The preparation and micellization behaviour of AB block copolymers of styrene and 4-nitrostyrene

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AB block copolymers of styrene and 4-nitrostyrene have been prepared. The 4-nitrostyrene monomer was synthesized by the nitration of 2-bromoethylbenzene, followed by dehydrobromination, and was purified by sublimation. The polymerization of styrene in tetrahydrofuran was initiated with s-butyllithium and the 'living' polystyryl anion was used to initiate the polymerization of 4-nitrostyrene. Block copolymer in the product was separated from polystyrene homopolymer by a fractionation procedure. The formation of well-defined block copolymers was verified by characterization of the polymers with respect to composition and molecular weight distribution and by studies of their micellization behaviour. Micelles were shown to form in toluene, a selectively bad solvent for poly(4-nitrostyrene). Differential scanning calorimetry indicated a microdomain structure in the solid state.

(Keywords: anionic polymerization; block copolymer; micelle)

INTRODUCTION

Recently, it has been demonstrated that poly(4-nitrostyrene) may be prepared by the nitration of polystyrene in 3-nitrotoluene, a solvent for substrate and product which is immiscible with the nitrating mixture[1]. Polymers and copolymers of 4-nitrostyrene may also be formed by free radical polymerization of the monomer[2–4]. A cationic initiator has been shown not to give appreciable copolymerization of 4-nitrostyrene with styrene[5], as might be expected given the strongly electron-withdrawing nature of the nitro group. As far as the authors are aware, there have previously been no reports of the polymerization of 4-nitrostyrene by an anionic mechanism, which offers potential for the formation of well-defined polymers and block copolymers. Here we show, for the first time, that 4-nitrostyrene may be polymerized anionically. A major problem is the insolubility of poly(4-nitrostyrene) in solvents which are suitable for anionic polymerization. This problem may be overcome in the formation of block copolymers by polymerizing the 4-nitrostyrene in the second stage, the first block serving to solubilize the copolymer. This paper describes the preparation of AB block copolymers of styrene and 4-nitrostyrene.

EXPERIMENTAL

Nitration of 2-bromoethylbenzene

Acetic acid (BDH, 195 cm^3) and acetic anhydride (BDH, 118 cm^3) were added to a round-bottomed flask equipped with a mechanical stirrer, a thermometer and two addition funnels. Nitric acid (s.g. 1.5, May and Baker, 84 cm^3) was added dropwise with vigorous stirring at 0°C. 2-Bromoethylbenzene (Fluka, 370 g) was added likewise over a 2.5 h period. The reaction mixture was left stirring at 30°C for a further 2.5 h.

The reaction mixture was poured into a suspension of ice (100 g) and sodium carbonate (BDH, 200 g). The suspension was filtered and the yellow crystalline residue washed with cold petroleum ether (60/80). The needle-like crystals of 2-bromoethyl-4-nitrobenzene were dried to constant weight (yield 113.4 g, 24.7%; m.p. 69.2–69.5°C).

Organic matter present in the aqueous mixture was extracted with diethyl ether (Aldrich, 4×250 cm^3) and dried using fused calcium chloride. After filtration the ether was removed and the 2-bromoethyl-4-nitrobenzene was recrystallized from petroleum ether (60/80). The crystals were filtered, washed with cold petroleum ether (60/80) and dried to constant weight (yield 80.6 g, 17.5%; m.p. 69.1–69.5°C).

The 2-bromoethyl-4-nitrobenzene was stored at −10°C and dehydrobrominated shortly before use.

Dehydrobromination

Triethanolamine (Fluka, 300 cm^3), water (100 cm^3) and a trace amount of 4-t-butylcatechol (Fluka) were added to a round-bottomed flask equipped with a Stark–Dean trap, a mechanical stirrer and an addition funnel. The flask was heated in an oil bath and, when the water began to reflux, 2-bromoethyl-4-nitrobenzene (50 g) was added. A yellow oil was collected. A further three portions of 2-bromoethyl-4-nitrobenzene were added at 3 h intervals.

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Crude 4-nitrostyrene was recrystallized from the yellow oil with hexane at −40°C and dried at 0°C under vacuum ($<10^{-3}$ mmHg) (yield 123.1 g, 95%; m.p 22°C).

