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# Oxyethylene/oxybutylene block copolymers as structure-directing agents in the preparation of mesoporous silica

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A systematic study was undertaken of block copolymers of oxyethylene (E) and oxybutylene (B) as structure-directing agents for the preparation of mesoporous silica. Five diblock copolymers ($E_{40}B_{10}$, $E_{54}B_{11}$, $E_{89}B_{10}$, $E_{56}B_{19}$ and $E_{56}B_{27}$) and three triblock copolymers ($E_{23}B_{11}E_{23}$, $E_{31}B_{12}E_{31}$ and $E_{47}B_{10}E_{47}$) were synthesized by anionic polymerization. A commercial triblock copolymer ($E_{43}B_{14}E_{43}$) was also utilized. The phase diagrams for these copolymers in aqueous solution exhibited a cubic phase formed by packing of micelles. Silica was prepared under acid conditions. A simple relationship was demonstrated between the *d*-spacing from X-ray diffraction of mesostructured silica prepared with the copolymers and a theoretical micelle radius calculated on the basis of the copolymer composition and architecture. Type IV nitrogen adsorption/desorption isotherms were obtained for calcined silica samples, with the step in the isotherm moving to higher $p/p^{o}$ on increasing B-block length, but the form of the isotherm changing little with E-block length. This may be interpreted in terms of a model of convoluted silica walls penetrating the micelle corona region.

## Introduction

Amphiphiles, such as low molar mass surfactants and block copolymers, can form a variety of mesostructures in concentrated solutions or blends, including body-centred cubic (bcc) or face-centred cubic (fcc) arrays of spherical micelles, hexagonal arrays of cylindrical micelles, lamellar structures and bicontinuous cubic structures.[1–3] When incorporated into a silica synthesis, similar mesostructures may be generated. Subsequent removal of the amphiphile by calcination gives a structured mesoporous material (pore dimensions 2–50 nm). This approach was proposed by Mobil researchers, who originally used cationic surfactants as structure-directing agents and who reported hexagonal (MCM-41), lamellar (MCM-50) and bicontinuous cubic (MCM-48) materials.[4,5] In recent years, a wide variety of amphiphiles have been used to produce a range of mesoporous inorganic products.

Mesostructured silica is normally obtained as a precipitate from a dilute solution containing the amphiphile and a silica precursor. The mechanism of formation of such precipitates is a subject of debate. It is commonly assumed that it involves the assembly of some kind of micelle–silicate complex. As has been discussed previously, a more likely mechanism is that it involves liquid–liquid separation, followed by microphase separation within the concentrated phase.[6]

The potential of block copolymers of hydrophilic oxyethylene (E), -[$OCH_2CH_2$]-, and hydrophobic oxybutylene (B), -[$OCH_2CH(C_2H_5)$]-, for structure-direction has been demonstrated previously.[7,8] The present contribution concerns a systematic study of $E_mB_n$ diblock and $E_mB_nE_m$ triblock copolymers. The objectives of this work were to investigate the relationship between the solution behaviour of copolymers and their structure-directing effects and to ascertain the extent to which silica mesostructure can be controlled by varying copolymer composition and architecture.

## Experimental

### Copolymer synthesis

Ethylene oxide and but-1-ene oxide were obtained from Fluka and dried twice over powdered $CaH_2$. 2-(2-Methoxyethoxy)ethanol and butane-1,2-diol were distilled under reduced pressure and stored over 4 Å molecular sieves. Standard vacuum line techniques were used for the transfer of the volatile monomers.

**EB diblock copolymers.** The initiator was prepared by dissolving potassium metal in a five-fold excess of 2-(2-methoxyethoxy)ethanol under nitrogen. The preparation of $E_{89}B_{10}$ is typical: ethylene oxide (26.34 g) was transferred under vacuum into an ampoule containing initiator (0.77 g). The temperature was increased from ambient to 80 °C over 8 days. Then but-1-ene oxide (5.01 g) was transferred into the ampoule under vacuum. The temperature was increased from ambient to 80 °C over 11 days.

