

# Non-aqueous polymer dispersions: dimensions of adsorbed AB block copolymers of polystyrene and poly(dimethyl siloxane) by small-angle neutron scattering

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Poly(methyl methacrylate) and polystyrene particles stabilized in *n*-heptane, Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane) and silicone fluid by AB block copolymers of polystyrene and poly(dimethyl siloxane) have been studied using small angle neutron scattering. Particle sizes calculated from the scattering intensity are in reasonable agreement with particle diameters estimated from electron micrographs. The intensity of scattering from poly(methyl methacrylate) particles stabilized with copolymers containing A blocks prepared from perdeuterostyrene was much higher than from polystyrene particles stabilized with the same block copolymers. It is proposed that the polystyrene blocks are molecularly dispersed in polystyrene particles and cluster into domains in poly(methyl methacrylate) particles. Scattering arising from the poly(dimethyl siloxane) blocks has been detected but could not be simply interpreted.

## INTRODUCTION

The interfacial properties of chain-like molecules in many polymeric and colloidal systems are dependent on the conformation of the chains adsorbed at the interface<sup>1</sup>. Chains adsorbed at the solid-liquid interface may be produced by anchoring block or graft copolymers to a dispersion of polymer particles. Such a dispersion is conveniently produced by polymerizing in the presence of a preformed copolymer a monomer dissolved in an organic diluent which is a precipitant for the polymer. The A blocks in the copolymer which are insoluble in the diluent anchor on or in the precipitating particles and the B blocks which are swollen by the diluent extend away from the particle surface. The surface layer of B blocks protects the particles from flocculation by a mechanism known as steric stabilization<sup>2</sup>.

Many of the studies on polymer dispersions in organic liquids have involved particles stabilized by graft copolymers which are invariably polydisperse<sup>2</sup>. AB block copolymers prepared by sequential 'living' anionic polymerization will have well defined block lengths and a narrow chain length distribution, so that stabilization of polymer dispersions should provide a constant layer thickness of B blocks around the particles. Stable dispersions of polystyrene (PS) and poly(methyl methacrylate)(PMMA) in *n*-alkanes have been prepared by polymerizing the monomers in the presence of AB block copolymers of polystyrene (PS) and poly(dimethyl

siloxane) (PDMS)<sup>3-5</sup>. Here, the results of an initial study by small angle neutron scattering of the dimensions of the PS and PDMS blocks in these well-defined dispersions are reported. The dimensions of the stabilizing B chains are of importance not only to steric stabilization in particular but also to the general problem of adsorbed chains at solid-liquid interfaces. The determination of the dimensions of the PS blocks for the PS and PMMA particles may indicate how the type of copolymer anchoring may be influenced by the degree of compatibility between the A blocks and the polymer molecules in the particles.

## EXPERIMENTAL

### *Block copolymers and dispersion polymerization*

PS-PDMS block copolymers containing protonated polystyrene PS(H) were synthesized by anionic polymerization using high vacuum techniques as described previously<sup>5</sup>. The same procedures were used for the preparation of AB block copolymers containing blocks of deuterated polystyrene PS(D) from perdeuterostyrene (Aldrich Chemical Co.). The characterization of the block copolymers with the techniques described elsewhere<sup>5</sup> yielded the molecular weight of the PS block  $M_A$ , the molecular weight of the PDMS block  $M_B$ , the polydispersity ( $<1.25$ ) defined as the ratio of the weight average and number average molecular weights  $\bar{M}_w/\bar{M}_n$ , and the copolymer composition determined from silicon analysis.

