately, leading to an increase in viscosity and an exotherm of 3 °C over 4 min. Samples for kinetic analyses were taken at various time intervals using a syringe under positive nitrogen pressure and diluted with D<sub>2</sub>O. This exposure to air led to the dark-brown reaction solution turning blue, indicating aerial oxidation of Cu(I) to Cu(II). Subsequent <sup>1</sup>H NMR analyses revealed the extent of conversion at a given time. Purification was achieved by adding base until the solution was at pH 9–10 and then adding silica. After stirring for 30 min., the silica (with the blue ATRP catalyst adsorbed onto it) was allowed to sediment and the colourless polymer solution was decanted. The methanol was removed under vacuum and the aqueous solution was freeze-dried overnight to produce white polymers in very high yield.

The statistical copolymers were prepared by dissolving the BMBA initiator in H<sub>2</sub>O at pH 10. The two monomers were then added to the reaction flask and the mixture was degassed. To this was added Cu(I)Cl and bpy and the reaction was allowed to continue overnight. For the block copolymer, the NaBMB initiator was dissolved in H<sub>2</sub>O at pH 10 and the monomethoxy-capped oligo(ethylene glycol) methacrylate (OEGMA) was added. After degassing, the CuCl and bpy ligand were added and the polymerisation was allowed to proceed for 30 min. An aliquot of the reaction solution was taken before addition of the degassed SEM monomer solution. The resulting diblock copolymers were precipitated in cold THF followed by treatment with silica in aqueous alkaline solution, as detailed above.

### Preparation of BaSO<sub>4</sub> particles

BaSO<sub>4</sub> was precipitated from a solution of concentration 0.3 mM with respect to BaSO<sub>4</sub>, in the presence of a given concentration of the PEG–SEM copolymers listed in Table 1. The copolymer was added such that the ratio of SO<sub>4</sub><sup>2-</sup> groups due to the SEM residues relative to Ba<sup>2+</sup> ions in solution was 1 : 10, 1 : 5, 1 : 2, 1 : 1, or 2 : 1. All glassware used was rigorously cleaned prior to use, according to a literature protocol.<sup>39</sup> Typically, a total solution volume of 20 cm<sup>3</sup> was employed. An aqueous solution of the copolymer was placed in a glass Petri dish, and the required volume of 6 × 10<sup>-3</sup> M BaCl<sub>2</sub> solution was added with stirring, followed by 6 × 10<sup>-3</sup> M Na<sub>2</sub>SO<sub>4</sub> solution. The solution was stirred for one minute. A clean, dry cover slide was placed on the base of the dish and the Petri dish was covered with Parafilm. The experiments were left undisturbed for five days prior to isolating the crystals. All experiments were repeated at least twice. Control experiments were also performed using identical methodologies in the absence of polymer, and in the presence

**Table 1** Summary of the molecular weight data for the synthesis of ME-SEM homopolymer, PEG-SEM and OEGMA-SEM diblock copolymers via ATRP at 20 °C

Theoretical composition	Solvent composition	Theoretical $M_n$	Aq-GPC $M_n$	$^1\text{H}$ NMR composition	$^1\text{H}$ NMR $M_n$
ME-SEM <sub>42</sub>	MeOH : H <sub>2</sub> O (3 : 1)	9700	11 600	ME-SEM <sub>39</sub>	9100
PEG <sub>7</sub> -SEM <sub>15</sub>	H <sub>2</sub> O	3800	–	PEG <sub>7</sub> -SEM <sub>19</sub>	4700
PEG <sub>7</sub> -SEM <sub>40</sub>	MeOH : H <sub>2</sub> O (3 : 1)	9500	–	PEG <sub>7</sub> -SEM <sub>36</sub>	8600
PEG <sub>22</sub> -SEM <sub>42</sub>	H <sub>2</sub> O	10 500	–	PEG <sub>22</sub> -SEM <sub>41</sub>	10 300
PEG <sub>45</sub> -SEM <sub>10</sub>	H <sub>2</sub> O	4300	–	PEG <sub>45</sub> -SEM <sub>11</sub>	4500
PEG <sub>45</sub> -SEM <sub>25</sub>	H <sub>2</sub> O	7700	–	PEG <sub>45</sub> -SEM <sub>26</sub>	7900
PEG <sub>45</sub> -SEM <sub>40</sub>	H <sub>2</sub> O	11 000	12 800	PEG <sub>45</sub> -SEM <sub>42</sub>	11 600
PEG <sub>113</sub> -SEM <sub>42</sub>	H <sub>2</sub> O	14 500	–	PEG <sub>113</sub> -SEM <sub>40</sub>	14 100
BMBA-OEGMA <sub>24</sub> -b-SEM <sub>20</sub>	H <sub>2</sub> O	14 700	–	BMBA-OEGMA <sub>27</sub> -b-SEM <sub>20</sub>	11 500