**EBE triblock copolymers.** The initiator was prepared by dissolving potassium metal in approximately 5 molar equivalents of butane-1,2-diol under nitrogen. The preparation of $E_{31}B_{12}E_{31}$ is typical: but-1-ene oxide (13.40 g) was transferred under vacuum into an ampoule containing initiator (1.58 g). The temperature was increased from ambient to 80 °C over 16 days. Then ethylene oxide (36.10 g) was transferred into the ampoule under vacuum. The temperature was increased from ambient to 80 °C over 10 days.

### Copolymer characterization

Gel permeation chromatography (GPC) of block copolymers was carried out in dimethylacetamide at 60 °C (Columns: PLGel 30 cm 2 × mixedB + 1 × 500A) or in tetrahydrofuran at ambient temperature (Columns: Waters HR 1,2 and 3).$^{13}$C

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NMR spectra were obtained in $CDCl_3$ using a Varian Unity 500 spectrometer.[9]

### Phase behaviour of copolymers in water

Phase diagrams were obtained using tube inversion experiments. Samples of copolymer in aqueous solution (0.5 g) at a range of concentrations were enclosed in small sample tubes (diameter 10 mm). The samples were observed while heating slowly ($<0.5\,^{\circ}C\,min^{-1}$) within the range 2–98 °C. The tubes were inverted every two minutes. Clouding, if any, was observed by eye. Gel phases were examined using a Nikon Optishot polarizing microscope equipped with a Mettler FP8 2HT hot stage temperature controller.

### Silica synthesis

Silica was prepared following the procedure of Zhao *et al.*[10] Block copolymer (0.15 g), distilled water (1.5 g) and 2 M HCl (6.0 g) were weighed into a 15 $cm^3$ sample tube. Tetraethoxysilane (TEOS) (0.78 g) was added to the polymer solution at 60 °C and the tube was shaken to mix the contents. A precipitate started to form within 10–20 minutes of the addition of TEOS. The reaction mixture was maintained overnight at 60 °C. The mother liquor was removed and the precipitate washed with water ($\sim 7 \times 12\ cm^3$) until the washings were pH > 5. The precipitate was oven-dried at 50 °C in air for 2 days. A portion was calcined for 2 h at 220 °C, followed by 6 h at 400 °C under flowing air. The rate of temperature increase was $1\,^{\circ}C\,min^{-1}$.

### Silica characterization

X-Ray diffraction patterns were obtained using a Bruker D8 X-ray diffractometer in Bragg–Brentano geometry and Cu $K_{\alpha 1}$ radiation ($\lambda = 1.54$ Å) at room temperature. The diffractometer was equipped with automatic variable slits, graphite monochromator and scintillation counter.

Nitrogen adsorption/desorption isotherms were obtained using a Coulter SA3100 surface area analyser. The samples were outgassed for 16 h at 150 °C before analysis. BET surface areas were calculated using data in the relative pressure range, $p/p^{o} = 0.05$–0.2. For some samples, "capillary filling" of mesopores may have occurred at relatively low partial pressures, but use of different $p/p^{o}$ ranges, up to $p/p^{o} = 0.3$, had little effect on the calculated surface areas.

## Results

### Copolymer characterization and phase behaviour

Average compositions from NMR and ratios of weight- to number-average molar mass, $\bar{M}_w/\bar{M}_n$, from GPC are given in Table 1 for five diblock copolymers (E-block lengths in the range 40–89; B-block lengths in the range 10–27) and three triblock copolymers (E-block lengths in the range 23–47; B-block lengths in the range 10–12) prepared in our laboratory and for a commercial (Dow) triblock copolymer ($E_{43}B_{14}E_{43}$). The polymers all possessed narrow molar mass distributions, as indicated by values of $\bar{M}_w/\bar{M}_n$ close to unity.