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**Table 1** Molecular weight data for AB block copolymers of PS and PDMS

Block copolymer	D/H	$M_A$	$M_B$
B1	PS(H)	20 000	3300
B15	PS(H)	8800	11 200
B16	PS(H)	43 600	13 700
B17	PS(H)	43 600	29 800
B20	PS(H)	12 700	3200
B22	PS(H)	33 400	13 800
B24	PS(H)	16 400	7600
B26	PS(D)	23 400	3300
B27	PS(D)	61 000	25 700

**Table 2** Dispersions in small angle neutron scattering experiments

Experiment	Particles	Particle diameter ( $\mu\text{m}$ )	Block copolymers	D/H (w/w block copolymer)	Diluent
A	PMMA	0.25	B15	0	Silicone fluid
B(i)	PMMA	0.48	B15	0	Freon 113
B(ii)	PS	0.21	B1	0	Freon 113
B(iii)	PS	0.32	B24	0	Freon 113
B(iv)	PS	0.36	B16	0	Freon 113
B(v)	PMMA	0.11	B20	0	Freon 113
B(vi)	PMMA	0.25	B15	0	Freon 113
C	PS	0.30	B26/B22	1/6	<i>n</i> -heptane
C	PS	0.30	B26/B22	1/3	<i>n</i> -heptane
D(i)	PMMA	0.20	B26/B24	1/6	<i>n</i> -heptane
D(ii)	PMMA	0.20	B26/B24	1/12	<i>n</i> -heptane
D(iii)	PMMA	0.20	B26/B24	1/2	<i>n</i> -heptane
D(iv)	PMMA	0.07	B27/B17	1/6	<i>n</i> -heptane
D(v)	PMMA	0.20	B26/B24	1/2	Freon 113

Polymer dispersions were prepared by polymerizing monomer in *n*-alkanes in the presence of PS–PDMS block copolymer. Anionic dispersion polymerization was employed for styrene<sup>3</sup>, and radical dispersion polymerization was used for methyl methacrylate<sup>5</sup>. Dispersions were washed by redispersion cycles which also served to exchange a diluent for a different one, e.g. Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane) and silicone fluid (F111/50 supplied by ICI Organics Division). Particle diameters were determined from transmission electron micrographs (*TEM*). Details of the block copolymers and the dispersions are given in *Tables 1* and *2*.

#### Small-angle neutron scattering

Small-angle neutron scattering experiments were carried out using the D11 and D17 spectrometers at ILL Grenoble<sup>6</sup>. The experimental conditions for samples in *Table 2* are summarized in *Table 3*. The dispersions were held in quartz cells 1 or 2 mm thick, the sample area being defined by a 1 cm diameter diaphragm. All normalization was made using the incoherent scattering from a water sample under identical experimental conditions<sup>7</sup>.

Contrast in a neutron scattering experiment arises from differences in the net scattering probabilities of neutrons from different nuclear species, the important parameter being the scattering length,  $b$ . (The difference between scattering lengths of hydrogen and deuterium is particularly important). If the net scattering length  $\Sigma b$  for the polymer repeat units differs considerably from that of the surrounding molecules, there is contrast and a scattering pattern for the polymer molecule may be observed. *Table 4* lists the values of  $\Sigma b$

for the various polymer repeat units and solvent molecules in these experiments. The values have been normalized to one PMMA unit. The observed scattering intensity from the sample is then proportional to the contrast factor  $B$  where

$$B = (\Sigma b_{\text{polymer}} - \frac{V_p}{V_s} \Sigma b_{\text{solvent}})^2 \quad (1)$$

where  $V_p/V_s$  takes account of specific volume effects.

Many examples of exploitation of neutron contrast factors may be found in two review articles by Richards and Macconnachie<sup>8</sup> and Higgins and Stein<sup>9</sup>.

Samples *C* and *D* in *Table 2* contained some PS(D) blocks. In each case by subtracting the scattering from an identical suspension with no deuteration, the signal of the PS(D) blocks themselves was to be extracted. For sample *A*, in silicone fluid, there is no contrast between the PDMS chains and the surrounding solvent. The signal of a spherical particle should be observed from the hard cores. Samples *B*(i–vi) have contrast between the PDMS and the solvent as well as the hard cores so that any signal from the PDMS chains will also be observed. For *A* and *B* samples the background sample subtracted is the solvent containing hydrogenous biphenyl with concentration chosen to give the same level of incoherent scattering as that from the dispersions.

