

Small-angle neutron scattering from a polystyrene-*b*-poly(methyl methacrylate) diblock copolymer in a selective solvent

Christopher J. C. Edwardst and Randal W. Richards*

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, UK

and Robert F. T. Stepto

Department of Polymer Science and Technology, University of Manchester Institute of Science and Technology, Manchester M60 1QD, UK

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Solutions of a polystyrene-*b*-poly(methyl methacrylate) diblock copolymer in *p*-xylene have been investigated using osmometry, viscometry, light scattering and small-angle neutron scattering. At 303 K the copolymer forms a dimer whilst at lower temperatures the number of molecules in the multimer increases. Small-angle neutron scattering from a selectively deuterated copolymer has enabled observation of the individual blocks in isolation from one another. From the observed scattering function and in conjunction with the data obtained from classical techniques, the dimer has been modelled as a central spherical core of poly(methyl methacrylate) with isolated polystyrene chains attached at the surface. A Monte Carlo calculation of the scattering function for such a structure agrees well with the experimentally obtained scattering.

(Keywords: block copolymer; multimerization; s.a.n.s.)

INTRODUCTION

Block copolymer conformation (spatial configuration) in dilute solution has attracted both experimental and theoretical effort for many years¹⁻¹². The interest arises from the thermodynamic incompatibility of the components which at high concentrations of copolymer leads to microphase separated structures^{13,14}. For a dilute solution of the copolymer in a common solvent for both components, two models have been proposed. A segregated conformation where unlike blocks occupy distinct regions in space thereby avoiding heterocontacts, and secondly a mutually interpenetrating random coil model. It has been suggested that the blocks in a segregated structure have similar conformations to the respective homopolymers, whilst expanded conformations should prevail in the mutually interpenetrating case. Counter arguments have been advanced and the experimental evidence in some cases is contradictory and confusing.

When a selective solvent is used, i.e. one which is thermodynamically better for one component of the block copolymer, the situation becomes somewhat clearer. Generally, a multimerization¹⁵ takes place and micellar structures have been deduced from the behaviour of such properties as intrinsic viscosity and Rayleigh ratio as functions of parameters such as temperature or concentration. Such studies on styrene-isoprene copolymers have been reported by Price and coworkers¹⁶⁻¹⁹ and light scattering results suggest that a

closed association process occurs. It has usually been assumed that the micellar multimer has a central spherical core of less soluble blocks, with the structure being stabilized in solution by the solvated blocks of the other component disposed at the periphery of the core. This hypothesis has been supported by transmission electron microscopy studies of polystyrene-*b*-polyisoprene block copolymer multimers notwithstanding the cautionary remarks made by the authors¹⁷.

Inagaki and coworkers have reported much work on the investigation of polystyrene-*b*-poly(methyl methacrylate) copolymers in both common and selective solvents. Of particular interest here are their conclusions for the diblock copolymer in *p*-xylene³, for which, at 303 K, they have proposed a multimer formed from 7 to 10 molecules; the morphology of the multimer being star-like, as deduced by comparing the particle scattering function with model calculations²⁰.

Whilst the combination of intrinsic viscosity and molecular weight studies gives vital clues to the multimer structure in solution, it cannot provide definitive answers. Light scattering provides a little more information but no *direct* evidence of multimer structure, the major limitation being due to the very small range of scattering vector accessible using visible light. The use of solvents with different refractive indices for light scattering can, in principle, provide a great deal of information. Unfortunately, thermodynamic effects make this approach highly questionable. The combination of a large range of scattering vector with the ability to vary block visibility, i.e. contrast, (without change in block conformation) is the most promising technique for investigation of multimolecular micelles. Small-angle X-

* To whom correspondence should be addressed.

† Present address: Unilever Research PLC, Port Sunlight Laboratory, Quarry Road East, Bebington, Wirral, Merseyside L63 3JW, UK.

ray scattering (SAXS) is a technique which offers a wide range of scattering vector and it has been used by Pleštil and Baldrian²¹ to study multimers of polystyrene-b-polybutadiene block copolymers. However, the electron density differences between the components and the solvent are not large and unambiguous evaluation of the data is difficult. Small angle neutron scattering (SANS) also provides a wide range of scattering vector and furthermore the use of selective deuteration of copolymer and/or solvent influences visibility markedly with no significant change in the thermodynamics of the block copolymer/solvent system. Although this technique has been much applied to block copolymers in the solid state^{13,22-25}, applications to solution studies are limited to two experimental studies²⁶⁻²⁸, neither of which deals with multimerization. We report here the use of small angle neutron scattering, in conjunction with classical techniques, in the study of a polystyrene-b-poly(methyl methacrylate) diblock copolymer in *p*-xylene solution. Experimentally obtained scattering functions are compared with the results of model calculations in an attempt to elucidate the structure of the multimer.