The purity of the crude product was found by gas–liquid chromatography to be 94% by weight, the impurity being a species with a higher boiling point. Mass spectroscopy indicated that the impurity was probably 2,4-dinitrostyrene. Careful purification of the monomer is essential for anionic polymerization. In the case of 4-nitrostyrene, purification by standard vacuum transfer procedures was not possible because of its relative involatility. Molecular distillation and zone refining also proved unsuccessful. However, it was found that it was possible to purify the monomer by sublimation. This was carried out prior to polymerization as described below.

Anionic polymerization

Three polymerizations were performed with different amounts of initiator. The polymerizations were carried out utilizing high vacuum techniques. The vacuum line comprised a glass manifold bearing high vacuum taps, two liquid nitrogen traps, a mercury diffusion pump and a rotary oil pump.

Reagents. Hexane was dried over sodium hydride for 48 h under a dry nitrogen atmosphere and distilled (68.5–69°C, 760 mmHg). The middle fraction was degassed and a quantity of s-butyllithium was added to react with impurities that would interfere with the polymerization. It was then distilled under vacuum prior to use.

4-Nitrostyrene was twice recrystallized from purified hexane at −40°C and then dried at 0°C. It was then sublimed into an ampoule, which was then sealed and stored in the dark.

Styrene was stirred over crushed calcium hydride under a dry nitrogen atmosphere for 72 h, distilled (56.5–57.5°C, 15 mmHg) and degassed. The monomer was vacuum transferred onto a sodium mirror and the required amount then distilled into an ampoule.

Tetrahydrofuran solvent (BDH) was stirred over a mixture of freshly cut sodium wire and recrystallized benzophenone under a dry nitrogen atmosphere. After 24 h the solvent was degassed and stored under a dry nitrogen atmosphere at 0°C.

s-Butyllithium initiator (Aldrich) was obtained as a solution in cyclohexane (ca. 1.1 mol dm^{-3}). The precise concentration was determined before each polymerization by the method of Gilman and Haubein[6].

Methanol was used as received and sealed under vacuum in an ampoule.

Polymerization. The polymerization was carried out in a glass vessel bearing two round-bottomed flasks, ampoules of styrene, 4-nitrostyrene and methanol, and a tap and socket for connection to the vacuum line. Each flask had a side arm with a serum cap and one had a second side arm with a tap.

The vessel was evacuated, tetrahydrofuran (250 cm^3) was distilled into one flask, and the vessel was isolated from the vacuum line. Styrene (0.5 cm^3) and s-butyllithium (1.0 cm^3) in that order were added to the solvent via the serum cap. The mixture took on the characteristic red colour of the polystyryl anion and was used to rinse the vessel before being returned to the first flask. The solvent was distilled into the second flask, used to rinse the vessel further and then returned to the first flask. Repeated distillations enabled all residual polymer to be removed from the glass walls. Finally, tetrahydrofuran (200 cm^3) was distilled into the second flask and the first flask was isolated from the rest of the vessel.

Styrene from an ampoule was released into the reaction flask and the mixture was cooled, with stirring, to −78°C. An appropriate quantity of s-butyllithium was injected via the serum cap and once the reaction had started the cap was removed by sealing a constriction. The reaction mixture was left at −78°C for 0.5 h, then allowed to warm to ambient temperature. After a further 0.5 h a sample of the reaction mixture was isolated in a side arm. 4-Nitrostyrene from an ampoule was added to the flask containing the 'living' polymer solution. The colour of the reaction mixture changed from bright red to brown and the viscosity of the solution increased. The reaction was allowed to proceed until slight precipitation was noted, when the polymerization was terminated with methanol from an ampoule. The solution then became green in colour and very viscous.

The terminated reaction mixture and the isolated polystyrene solution from the side arm were each filtered and added to an excess of Analar methanol with stirring to precipitate the polymer. The product was filtered off, washed with methanol and dried to constant weight under vacuum.

Fractionation

The block copolymer was separated from unreacted polystyrene homopolymer in the product by a fractionation procedure. A solution of the product (0.2% by weight) in toluene was prepared in a pear-shaped vessel equipped with a mechanical stirrer and held in a water bath at 30°C. The block copolymer was expected to form a micellar solution in this solvent. Hexane, a non-solvent for both blocks of the copolymer, was added dropwise to the vigorously stirred solution until an increasing turbidity was noted. Whilst continuing to stir, the temperature was increased until the additional turbidity had disappeared, then the solution was allowed to cool slowly back to 30°C. The stirrer was switched off and the precipitated phase was allowed to settle. The supernatant was siphoned off. The precipitated phase was redissolved in toluene, the bulk of the solvent removed by evaporation and the copolymer dried to constant weight under vacuum. The procedure was repeated a number of times to obtain a series of pure copolymer fractions which were then recombined.