#### Analysis

The isotropic scattering observed on the multidetector is grouped according to radial distance from the beam centre to give a radial distribution of scattered intensities  $I(r)$ . The angle of scatter,  $\theta$ , is then given by  $r/D$  where  $r$  is the radial distance and  $D$  the distance sample–detector. The scattering wave vector

$$K = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} = \frac{2\pi}{\lambda} \frac{r}{D}$$

From  $I(r)$  the normalized scattered intensity  $I(K)$  is obtained using water scattering data.

This data may then be compared with calculations for various model functions. A number of scattering functions

**Table 3** Experimental conditions for neutron small angle scattering

Sample	$D(v)$	A, B (i) C, D (i–iv)	B (ii–vi)
Sample-detector distance (m)	2.56	2.8	2.56
Wavelength $\lambda$ (Å)	9.96	15	7.9
Resolution $\Delta\lambda/\lambda$ (%)	8	10	8
Range $K$ -vector ( $\text{Å}^{-1}$ )	0.017–0.086	0.01–0.05	0.022–0.108
Apparatus	D11	D17	D11

**Table 4** Net scattering length densities ( $\times 10^{-12}$  cm/PMMA unit)

PDMS	0.12	
PS(H)	2.2	PS(D) 10.2
PMMA	1.5	
Freon 113	5.2	
<i>n</i> -heptane	–1.06	
Silicone fluid	0.12	

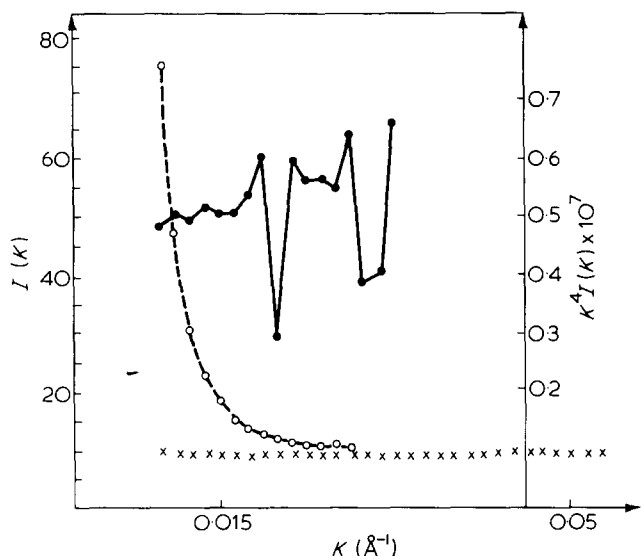


Figure 1 ○,  $I(K)$  and ●,  $K^4 I(K) \nu K$  for a sample A (PMMA) particles in silicone fluid. Signal from fluid alone x

were used in the analysis of the present data.

(a) For a monodisperse polymer sample in solution at concentration  $c$  the Zimm treatment<sup>10</sup> gives

$$\frac{\chi c}{I(K)} = \frac{1}{M} \left\{ 1 + \frac{K^2 \langle s^2 \rangle}{3} \right\} + 2A_2 c \quad (2)$$

where  $M$  is the molecular weight of the polymer,  $\langle s^2 \rangle$  the mean squared radius of gyration and  $A_2$  the second virial coefficient. A plot of  $c/I(K) \nu K^2$  is linear and by extrapolation  $\langle s^2 \rangle$  and  $M$  may be obtained from the slope and intercept respectively. The constant  $\chi$  contains the contrast factor  $B$  and instrumental parameters. Examination of the Zimm equation above shows that while  $\langle s^2 \rangle$  values are independent of normalization and a precise knowledge of the contrast factors, the values of  $M$  do depend on these parameters and are correspondingly less accurate. For a polydisperse system the values of  $M$  and  $\langle s^2 \rangle$  become the weight average  $\bar{M}_w$  and the  $z$  average  $\langle s^2 \rangle_z$ . Under  $\theta$  conditions (and in the bulk)  $A_2 \approx 0$  and no concentration dependence is observed.