of the ME-SEM homopolymer, the PEG macro-initiator ( $D_p = 45$ ), and the SEM monomer.

Larger quantities of material were required for TGA, XRD and FTIR analysis. In this case, the volume of the experiment was scaled-up and the particles were isolated by centrifugation. Repeated washing-centrifugation cycles removed any copolymer remaining in solution, and the particles were finally washed with acetone and were dried. Approximately 25 mg of BaSO<sub>4</sub> was obtained per litre of solution.

### Characterization

**Polymers.**  $^1\text{H}$  NMR spectra were recorded in either D<sub>2</sub>O or CDCl<sub>3</sub> using a DPX 300 spectrometer. Molecular weights were determined by aqueous gel permeation chromatography (GPC) using two PL aquagel-OH columns (type 30 and 40; ex. Polymer Laboratories, UK) in series with a refractive index detector. Poly(sodium styrene-4-sulfonate) standards (mp 2290–208 000 g mol<sup>-1</sup>; ex. PSS, Germany) were used with a mobile phase of 70% 0.2 M NaNO<sub>3</sub> + 0.01 M NaH<sub>2</sub>PO<sub>4</sub> (adjusted to pH 7) and 30% methanol co-solvent at a flow rate of 1.0 mL min<sup>-1</sup>.

**BaSO<sub>4</sub> particles.** The morphology of the particles produced was determined by examining the particles precipitated on the glass cover slide. Crystals were examined both by optical microscopy and scanning electron microscopy (SEM). Samples were prepared for SEM by mounting a portion of the cover slide on an aluminium stub using adhesive carbon tape, and then sputter-coating with a thin layer of gold prior to viewing. The samples were examined using a JEOL 6300F SEM instrument, fitted with a field emission source and operating at 5 kV. Mean particle sizes were determined by SEM analysis of at least 100 particles per sample.

The composition of the particles was evaluated using thermogravimetric analysis (TGA), X-ray diffraction (XRD) and FTIR spectroscopy. TGA were performed using a Perkin-Elmer TGA-7 instrument, and the samples were heated up to 800 °C at a scan rate of 20 °C min<sup>-1</sup> in air. XRD was carried out using a Cu K $\alpha_1$  source, and an INEL CPS-120 curved position sensitive detector, as reported in the literature.<sup>40</sup> FTIR spectra were recorded on a Nicolet Magna 550 spectrometer (Series II). These techniques were used to analyse the BaSO<sub>4</sub> particles produced using PEG<sub>45</sub>-SEM<sub>42</sub> at a 2 : 1 SO<sub>4</sub> : Ba ratio, and the results were compared with BaSO<sub>4</sub> control particles precipitated in the absence of any copolymer. Any differences between the data obtained were attributed to the presence of the PEG-SEM copolymer occluded/intercalated within the BaSO<sub>4</sub> particles.