Gel permeation chromatography

Molecular weight distributions were investigated by gel permeation chromatography (g.p.c.), utilizing three columns (Polymer Laboratories PL gel, nominal pore sizes 10^5 Å, 10^4 Å and 500 Å) operated at 70°C with *N,N*-dimethylacetamide as the eluent at a flow rate of 1.0 cm^3 min^{-1}. A differential refractometer (Waters 501) was employed as the detector. The system was calibrated with polystyrene standards and with samples of poly(4-nitrostyrene) of known molecular weight.

Nuclear magnetic resonance spectroscopy

^{1}H nuclear magnetic resonance (n.m.r.) spectra of the copolymers were recorded using a Bruker AC300 spectrometer operating at 300 MHz. Samples were dissolved in deuterated dimethyl sulphoxide (0.01 g cm^{-3}). The mole fraction of 4-nitrostyrene units x_N was evaluated from the integral A of the peak for aromatic protons *ortho* to the

nitro group (at 7.9 ppm) and the overall integral B for other aromatic peaks using $x_N = 5(A/B)/[2+3(A/B)]$.

Elemental analysis

Elemental analysis of the copolymers was carried out by the Department of Chemistry Microanalytical Service, University of Manchester. The mole fraction of 4-nitrostyrene units x_N was evaluated from the percentage nitrogen by weight $N\%$ or the percentage carbon by weight $C\%$ using $x_N = 104N\%/(1400-45N\%)$ or $x_N = (9600-104C\%)/45C\%$.

Static light scattering

Apparent weight-average molecular weights $\bar{M}_w$ for the block copolymers and block copolymer micelles were determined by static light scattering utilizing a Sofica PGD 40B photometer with incident light of wavelength 546 nm. The scattered light intensity was monitored at nine angles from 30 to 142.5° for each solution studied. Molecular solutions were studied in *N,N*-dimethylformamide at 90°C, and micellar solutions in toluene at 30°C. Refractive index increments were determined with a Brice–Phoenix differential refractometer.

For micellar solutions the angular dependence of scattering was markedly dependent on concentration, making it difficult to evaluate accurately the z-average root-mean-square radius of gyration $\langle \bar{s}^2 \rangle_z^{1/2}$ in the normal way. Estimates were obtained in either of two ways: by determining $\langle \bar{s}^2 \rangle_z^{1/2}$ at various finite concentrations and extrapolating the results to infinite dilution, or by fitting a model to the experimental scattering data utilizing the Percus-Yevick theory[7].

Dynamic light scattering

The z-average diffusion coefficients $\bar{D}_z$ for the block copolymer micelles in toluene were determined over a range of temperatures and concentrations by dynamic light scattering using a Malvern PCS100 SM photon correlation spectrometer. Incident light of wavelength 632.3 nm was provided by a Spectra-Physics 124B helium–neon laser operating at 35 mW.

Reciprocal z-average hydrodynamic radii were evaluated from the diffusion coefficients utilizing the Stokes–Einstein relationship $D = RT/N_A 6\pi\eta r_h$, where R is the gas constant, T is the absolute temperature, η is the solvent viscosity and r_h is the hydrodynamic radius.

Electron microscopy

Electron micrographs of collapsed block copolymer micelles were obtained with a JEOL 100CX transmission electron microscope. Micellar solutions of the block copolymers were prepared in toluene at concentrations below 10^{-3} g cm^{-3}. Ultrasound from a Lucas Dawes soniprobe aided preparation of the solutions. Specimens were dried on a freshly cleaved mica surface, shadowed with platinum at an angle of 40°, coated with carbon then detached from the mica by flotation on water. Copper grids were used to support the specimens for electron microscopy.

Micellar diameters were determined by the method of Riegelhuth and Watkins[8] for 300–400 particles from each sample. Hence, average particle volumes and, assuming the density to be unity, molecular weights were evaluated.

Differential scanning calorimetry

Glass transition temperatures were evaluated by differential scanning calorimetry (d.s.c.) using a Perkin–Elmer DSC4 calorimeter. Block copolymers were dissolved in *N,N*-dimethylacetamide and reprecipitated in a finely divided state in warm water. After stirring for 0.5 h the copolymers were filtered, washed with water and Analar methanol, and dried to constant weight under vacuum. Samples were weighed into aluminium pans and lids were attached under a dry nitrogen atmosphere in a dry box. Samples were annealed in the calorimeter by heating to 210°C at 100°C min^{-1}, maintaining at that temperature for 10 min, then cooling rapidly to 0°C. D.s.c. curves were recorded three times at various heating rates, a fresh sample being used for each heating rate.