(b) A solution of spherical particles of radius  $R$ , in the limit of  $K \gg R^{-1}$ , shows characteristic Porod scattering<sup>11</sup>

$$I(K)K^4 = \text{constant} = 2\pi n B' S$$

where  $S$  is the surface area of the sphere and  $B'$  the contrast per unit volume.

$$n = \text{number of particles} = \frac{c}{\rho \times V}$$

where  $c$  is the concentration of particles mass/cm<sup>3</sup>;  $\rho$  is their density;  $V$  is their volume. Thus

$$I(K)K^4 = 2\pi B' \frac{c}{\rho} \cdot S/V \quad (3)$$

and the diameter of the particle may be obtained from the surface to volume ratio  $S/V$ .

(c) Scattering from a sphere of radius  $R$  when  $K \sim R^{-1}$

$$I(K) = 9B'V^2 \frac{j_1^2(KR)}{K^2R^2} \quad (4)$$

this is an oscillating function with period defined by  $R$ . Scattering from a thin disc of radius  $R$  when  $K \sim (2R)^{-1}$

$$I(K) = \frac{B'}{K^2R^2} \left[ 1 - \frac{j_1(2KR)}{KR} \right] \quad (5)$$

this function also oscillates.

Scattering from a hollow sphere (inner and outer radii  $R_1$  and  $R_2$ )

$$I(K) = 32 \frac{\pi^5 B'}{K^3} R_2^{3/2} J_{3/2} \frac{(KR_2)}{2} - R_1^{3/2} J_{3/2} \frac{(KR_1)^2}{2} \quad (6)$$

which is also an oscillating function;  $j_1$  and  $J_{3/2}$  are Bessel functions.

## RESULTS

### Spherical particles in dispersion

Figure 1 shows  $I(K) \nu K$  for sample A where the only contrast is for the hard PMMA centres and PDMS chains are invisible. The signal is effectively zero for  $K > 0.03 \text{ \AA}^{-1}$ . Inset in the figure is a plot of  $I(K)/K^4 \nu K$  (Porod plot). Before the signal disappears there is clearly a region where  $I(K)/K^4$  is constant. A value of the radius  $R$  for the particles from this region is  $0.2 \text{ \mu m}$  (using equation 3). This is a  $z$ -average and is to be compared to an  $n$ -average value of  $0.13 \text{ \mu m}$  obtained by TEM. Within experimental error (note the strong  $K$ -dependence) the agreement is gratifying. When the solvent is Freon a more complicated situation arises since as Table 4 indicates there is a contrast both for the cores and the PDMS chains. In Figure 2 the results for samples B(i) at two concentrations are shown  $c/I(K)$  against  $K^2$  (inset is a Porod plot). In this case, we see two regions of behaviour. At low  $K$  there is scattering characteristic of spherical particles, but note that the intensity is independent of particle concentration. At higher  $K$  a region of approximately linear  $K^2$  behaviour is seen where intensity is approximately proportional to concentration. This high  $K$  'tail' to the scattering will be

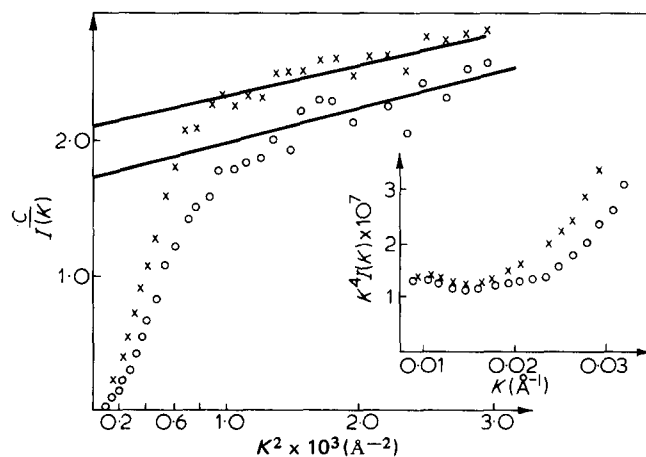


Figure 2  $c/I(K) \nu K^2$  for sample B (i) (PMMA particles). x, 10% solution; ○, 5% solution in Freon. Inset  $K^4 I(K) \nu K$  for same samples