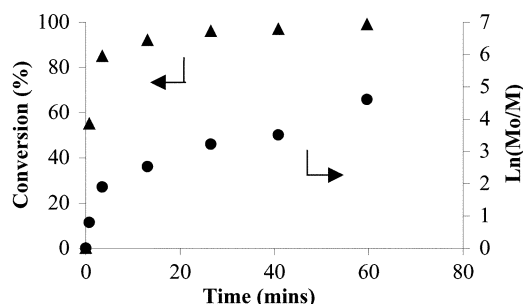
## Results and discussion

### 1. Copolymer synthesis and characterization

The results of our homopolymer and copolymer syntheses are summarised in Table 1. Excellent yields (>90%) were obtained in all cases. Control over the degree of polymerisation of the

SEM blocks was achieved simply by varying the monomer : (macro-)initiator ratio, as in conventional ATRP. Four near-monodisperse, PEG-based macro-initiators were employed in this study, with  $D_p$ 's of 7, 22, 45 and 113, respectively. This approach allowed both the PEG and SEM block lengths to be varied independently. In addition, the SEM homopolymer employed in the control experiments was prepared using the ME-Br initiator, which was selected because the morpholine group provided a convenient NMR label.

Kinetic data for one of the SEM polymerisations is presented in Fig. 2. In this particular example the target degree of polymerisation of the SEM block was 42. The conversion vs. time curve confirms that this polymerisation was rapid, with over 95% conversion being achieved within 15 minutes at 20 °C. The semi-logarithmic plot of this conversion data is also depicted. This indicates first order kinetics with respect to monomer initially (up to 85% conversion), followed by marked deviation from linearity at higher conversions. Such deviations are usually interpreted in terms of a non-constant (*i.e.* decreasing) polymer radical concentration, which suggests less than ideal living character.<sup>19</sup> Based on our poly(sodium styrene-4-sulfonate) calibration, the  $M_n$  of the SEM homopolymer was 11 600 g mol<sup>-1</sup> ( $M_w/M_n = 1.76$ ) and the  $M_n$  of the PEG-SEM diblock copolymer was 12 800 g mol<sup>-1</sup> ( $M_w/M_n = 1.69$ ). Although the aqueous GPC chromatograms indicated unimodal, symmetrical peaks, the polydispersities of both the SEM homopolymer and the PEG-SEM diblock copolymer are too high to be able to claim that the polymerisation is well controlled. Given that the SEM monomer is polymerised as a 25% solution in the presence of water, the relatively poor control obtained is perhaps not surprising. Both our group<sup>41</sup> and others<sup>42</sup> have reported that, although the rate of polymerisation is significantly increased by the addition of small quantities of water, control over such polymerisations is often compromised. Nevertheless, the use of ATRP is justified since the mean degrees of polymerization ( $D_p$ ) of the SEM chains were relatively low according to the GPC analyses [ $D_p = 51$  for the ME-SEM homopolymer and  $D_p = 47$  for the PEG-SEM diblock copolymer].<sup>43</sup>



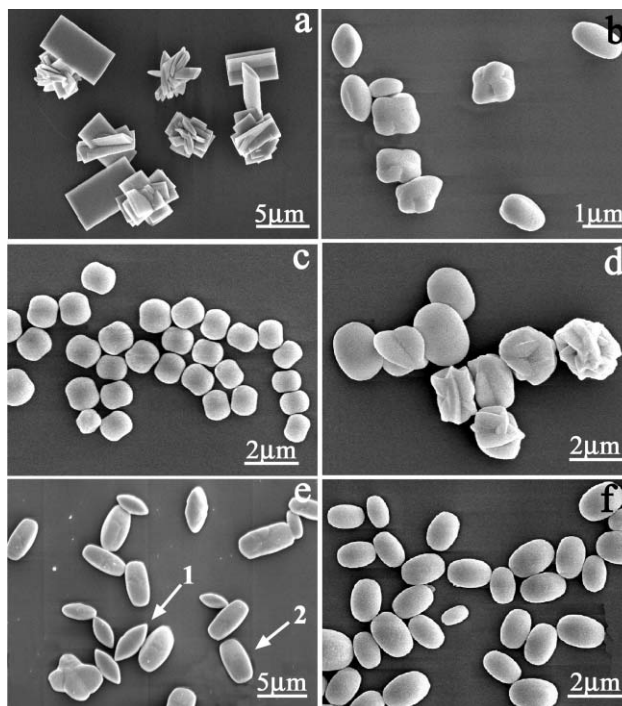
**Fig. 2** Kinetic data for the ATRP of ammonium 2-sulfonatoxyethyl methacrylate (SEM) in 3 : 1 H<sub>2</sub>O : MeOH at 20 °C using a ME-Br initiator. Experimental conditions: [SEM]<sub>0</sub> = 25 w/v%, ME-Br : Cu(I)Cl : bpy 1 : 1 : 2.5. The target  $D_p$  was 42;  $^1\text{H}$  NMR analysis indicated that the actual mean  $D_p$  was 40.