Phase diagrams in water for the copolymers prepared in our laboratory are shown in Fig. 1. The phase diagram for the commercial copolymer, $E_{43}B_{14}E_{43}$, has been reported previously.[7] Some features in these phase diagrams may be metastable. The significant point is that all the copolymers exhibit an extensive non-birefringent (cubic) gel region in the phase diagram. Previous work on similar copolymers has shown the isotropic cubic gel to be formed by packing spherical micelles of a similar size to those that exist in dilute solution.[11] In general, it has been found for $E_mB_n$ copolymers that when corona blocks are large relative to the core ($m/n \geqslant 10$) the micelles act as soft spheres and a bcc structure is obtained.[12] Copolymers with shorter corona blocks give micelles that behave as hard spheres and form fcc structures at low concentration, but may give bcc structures at high concentration.[12] Very short corona blocks promote a transition from spherical to elongated micelles.[13] It should be noted that the phase diagram can be sensitive to the distribution of block sizes as well as to the overall composition.[7]

The phase behaviour of the block copolymers will be modified to some extent under the conditions of a silica synthesis.[7] Nevertheless, it might be expected that a copolymer which tends to form a packed-micelle cubic phase in aqueous solution would be likely to generate a similar structure in a silica synthesis.

### Silica characterization

X-Ray diffraction results for uncalcined and calcined silica products prepared with the copolymers are given in Table 1 and an example is shown in Fig. 2. Products obtained with the triblock copolymers exhibited a single diffraction peak. With the diblock copolymers, additional reflections were observed. For $E_{40}B_{10}$ and $E_{54}B_{11}$ the results are consistent with a bcc structure (space group *Im*3*m*). These products appear similar in structure to SBA-16 prepared by Stucky's group using the triblock copolymer $E_{106}P_{70}E_{106}$, where P is an oxypropylene unit.[10] For other samples there was insufficient evidence conclusively to assign a structure. Values of radius ('pore' + ½ 'pore wall') calculated on the basis of bcc structures are included in Table 1. On calcination there was some contraction but the essential mesostructure was retained.

Nitrogen adsorption/desorption isotherms (volume of nitrogen adsorbed per unit mass of material, $V_{ads}$, reduced to standard temperature and pressure, *versus* relative pressure, $p/p^{o}$) for calcined materials are shown in Fig. 3. Desorption curves were only obtained for $p/p^{o} > 0.4$. Essentially type IV isotherms were obtained, typical of mesoporous solids.[14]

**Table 1** Molecular characteristics of copolymers, XRD *d*-spacings and radius ('pore' + ½ 'pore wall') calculated on the basis of a bcc structure, $r_{bcc}$, for uncalcined and calcined silica products, and BET surface area, *A*, for calcined silica products

| Copolymer | | Uncalcined silica | | Calcined silica | | |
|---|---|---|---|---|---|---|
| Composition | $M_w/M_n$ | *d*-spacing/nm | $r_{bcc}$/nm | *d*-spacing/nm | $r_{bcc}$/nm | $A/m^2\,g^{-1}$ |
| $E_{40}B_{10}$ | 1.04 | 7.76, 5.56 | 4.8 | 6.88, 4.85, 3.96 | 4.2 | 805 |
| $E_{54}B_{11}$ | 1.03 | 8.64, 6.15, 5.07 | 5.3 | 7.72, 5.48, 4.48 | 4.7 | 735 |
| $E_{89}B_{10}$ | 1.03 | 9.67, 6.39, 5.63 | 5.9 | 8.78, 5.55, 5.15 | 5.5 | 667 |
| $E_{56}B_{19}$ | 1.02 | 10.54 | 6.5 | 9.12 | 5.6 | 656 |
| $E_{56}B_{27}$ | 1.02 | 13.60 | 8.3 | 11.88 | 7.3 | 502 |
| $E_{23}B_{11}E_{23}$ | 1.11 | 5.97 | 3.7 | 5.72 | 3.5 | 678 |
| $E_{31}B_{12}E_{31}$ | 1.10 | 6.45 | 4.0 | 5.78 | 3.6 | 671 |
| $E_{47}B_{10}E_{47}$ | 1.08 | 6.49 | 4.0 | 5.79 | 3.5 | 602 |
| $E_{43}B_{14}E_{43}$[a] | 1.08 | 7.36 | 4.3 | 6.52 | 4.0 | 634 |

[a] Commercial sample (Dow).