Table 5 Particle radius for Freon solutions and one silicone solution

Sample	Composition	<i>n</i> average <i>R</i> by TEM (μm)	<i>z</i> average <i>R</i> (μm) by neutrons (conc)
A	PMMA	0.13	0.22 (10%)
B (i)	PMMA	0.24	0.53 (10%) 0.025 (5%)
B (ii)	PS	0.11	0.26
*B (iii)	PS	0.16	0.41
*B (iv)	PS	0.18	0.7
B (v)	PMMA	0.05	0.21
B (vi)	PMMA	0.13	0.26

\* Very rough estimates — there is not really a region of  $K^4$  behaviour. All B (ii)–B(iv) experiments were performed in a higher  $K$ -range ∴ narrow region of  $K^4$

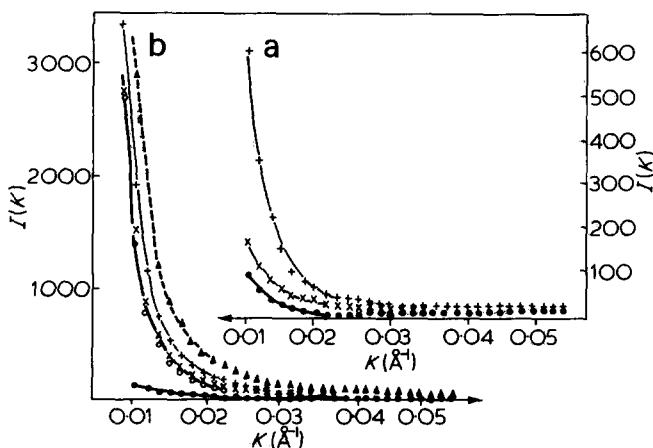


Figure 3 (a) Sample C(PS) particles PS(D)/PS(H) ratio; x, 1:6 PS(D) 23,400; +, 1:3; ●, undeuterated; (b) Sample D(PMMA) particles (0.2 μm) in *n*-heptane PS(D)/PS(H) ratio; +, 1:6, x, 1:12, ▲, 1:2 (PS(D) 23,400); ○, 1:6 PS(D) 61,000; ●, undeuterated

discussed later. The  $K^4$  dependent region leads to differing values of the particle radius for the two different concentrations. However the absolute intensity  $I(K)$  and hence the value of  $R$  obtained is directly proportional to the calculated  $B'$  contrast factor, so that even the simplest interparticle interaction, which changes the PDMS distribution and thus the mean contrast from hard core to surrounding solvents, may affect the calculation of  $R$ . Values calculated for all the *B* samples assuming a direct contrast between core and Freon, are listed in Table 5. The effect of PDMS on this contrast can only reduce the  $R$  values obtained giving better agreement with TEM values.

In Figures 3 and 4 a similar particle shape scattering pattern can be seen for the particles with PS(D) blocks. The fact that this signal persists at low  $K$  in Figure 4 where scattering from undeuterated particles has been subtracted indicates clearly the problems of working with these systems. The deuteration itself changes the overall contrast for the particle cores, so that this contribution is never perfectly subtracted. The overall strategy must be to use as large particles as possible so that the signal is confined to low  $K$  (Figure 1 shows that the particle signal is quickly damped out in this  $K$ -range) and PS(D) blocks with low  $M_A$  so that the Guinier range is reasonably well separated from the sphere signal.