Moreover, since near-monodisperse PEG blocks were used as macro-initiators, the diblock copolymers are reasonably well-defined in terms of their architecture, if not their molecular weight distribution.

Assigned  $^1\text{H}$  NMR spectra of a PEG-based ATRP macro-initiator ( $D_p = 45$ ), a ME-SEM<sub>39</sub> homopolymer, a PEG<sub>45</sub>-SEM<sub>42</sub> diblock copolymer and MEBr initiator are shown in Fig. 3. The ethylene glycol residues of the PEG block give rise to signals at  $\delta$  3.7–3.8, while the SEM residues have several characteristic signals at  $\delta$  0.8–2.2 (methacrylate backbone) and  $\delta$  4.2 (oxymethylene protons attached to the ester carbonyl and also the sulfate groups). Comparison of the peak integrals due to the methacrylate backbone with those of the ethylene glycol units allows the average  $D_p$  of the SEM block to be calculated. In the case of the ME-SEM homopolymer, the terminal morpholine group has unique NMR signals at  $\delta$  2.3 and  $\delta$  2.6 which can be used as an NMR label for estimating the SEM block length.

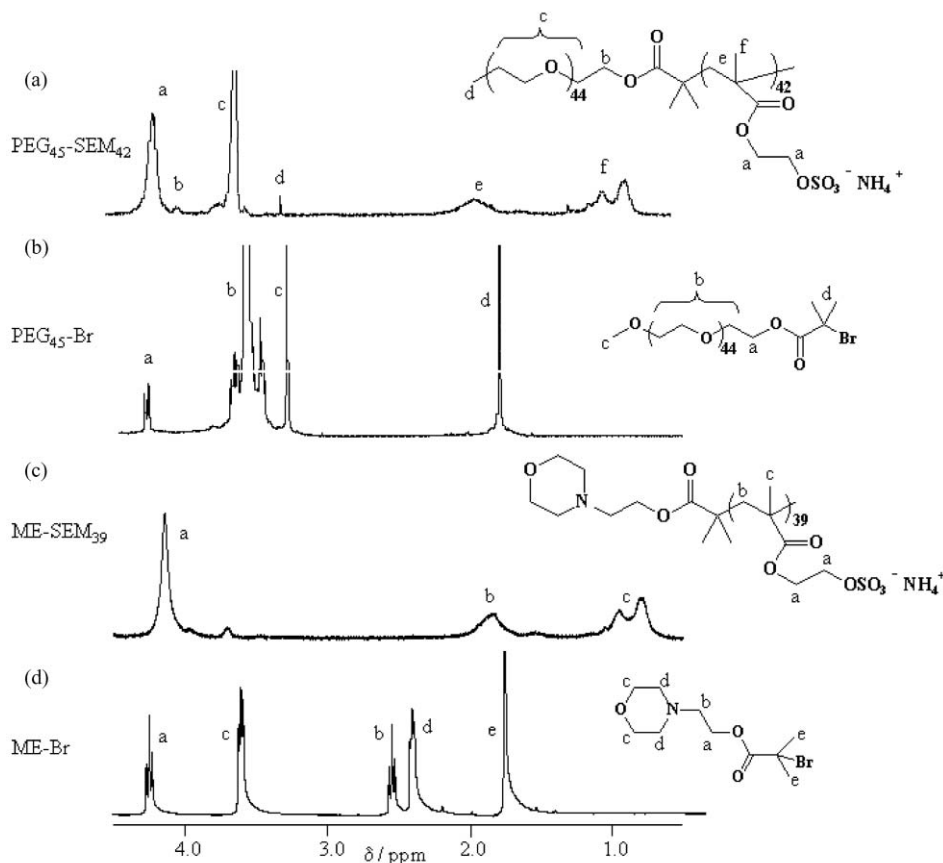
## 2. BaSO<sub>4</sub> precipitation

BaSO<sub>4</sub> precipitated in the absence of polymer additives exhibited two characteristic morphologies, namely rectangular tablets, and the form of rosettes known as ‘rock roses’ or ‘desert roses’ (Fig. 4a). Each desert rose actually comprises a number of tabular crystals and probably forms *via* continuous nucleation and growth of smaller crystals on existing larger ones. The average length of the rectangular tablets was approximately 6  $\mu\text{m}$ . Addition of copolymers to the crystallising solution had a marked effect on the size, shape and homogeneity of the particles, depending on both the block composition and the copolymer concentration. In particular, the relative block lengths are shown to be crucial in determining the degree of control. Neither the PEG homopolymer, nor the SEM monomer had any influence on BaSO<sub>4</sub>