RESULTS AND DISCUSSION

Molecular characterization of the polymers

Three copolymers were obtained, designated B14, B16 and B17. In each case, polystyrene homopolymer, isolated prior to addition of the second monomer, was shown by g.p.c. to possess a narrow molecular weight distribution. Values of $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ for the polystyrene samples are given in *Table 1*, and may be considered to apply to the styrene blocks in the copolymers.

Figure 1 shows for one polymerization the g.p.c. curves of the polystyrene, the crude block copolymer and the block copolymer isolated by fractionation. The g.p.c. curve for the crude product is seen to be bimodal; there is a peak corresponding to unreacted homopolymer and a larger peak at lower elution volume (higher molecular weight) which may be attributed to the block copolymer. The fractionated product is seen to be free of homopolymer.

Table 2 gives the compositions of the block copolymers. The mole fraction of 4-nitrostyrene units x_N was evaluated by two independent methods, ^{1}H n.m.r. and elemental analysis, and good agreement was obtained.

Molecular weight data for the block copolymers are summarized in *Table 3*. $\bar{M}_w/\bar{M}_n$ was evaluated from g.p.c. curves both with a polystyrene calibration and with a poly(4-nitrostyrene) calibration. The two calibrations were found to give virtually the same results for the polydispersity. $\bar{M}_n$ was calculated independently from a knowledge of the $\bar{M}_n$ for the styrene block and the wt% of 4-nitrostyrene. $\bar{M}_w$ was determined independently by

Table 1 Average molecular weights for the polystyrene homopolymers

Polymer	$\bar{M}_n$ (g mol^{-1})	$\bar{M}_w$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$
B14PS	69 000	75 200	1.09
B16PS	18 100	19 900	1.10
B17PS	181 000	199 100	1.10

Table 2 Compositions of the block copolymers

Polymer	x_N[a]	x_N[b]	Amount of 4-nitrostyrene (wt%)
B14	0.40±0.02	0.43±0.02	50
B16	0.42±0.02	0.45±0.02	52
B17	0.19±0.01	0.17±0.02	24

[a] From ^{1}H n.m.r.
[b] From elemental analysis

static light scattering. These different methods give results in realistic agreement.

The results are consistent with the formation of well-defined block copolymers. They show that copolymers B14 and B16 have similar proportions of each monomer, but B14 is much higher in molecular weight. For copolymer B17, the 4-nitrostyrene block is intermediate in size between that in B14 and that in B16, but the styrene block is much larger. To confirm that block copolymers were indeed obtained, rather than mere mixtures of homopolymers, the behaviour of the polymers in a selective solvent was investigated.

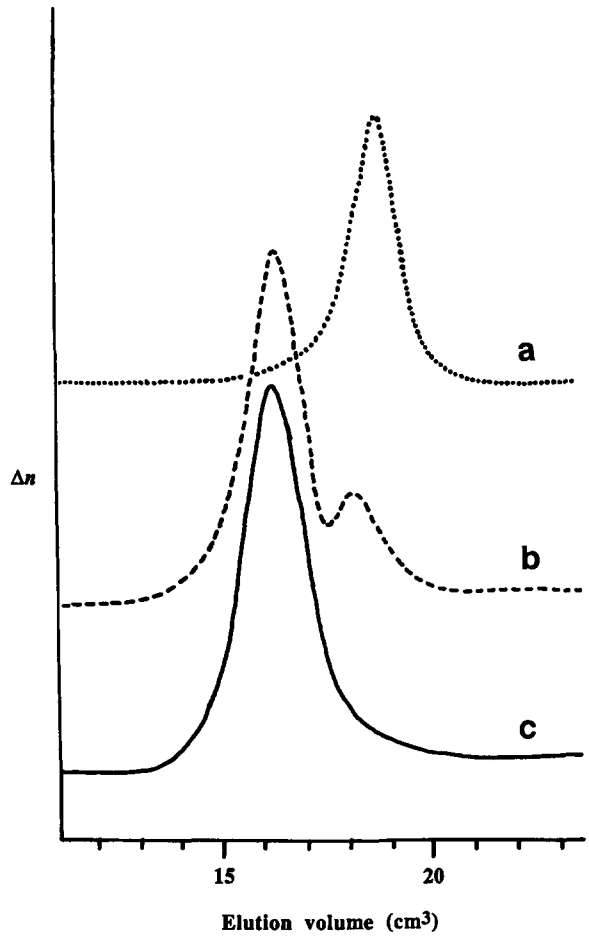

Figure 1 G.p.c. curves for (a) polystrene B17PS, (b) crude block copolymer B17 and (c) purified block copolymer B17