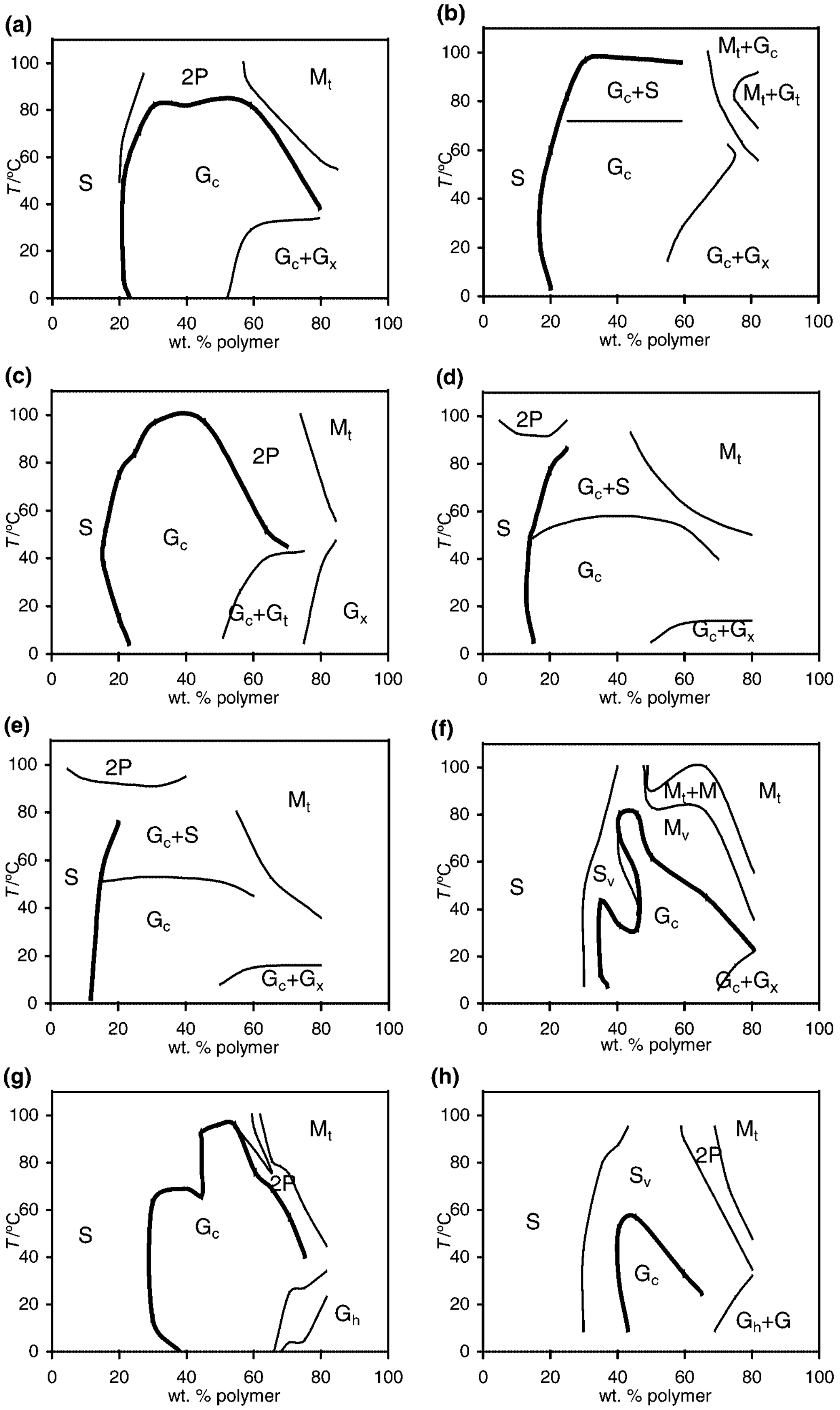

**Fig. 1** Phase diagrams for (a) $E_{40}B_{10}$, (b) $E_{54}B_{11}$, (c) $E_{89}B_{10}$, (d) $E_{56}B_{19}$, (e) $E_{56}B_{27}$, (f) $E_{23}B_{11}E_{23}$, (g) $E_{31}B_{12}E_{31}$ and (h) $E_{47}B_{10}E_{47}$ in aqueous solution. Key: S = clear solution, $S_v$ = viscous clear solution, $G_c$ = clear gel (cubic), $G_t$ = turbid gel, $G_x$ = birefringent turbid gel, $G_h$ = birefringent turbid gel (hexagonal), M = clear mobile phase, $M_v$ = viscous clear mobile phase, $M_t$ = turbid mobile phase, 2P = two phases.

However, for products prepared using block copolymers with short B-blocks, the step in the isotherm was not very pronounced and occurred at low $p/p^o$ values. It has been observed previously that mesoporous silicas prepared under acidic conditions exhibit different sorption behaviour to materials of similar lattice spacing prepared under alkaline conditions, with a step in the isotherm at much lower $p/p^o$ values, indicating either convoluted surfaces or the presence of

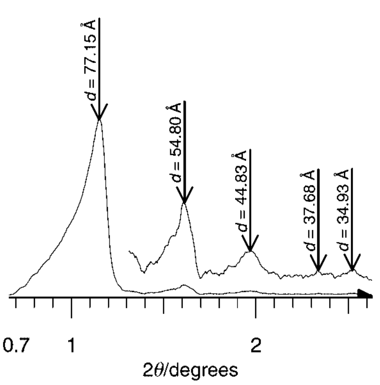

**Fig. 2** X-Ray diffraction pattern for calcined silica prepared with $E_{54}B_{11}$.

micropores.[6,7,15] For diblock copolymers, on increasing the B-block length the step in the isotherm moved to higher $p/p^o$ (see Fig. 4) and a pronounced hysteresis was observed. The step in a type IV isotherm is generally interpreted as being associated with capillary condensation in the mesopores.