**Fig. 4** Scanning electron micrographs of BaSO<sub>4</sub> particles precipitated (a) in the absence of any polymer; and in the presence of (b) ME-SEM<sub>39</sub> homopolymer at  $[\text{SO}_4^{2-}]_{\text{polymer}} : [\text{Ba}^{2+}] = 1 : 1$ ; (c) ME-SEM homopolymer at 2 : 1; (d) PEG<sub>45</sub>-SEM<sub>11</sub> at 1 : 10; (e) PEG<sub>45</sub>-SEM<sub>42</sub> at 2 : 1 and (f) PEG<sub>113</sub>-SEM<sub>40</sub> at 2 : 1. In image (e) angular and rounded particles are labeled 1 and 2 respectively.

precipitation, even at the highest concentrations investigated. The inactivity of the PEG homopolymer is consistent with previous observations on the weak interaction of non-ionic



**Fig. 3** Assigned  $^1\text{H}$  NMR spectra of (a) a PEG<sub>45</sub>-SEM<sub>42</sub> diblock copolymer; (b) the PEG<sub>45</sub>-Br macro-initiator; (c) a ME-SEM<sub>39</sub> homopolymer and (d) the ME-Br initiator.

polymers with BaSO<sub>4</sub> and CaCO<sub>3</sub>.<sup>13,16</sup> In contrast, the ME-SEM homopolymer had some effect on the BaSO<sub>4</sub> morphology, depending on the concentration used. At 1 : 10 SO<sub>4</sub><sup>2-</sup> : Ba<sup>2+</sup>, the lowest concentration used, both the plate and rosette BaSO<sub>4</sub> morphologies appeared more rounded, and there was a broad distribution of particle size and morphologies. Higher copolymer concentrations enhanced this effect, producing rounded, irregularly shaped particles, but with narrower particle size distributions. At a 1 : 1 ratio, the particles could not be identified as either tablet or desert-rose in origin (Fig. 4b). Further increase in the polymer concentration to 2 : 1 resulted in a uniform population of 1.5 μm particles, which exhibited a constriction round the centre to give a slight dumbbell character (Fig. 4c). In contrast to the SEM monomer, the ME-SEM homopolymer, which was added such that the concentration of SEM residues was the same in both cases, did affect crystal growth. This indicates that the changes in crystal growth occur because of this polymer's interaction with the particle surface, as opposed to supersaturation effects due to complexation of Ba<sup>2+</sup> ions in solution. Additionally, cooperative (multi-site) interactions of the SEM residues with the inorganic BaSO<sub>4</sub> particles are essential. Isolated, individual sulfate groups due to SEM monomer will be much more weakly adsorbed onto the particle surface in comparison; this is clearly not sufficient for effective crystal habit modification.