Polystyrene blocks-conformation

Figure 3 shows the scattering function  $I(K)$  plotted against wave vector  $K$  for samples *C* and *D* (i–iv). The in-

tensity scattered from the PS samples relative to the background sample is an order of magnitude less than that from the PMMA samples with corresponding concentrations of PS(D) blocks relative to their background. This implies that there are larger scattering objects in the PMMA samples and hence aggregates of PS(D) blocks. Figure 4 shows a plot  $c/I(K)$  against  $K^2$  for the *C* samples. At low  $K$  there is a region of sharply varying signal arising from the spherical particle shape as described in the previous section, but above  $K^2 \sim 10^{-3} \text{ \AA}^{-2}$  a linear  $K^2$  region is observed for both samples with intensity approximately proportional to concentration of PS(D) blocks. From this region (using equation 2 and assuming  $A_2 = 0$ ) it is possible to obtain values of  $\bar{M}_w$  and  $\langle s^2 \rangle_z$ . The values of  $(\langle s^2 \rangle_z)^{1/2}$  obtained are 55 Å and 60 Å respectively for the 1:6 and 1:3 PS(D)/PS(H) ratios. The value for bulk polystyrene would be 43 Å<sup>12</sup>. Because of the difference in  $M_A$  between the deuterated and hydrogenous copolymers the actual concentration of deuterated blocks/particle is uncertain to within a factor 2 or 3 (that is to say the 1:6 and 1:3 ratios are uncertain). This gives rise to the same uncertainty in the values of  $\bar{M}_w$  obtained from the intercepts in Figure 4. It is only possible to say that the values of 72 000 and 63 000 obtained are within the same order as the number average value  $M_A = 23 000$  measured by g.p.c. within this uncertainty of 2 or 3. As remarked above the large increase in intensity seen in Figure 3 when the same copolymers are incorporated in PMMA particles, implies that the PS(D) blocks are forming aggregates. Figure 5 shows a plot of  $c/I(K) v K^2$  for sample *D*(i). There is no linear region from which a value of  $\langle s^2 \rangle$  can be obtained — this was true for all the *D* samples. The scattered intensity from *D*(i) may be compared with curves calculated for the model systems as described in analysis (c) earlier. An even distribution of the PS(D) over the surface of the particle might appear as a thin hollow sphere in the

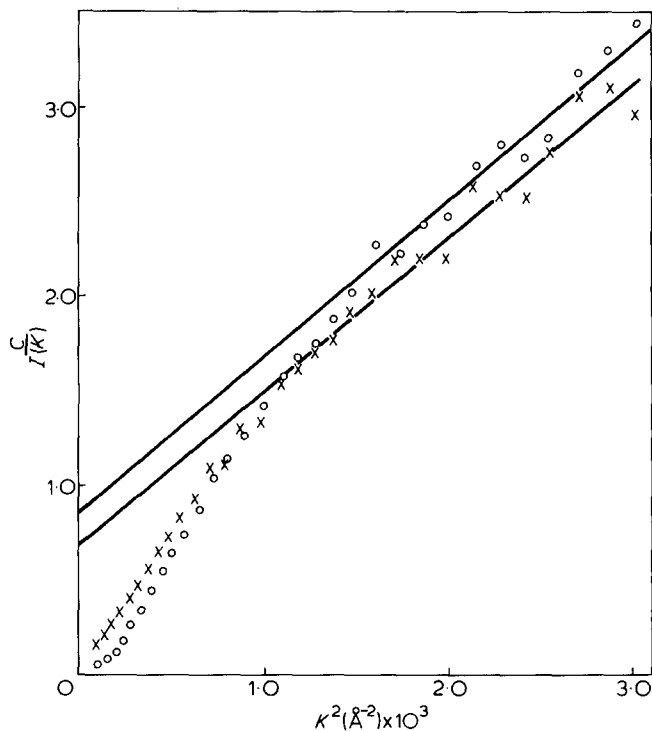


Figure 4  $c/I(K)$  against  $K^2$  for sample C(PS) particles containing PS(D) blocks with undeuterated particle signal subtracted PS(D)/PS(H), ○ 1:3, x 1:6