[14] The hysteresis is of type H2, suggestive of a three-dimensional cage structure. The length of the E-block, over the range studied, had relatively little effect on the form of the isotherm.

BET analysis of nitrogen adsorption data gave high surface areas, as can be seen in Table 1. When diblock copolymers were used as structure-directing agents the surface area decreased as *d*-spacing increased. Triblock copolymers gave materials with slightly lower BET surface areas than diblocks, for a similar *d*-spacing. The nitrogen sorption data indicate that pores created on calcination are accessible and interconnected. Thus windows or channels in the silica walls must be formed during the synthesis or generated on calcination. Ryoo *et al.*[16] have provided evidence that in mesoporous hexagonal SBA-15 silica, prepared with a poly(oxyethylene)-*block*-poly(oxypropylene)-*block*-poly(oxyethylene) triblock copolymer, the large mesopores are connected by disordered small pores in the mesopore walls.

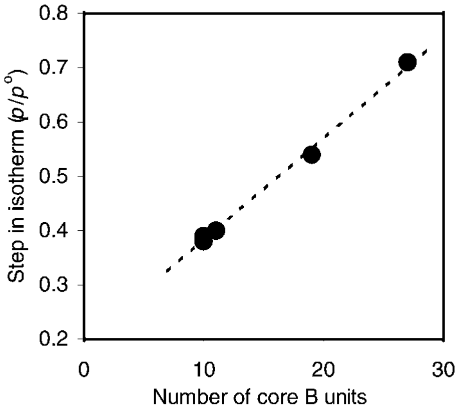

**Fig. 4** Variation of the position of the step in the nitrogen adsorption isotherm for calcined silica products with the number of B units in $E_mB_n$ diblock copolymers used as structure-directing agents.