The series of PEG<sub>X</sub>-SEM<sub>Y</sub> copolymers and also a semi-branched OEGMA-SEM diblock copolymer (see Table 1) were studied as crystal habit modifiers for the *in situ* crystallisation of BaSO<sub>4</sub>. The PEG<sub>X</sub>-SEM<sub>Y</sub> copolymers were selected such that the effect of varying the respective PEG and SEM block lengths could be independently investigated. In the case of PEG<sub>7</sub>-SEM<sub>19</sub>, both block lengths are relatively short and this copolymer exhibited minimal effect on BaSO<sub>4</sub> precipitation, with rectangular tablets and rosettes being produced. Slight rounding of these particles occurred at high polymer concentrations. However, a moderate increase in the degree of polymerisation of either of these blocks produces much more active copolymers, as exemplified by the results obtained using PEG<sub>7</sub>-SEM<sub>36</sub> and PEG<sub>45</sub>-SEM<sub>11</sub>. Low concentrations of either of these copolymers yielded populations of particles, which contained rounded forms of the rectangular tablets and desert roses (Fig. 4d). More profound morphological changes were observed using a 2 : 1 concentration ratio. In the presence of PEG<sub>7</sub>-SEM<sub>36</sub> angular, lozenge-shaped BaSO<sub>4</sub> particles were principally obtained, together with a small number of irregularly shaped particles. The lozenge-shaped particles were fairly homogeneous in size, exhibiting lengths of approximately 2 μm. The PEG<sub>45</sub>-SEM<sub>11</sub> was less effective in controlling size and morphology, producing a number of small (1 μm) ovoid particles, together with irregularly shaped particles.

The effect of holding one block length constant, while varying the length of the other block was also studied. The constant PEG series included the copolymers PEG<sub>45</sub>-SEM<sub>11</sub>, PEG<sub>45</sub>-SEM<sub>26</sub> and PEG<sub>45</sub>-SEM<sub>42</sub> while the (approximately) constant SEM series included the copolymers PEG<sub>7</sub>-SEM<sub>36</sub>, PEG<sub>22</sub>-SEM<sub>41</sub>, PEG<sub>45</sub>-SEM<sub>42</sub> and PEG<sub>113</sub>-SEM<sub>40</sub>. All of these copolymers produced similar BaSO<sub>4</sub> particles at low concentrations (1 : 10), comprising rounded forms of the rectangular tablets and rosettes. Differences in the interactions of these copolymers with the growing BaSO<sub>4</sub> particles were more apparent at higher copolymer concentrations. Examining first the constant SEM block length series at a 2 : 1 ratio, electron microscopy studies revealed lozenge-shaped particles, which were either rather angular or rounded in form, in all cases (Fig. 4e). For the short PEG chain (PEG<sub>7</sub>-SEM<sub>36</sub>), the particles were principally angular. However, the proportion of rounded particles increased with the PEG block length, until only rounded particles were produced with the PEG<sub>113</sub>-SEM<sub>40</sub> polymer (Fig. 4f). Some irregularly shaped particles were also produced using copolymers with shorter PEG block lengths

(e.g. PEG<sub>7</sub>-SEM<sub>36</sub> and PEG<sub>22</sub>-SEM<sub>41</sub>). Increased particle uniformity was also observed in the constant PEG series as the SEM block length was increased. Morphological control was relatively poor using the PEG<sub>45</sub>-SEM<sub>11</sub> copolymer: small ovoid particles, together with irregularly-shaped particles were precipitated. However, use of both PEG<sub>45</sub>-SEM<sub>26</sub> and PEG<sub>45</sub>-SEM<sub>42</sub> diblock copolymers enabled improved control, with lozenge-shaped particles being produced. While both angular and rounded particles were observed with PEG<sub>45</sub>-SEM<sub>26</sub>, the particles were principally rounded using the PEG<sub>45</sub>-SEM<sub>42</sub> diblock copolymer.