Table 3 Average molecular weights for the block copolymers

Polymer	$\bar{M}_w/\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$[b]	$\bar{M}_n$[c] ($g\,mol^{-1}$)	$\bar{M}_w$[d] ($g\,mol^{-1}$)
B14	1.21	1.20	139 000	156 000 ± 16 000
B16	1.29	1.31	38 000	46 000 ± 4 600
B17	1.21	1.21	238 000	261 000 ± 26 000

[a] From g.p.c. (polystyrene calibration)
[b] From g.p.c. (poly(4-nitrostyrene) calibration)
[c] From composition
[d] From static light scattering

Micellization behaviour

Figure 2 is an electron micrograph of structures isolated from a solution of block copolymer B14 in toluene, which is a good solvent for the polystyrene block but a bad solvent for the poly(4-nitrostyrene) block. The structures, which are extremely regular in size, are almost certainly micellar in nature, comprising a poly(4-nitrostyrene) core and a polystyrene fringe. Similar structures were observed for the other block copolymers. The formation of micelles in a selective solvent is characteristic of the behaviour of block copolymers[9].

Table 4 gives estimates of the weight-average molecular weights and size distributions of the block copolymer micelles, derived from electron microscopy results. The micelles were found to possess very narrow size distributions, narrower than those of the unassociated block copolymers. Sharpening of the size distribution on association may be predicted by statistical arguments[10,11]. There is some uncertainty in the average molecular weights derived from electron microscopy because of distortion of the particles which occurs on isolation. Further information was obtained by static light scattering.

The static light scattering behaviour of the block copolymers in toluene at 30°C and at low concentrations (down to $2 \times 10^{-4}\,g\,cm^{-3}$) could be interpreted simply in terms of 'hard spheres', and indicated in every case

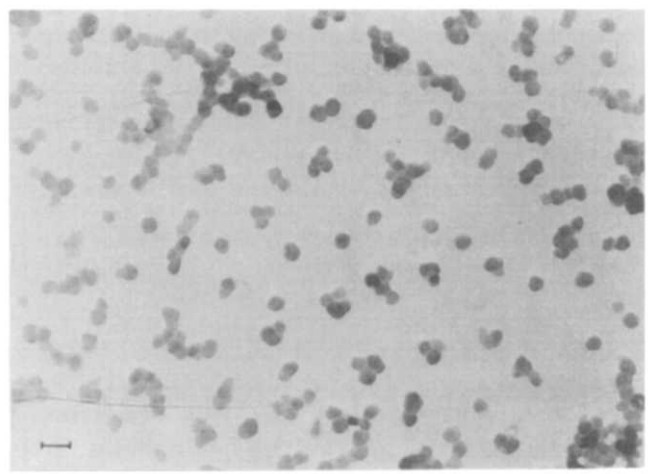

Figure 2 Transmission electron micrograph of micellar structures isolated from a solution of block copolymer B14 in toluene. The scale bar indicates 100 nm

Table 4 Results from electron microscopy and static light scattering for block copolymer micelles

Polymer	$10^{-6}\bar{M}_w$[a] ($g\,mol^{-1}$)	$\bar{M}_w/\bar{M}_n$[a]	$10^{-6}\bar{M}_w$[b] ($g\,mol^{-1}$)	$10^6 A_2$[b] ($cm^3\,g^{-2}\,mol$)	$\langle \bar{s}^2 \rangle_z^{1/2}$[b] (nm)	Aggregation number
B14	11.7	1.12	13.8	3.7	23.1	88
B16	3.9	1.09	4.1	22.0	19.7	89
B17	20.4	1.11	22.4	4.6	29.6	94