## Discussion

### Effect of the molecular structure of the copolymer on the dimensions of the silica mesostructure

If block copolymers act as structure-directing agents, then the dimensions associated with silica mesostructures should relate to the dimensions of copolymer micelles and thus to copolymer composition and architecture. Research on the association

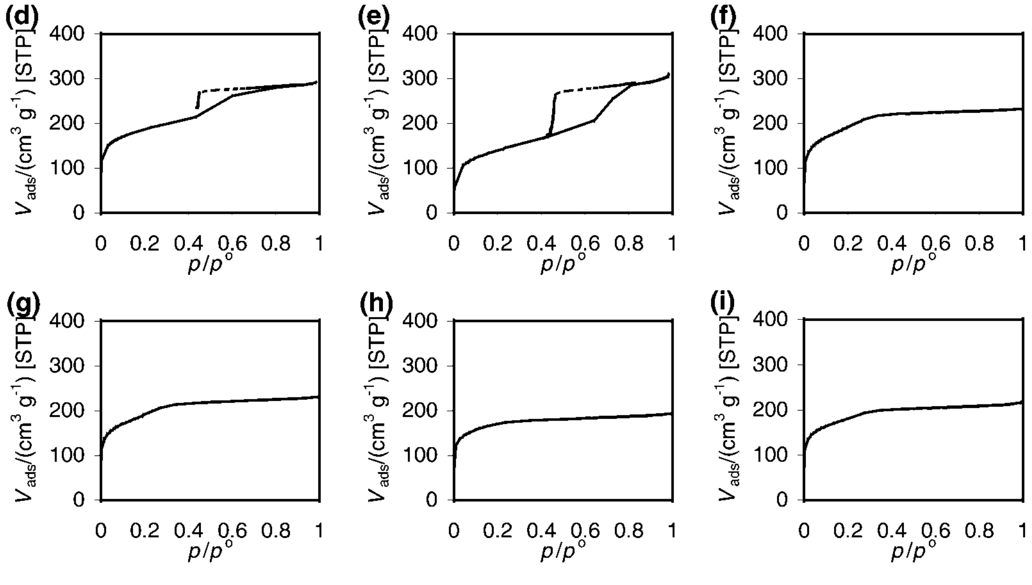

**Fig. 3** Nitrogen adsorption (solid line) and desorption (dashed line) isotherms for calcined silica prepared with (a) $E_{40}B_{10}$, (b) $E_{54}B_{11}$, (c) $E_{89}B_{10}$, (d) $E_{56}B_{19}$, (e) $E_{56}B_{27}$, (f) $E_{23}B_{11}E_{23}$, (g) $E_{31}B_{12}E_{31}$, (h) $E_{47}B_{10}E_{47}$ and (i) $E_{43}B_{14}E_{43}$.

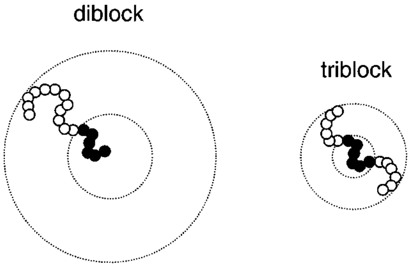

**Fig. 5** Comparison of micelles formed by diblocks and triblocks of the same overall composition.

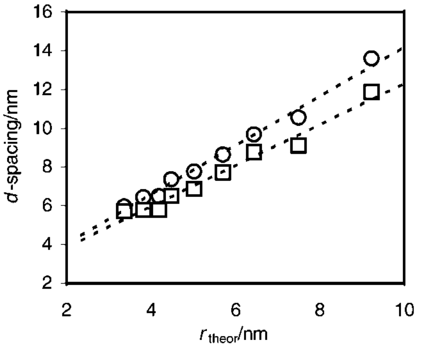

**Fig. 6** Dependence of *d*-spacing for uncalcined (○) and calcined (□) silica products on $r_{\text{theor}}$ calculated on the basis of copolymer composition and architecture.