The OEGMA<sub>27</sub>-SEM<sub>20</sub> diblock copolymer was markedly less effective in producing uniform particles. Compared to the linear PEO block, the OEGMA block is 'semi-branched', in that it has a methacrylate backbone and pendent oligo(ethylene glycol) side-chains. This architecture (or perhaps the relatively short block length) is apparently not optimal for efficient interaction with the precipitating inorganic phase. At low copolymer concentrations (SO<sub>4</sub><sup>2-</sup> : Ba<sup>2+</sup>, 10 : 1) rounded forms of the tablets and rosettes were observed. Higher concentrations resulted in a range of particle morphologies. A small number of lozenge-shaped particles were produced, together with irregularly shaped particles. Due to its poor morphological control, no further experiments were carried out with this copolymer.

The chemical composition of the lozenge-shaped BaSO<sub>4</sub> particles [produced using the PEG<sub>45</sub>-SEM<sub>42</sub> copolymer at a 2 : 1 SO<sub>4</sub><sup>2-</sup> : Ba<sup>2+</sup> ratio] was assessed using TGA, FT-IR spectroscopy and XRD. TGA indicated relatively large mass losses of up to 8 wt%, at 800 °C, which were attributed to pyrolysis of the organic copolymer component. This was borne out by control TGA experiments on the copolymer alone, which indicated that most of the mass loss occurred below 400 °C. Furthermore, significantly lower mass losses (2% or less) were observed in TGA runs with pure BaSO<sub>4</sub> particles prepared in control experiments in the absence of copolymer. The relatively high copolymer content of the BaSO<sub>4</sub> particles suggests that a significant proportion of the copolymer is occluded *within* the particles, rather than merely adsorbed at the particle surface. Based on this result alone, the BaSO<sub>4</sub> particles are most likely polycrystalline in nature, as opposed to single crystals. Powder XRD studies, carried out on BaSO<sub>4</sub> samples prepared in the presence and absence of the SEM-based copolymers, confirmed this analysis. The diffractograms were subjected to Rietveld analysis, which revealed significant peak broadening in the copolymer-precipitated BaSO<sub>4</sub> particles. The broadening was consistent with a mean particle size of 87 nm, clearly demonstrating that the lozenge-shaped particles are polycrystalline. In contrast, the pure BaSO<sub>4</sub> particles prepared in the absence of any copolymer were single crystals. FT-IR spectroscopy studies also confirmed the presence of significant levels of copolymer associated with the BaSO<sub>4</sub> particles, since a weak band at 1723 cm<sup>-1</sup> was observed. An FT-IR spectrum of the PEG<sub>45</sub>-SEM<sub>42</sub> copolymer enabled this feature to be assigned to the carbonyl ester of the SEM residues, whereas no such band was observed in the spectrum of the pure BaSO<sub>4</sub> particles.

The dramatic change in morphology that occurs between particles produced at low (1 : 10 SO<sub>4</sub><sup>2-</sup> : Ba<sup>2+</sup>) and high (2 : 1 SO<sub>4</sub><sup>2-</sup> : Ba<sup>2+</sup>) copolymer concentrations suggests that a change in the mechanism of particle growth occurs. At low copolymer concentrations, the BaSO<sub>4</sub> morphologies exhibit only minor modifications compared to the control experiments, and rounded versions of both the rectangular tablet and desert rose forms are observed. These morphologies suggest that the particles are either still single crystals, or comprise a number of inter-grown single crystals (the rosettes). In contrast, the particles produced at high copolymer concentrations have distinctly different morphologies compared to the corresponding control experiments and only the polycrystalline,

lozenge-shaped particles are observed. During nucleation, the copolymer most likely binds to the surfaces of the growing particles, hence inhibiting crystal growth. Depending on the copolymer concentration, growth of the crystal nuclei may be sufficiently retarded such that aggregation may proceed more rapidly than further growth, producing polycrystalline particles. Alternatively, the adsorbed copolymers may reduce the surface charge on the particles, which would accelerate aggregation. Both processes would be expected to promote aggregation over single crystal formation at high copolymer concentrations.