[a] From electron microscopy
[b] From static light scattering

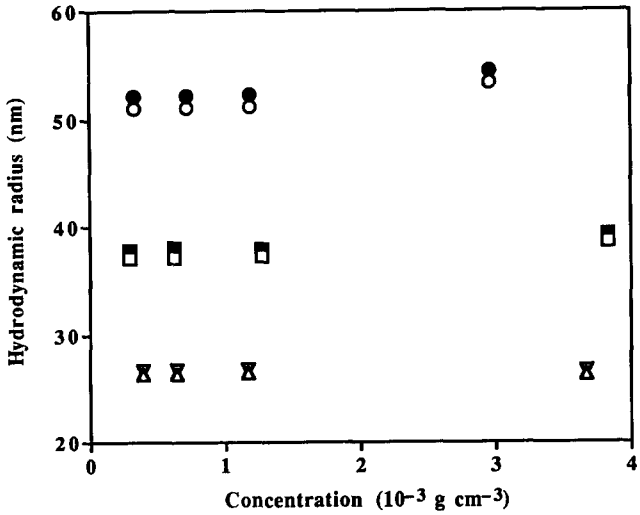

Figure 3 Dependence of the hydrodynamic radius on concentration for block copolymer micelles of B17 at 25°C (○) and 65°C (●), B14 at 25°C (□) and 65°C (■), and B16 at 25°C (△) and 65°C (▽)

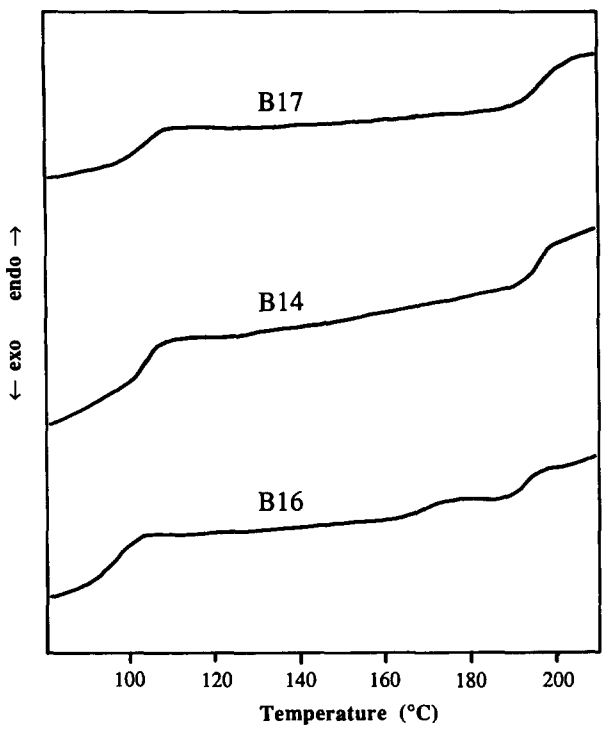

Figure 4 D.s.c. curves for block copolymer samples B17, B14 and B16 at a heating rate of 10°C min^{-1}

Table 5 Results from differential scanning calorimetry for the block copolymers

Polymer	Styrene block T_g(°C)	4-Nitrostyrene block T_g(°C)
B14	101.4	193.9
B16	94.2	193.3
B17	102.2	194.2

that the micelle/free chain equilibrium was overwhelmingly in favour of micelle formation. Weight-average molecular weights determined by static light scattering from dilute solutions are given in *Table 4*, together with second virial coefficients, *z*-average root-mean-square radii of gyration and aggregation numbers in toluene at 30°C.

Diffusion coefficients, and hence hydrodynamic radii, were determined by dynamic light scattering over a range of concentrations and temperatures. The dependence of r_h on concentration is shown in *Figure 3* for temperatures of 25 and 65°C. Micelles are clearly present down to the lowest concentrations measured throughout the temperature range. These results also indicate that the micelle/free chain equilibrium is strongly in favour of micellization. There is very little increase in r_h with temperature.

Swelling experiments were carried out separately with high molecular weight poly(4-nitrostyrene) in toluene, which showed a maximum increase in weight of 4% at 110°C. It is likely, therefore, that there would be very little solvent swelling of the micelle cores, even at high temperature.

Differential scanning calorimetry

Figure 4 shows the d.s.c. curves for the block copolymers at one heating rate (10°C min^{-1}). In each case two clear inflections are visible which may be attributed to the glass transitions for the two blocks. The values obtained for the glass transition temperature T_g of each block, determined as the midpoint of the inflection at the slowest heating rate used (5°C min^{-1}), are given in *Table 5*. The values of T_g are close to those for the homopolymers[1]. The existence of two distinct glass transitions indicates that microdomains are present in the solid state in all three systems. For B16, the lowest molecular weight polymer, there is evidence in *Figure 4* of a third, intermediate, transition which appeared more pronounced at higher heating rates. This suggests a significant amount of interfacial mixing in this case.

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