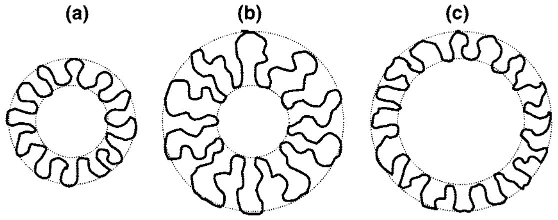

**Fig. 7** Schematic illustration of mesopores with convoluted or microporous walls: (a) and (b) have the same core mesopore size but different overall dimensions; (b) and (c) have different core mesopore sizes but the same overall dimensions.

behaviour of poly(oxyalkylene) copolymers has been reviewed by Booth and Attwood.[17] In general, triblock copolymers form micelles of approximately half the radius of diblock copolymers of the same overall composition, because both ends of a triblock must emerge from the micelle core into the corona (Fig. 5). Neutron scattering experiments on $E_mB_n$ copolymers have indicated that in the micelle core the B chain is stretched to about 60% of its fully extended length and that in the corona the dimensions of the E chain are approximately twice its radius of gyration.[12,18] Consequently, the ratio of corona size to core radius is expected to be of the order of $2.1m^{1/2}/n$. On this basis, given that the fully extended length per B unit is 0.36 nm, a theoretical micelle radius, $r_{\text{theor}}$, may be calculated. For an $E_mB_n$ diblock copolymer eqn. (1) applies.

$$r_{\text{theor}}/\text{nm} = 0.216n[1+(2.1m^{1/2}/n)] \qquad (1)$$

For an $E_mB_nE_m$ triblock copolymer, as explained above, it is appropriate to use ($n$/2) in place of $n$ in eqn. (1). Different experimental methods will, of course, give different numerical values of micelle radius. Furthermore, this model is likely to break down for very short or very long blocks. Nevertheless, if the copolymer acts as a structure-directing agent, the characteristic length observed within the product by X-ray scattering should, to a first approximation, scale with $r_{\text{theor}}$. Fig. 6 shows a simple relationship between the *d*-spacing obtained for silica products and $r_{\text{theor}}$ calculated on the basis of the molecular structure of the copolymer. This provides clear evidence of a genuine structure-directing effect and offers a basis for making predictions.

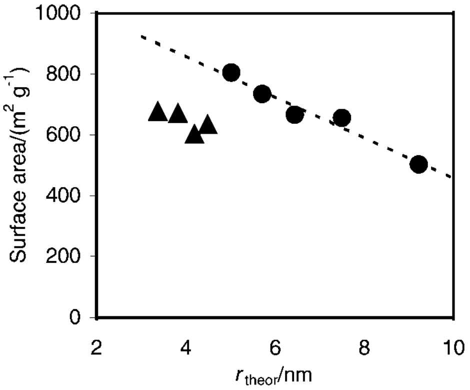

**Fig. 8** Dependence of BET surface area for calcined silica prepared with diblock (●) and triblock (▲) copolymers on $r_{\text{theor}}$ calculated on the basis of copolymer composition and architecture.

### Effect of the molecular structure of the copolymer on the surface properties of the silica

The length of the B-block was found to have a profound effect, but the length of the E-block a relatively small effect, on the form of the nitrogen adsorption/desorption isotherms (Fig. 3 and 4). It has already been commented that silica prepared under acid conditions may have walls that are convoluted and/or contain channels. This is particularly likely to be the case when using amphiphiles incorporating poly(oxyethylene) blocks, as the micelle coronas are highly swollen with solvent. A simple model is illustrated in Fig. 7, which indicates how increasing E-block length may increase mesostructure dimensions without increasing the core mesopore size, whilst increasing B-block length will swell the mesopore core.

As discussed above and indicated in Fig. 5, a triblock may be regarded in the first instance as behaving in the same way as the diblock that would be generated by scission at its mid-point. However, the surface properties of the silica show a subtle difference between triblocks and diblocks, as illustrated by Fig. 8, in which BET surface area is plotted against $r_{\text{theor}}$. Triblocks appear to give lower surface areas than equivalent diblocks. This may reflect a more hydrophilic micelle core that is obtained with a diblock. In a diblock, prepared as in this work, the B-chain has a hydroxy end and so a significant amount of water may penetrate the core.[18]

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