Our results demonstrate that SEM-based copolymers are active in controlling BaSO<sub>4</sub> precipitation, generating particles of uniform size and defined morphologies. While the ME-SEM homopolymer influenced crystal growth to produce uniform particles with a 'dumbbell' morphology, the PEG-SEM diblock copolymer produced a more dramatic change in particle morphology. Here, the lengths of both the PEG and SEM blocks were important in achieving effective morphological control and the most morphologically uniform particles were obtained with the PEG<sub>45</sub>-SEM<sub>42</sub> and PEG<sub>113</sub>-SEM<sub>40</sub> copolymers. The copolymer binds to the particle *via* the anionic SEM block, and it is envisaged that the non-ionic, highly hydrophilic PEG block is oriented into solution, acting as a steric stabiliser. Access of ions to the growing crystal will be limited according to the surface concentration and layer thickness of the copolymer chains, which will in turn depend on the lengths of the two blocks. This will determine the rate of crystal growth, and will modify the single crystal morphology due to non-specific binding of the copolymer to crystal faces. The adsorbed copolymer will also alter the surface chemistry of the growing crystals, which may promote aggregation. This process is also clearly dependent on the relative block lengths. Therefore, precise control of particle morphology requires judicious selection of both the PEG and SEM block lengths.

## Conclusions

In summary, a new range of sulfate-based diblock copolymers can be readily prepared in high yield *via* ATRP in protic media at 20 °C. Although the PEG blocks are near-monodisperse, aqueous GPC studies revealed that the SEM blocks are relatively polydisperse, presumably due to the very rapid rate of the SEM homopolymerisation in the presence of water. Nevertheless, <sup>1</sup>H NMR spectroscopy studies confirmed that the SEM blocks had relatively low average degrees of polymerization, as expected for ATRP; moreover, the use of a 'macro-initiator' route ensured that well-defined block architectures were obtained. This approach enabled a series of PEG-SEM diblock copolymers to be synthesised in which the PEG and the SEM block lengths were independently varied. Thus the influence of block composition on the ability of these copolymers to modify the crystal habit of *in situ*-prepared BaSO<sub>4</sub> could be studied.

In the absence of any copolymer, the BaSO<sub>4</sub> phase was precipitated from dilute aqueous solution as single crystals, but the particle morphology was relatively ill-defined (micrometer-sized polydisperse platelets). Control experiments using PEG homopolymer confirmed that this non-ionic polymer had little or no effect as a crystal habit modifier. However, in the presence of a SEM homopolymer, the BaSO<sub>4</sub> particle morphology was modified profoundly and particles with a slight dumbbell character were produced, presumably due to the anionic sulfate groups on the polymer chains interacting with the BaSO<sub>4</sub> lattice. Use of PEG-SEM diblock copolymers led to the formation of particles with regular ovoid morphologies. Here the non-interacting PEG block is believed to act as a steric stabilizer. X-Ray diffraction studies of near-monodisperse 'lozenge'-shaped BaSO<sub>4</sub> particles prepared using a

PEG<sub>45</sub>-SEM<sub>42</sub> diblock copolymer indicated that the inorganic phase was polycrystalline. Both FTIR spectroscopy and thermogravimetric analyses indicated that a significant amount of copolymer was incorporated within the particles.

## Acknowledgement

EPSRC is acknowledged for funding this research programme (GR/M03351 and GR/R29260). Avecia is thanked for additional financial support for KLR and Laporte Performance Chemicals (Hythe, UK) is thanked for CASE support for JVMW and also for the kind donation of the SEM monomer. Dr M. J. Percy at Sussex University is acknowledged for his assistance with the thermogravimetric analyses. We thank the Department of Materials, Queen Mary, for access to electron microscopy facilities. Finally, we thank Dr Rory Wilson, Department of Biophysics in Relation to Dentistry, Queen Mary, for carrying out the XRD experiments, and Dr Ram Seshadri, Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, for his analysis of the XRD spectra.

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