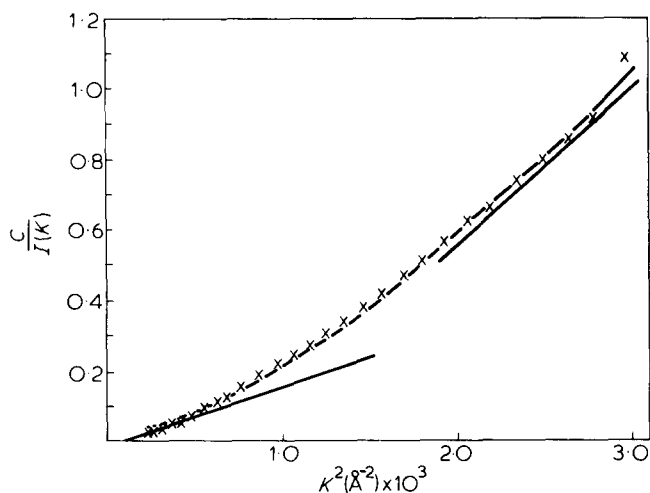


Figure 5  $c/I(K)$  against  $K^2$  for sample D(i) (PMMA particles containing PS(D) blocks). Signal from undeuterated particles has been subtracted

scattering pattern. A tentative suggestion is that the PS(D) is irregularly distributed over the surface of a particle in approximately phase-separated domains, since the oscillating intensity expected from a thin hollow sphere is not observed (equation 6) in Figure 6. The curves for either thin discs of spherical domains (equations 4,5) give a reasonable fit to the data if the low  $K$  scattering is ignored and assumed to arise from the spherical particle shapes.

#### The high- $K$ 'tail'-PDMS scattering

It is tempting to interpret the linear region in Figure 2 observed for all  $B$  samples as scattering from PDMS chains. However, while the slopes would lead to reasonable values of  $\langle s^2 \rangle_z$  for some of the samples, in others these values are an order of magnitude smaller than  $\theta$ -dimension for free chains having these  $M_B$  values. Also, the intensity of the scattering is too large to arise from individual PDMS chains; it would lead in some cases to values of  $\bar{M}_w$ , taken from the intercept, an order of magnitude too large. A correlation between PDMS blocks over the particle surface could give rise to such an intense signal. The only way to unravel the signal from the PDMS blocks is to attack the problem as for the PS blocks and to deuterate some of them.

#### CONCLUSIONS

The spherical shape of the particles gives rise to a strong  $K^4$  dependent signal at low  $K$ , the intensity of which correlates reasonably well with the size of the particle determined by TEM.

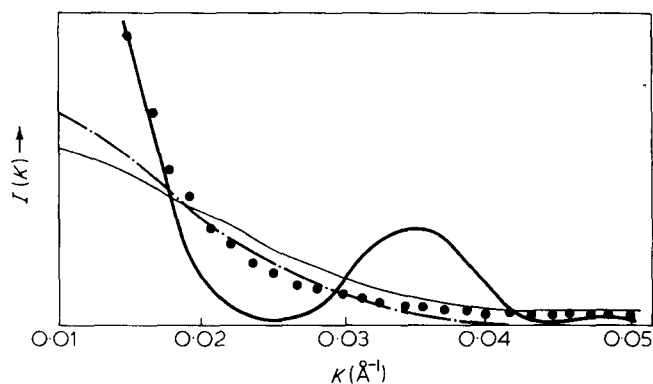


Figure 6  $I(K)$  v  $K$  for sample D(i) with signal from undeuterated particles subtracted. ●●●, data; —, model calculations for hollow sphere  $R_1 = 0.1 \mu\text{m}$   $\Delta R = 20 \text{Å}$ ; - - - -, model calculations for spheres  $R = 100 \text{Å}$ ; —, model calculations for thin discs  $R = 100 \text{Å}$

In PS particles the PS(D) blocks are molecularly dispersed with  $\langle s^2 \rangle_z \geq$  bulk value, whereas in PMMA particles PS(D) blocks are clustered or aggregated. There is a signal associated with the PDMS blocks but its exact origin is not clear.

#### ACKNOWLEDGEMENTS

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