SCATTERING THEORY

Light scattering, in common with SAXS and SANS, provides scattered intensities at small scattering vector, Q , where $|Q| = (4\pi/\lambda)\sin(\theta/2)$, for radiation of wavelength, λ , in the scattering medium, and scattering angle, θ . Typically, the wavelengths used in light scattering are circa 400 nm whilst SAXS and SANS wavelengths range from 0.15 to 2 nm, and the equations developed for light scattering from copolymers may be applied to the analysis of SANS data for such systems with only minor modifications.

It has been previously noted by Stockmayer and coworkers²⁹ that the molecular parameters obtained for copolymers by light scattering displayed large variations when different solvents are used. The analysis of such behaviour was provided by Bushuk and Benoit³⁰, and further extended by Leng and Benoit³¹. The pivotal result of these analyses is that the intensity of scattering from copolymer solutions at any one scattering vector and the variation with scattering vector depends on both the 'contrast' between copolymer and solvent and the copolymer composition.

A general expression for SANS from a polymer solution after the subtraction of background intensity and in the absence of interference effects can be written as:

$$I(Q) = K^* c M (\rho_p - \rho_m)^2 P(Q) \quad (1)$$

K^* = instrument constant

c = polymer concentration

M = molecular weight

$(\rho_p - \rho_m)^2 = K^2$ = contrast factor

ρ_p = coherent scattering length density of polymer

ρ_m = coherent scattering length density of medium

$P(Q)$ = scattering law of the scattering particle which describes the Q variation of the scattered intensity

As in light scattering, SANS data from copolymer solutions may be plotted in the well known Zimm

format³² and extrapolated to give radius of gyration ($c=0$ line), the second virial coefficient ($Q=0$ line), and the molecular weight (from the intercept at $Q=0, c=0$).

For copolymers, the molecular weight obtained is an apparent value, related to the true molecular weight, M_C , and that of the blocks, M_A, M_B , by the equation

$$M_{App} = (K_A K_B / K_C^2) M_C + (K_A (K_A - K_B) / K_C^2) w_A M_A + (K_B (K_B - K_A) / K_C^2) w_B M_B \quad (2)$$

where w_i is the weight fraction of component i in the copolymer, K_i is the contrast factor for component i , subscript C pertains to the whole molecule and $K_C = w_A K_A + w_B K_B$

Likewise, the scattering function at $c=0$ is given by

$$P(Q) = 1/K_C^2 [w_A^2 K_A^2 P_A(Q) + w_B^2 K_B^2 P_B(Q) + 2w_A w_B K_A K_B Q_{AB}(Q)] \quad (3)$$

where $Q_{AB}(Q)$ is a scattering function for cross correlations between the blocks, and $P_i(Q)$ is the scattering function for the i th component of the copolymer. Usually, for polymer molecules, $P_i(Q)$ is represented by the Debye³³ equation for randomly oriented point scatterers

$$P_i(Q) = 2/(Q^2 R_g^2)^2 [\exp\{-Q^2 R_g^2\} - 1 + (Q^2 R_g^2)] \quad (4)$$

where R_g is the radius of the macromolecule. For $QR_g \leq 1$ then

$$P_i(Q) = 1 - Q^2 R_g^2 / 3$$

Both equations (2) and (3) can be considerably simplified if either K_A or K_B is zero, thus if $K_B = 0$, then equation (3) reduces to:

$$P(Q) = P_A(Q) \quad (5)$$

thus providing the scattering function for the A part of the copolymer. Under similar conditions equation (2) reduces to

$$M_{App} = M_A / w_A \quad (6)$$

thereby allowing calculation of the molecular weight of the A part of the copolymer. Exploitation of these facets using light scattering is limited by the small range in refractive index differences between solvents and organic polymers³⁴. Such limitations are not so restrictive in SANS due to the large difference in coherent scattering lengths between hydrogen and deuterium, enabling contrast factors approaching zero to be obtained by employing appropriate mixtures of hydrogenous and deuterated solvents. This attribute of SANS has been exploited in the study reported here.

Contrast factors

Although there is greater flexibility in SANS contrast factors relative to those for light scattering, the probability of obtaining a polymer/solvent combination with exactly zero contrast factor and the required thermodynamic properties, is not great. The best that can be obtained in practice is a large difference between the

contrast factors of the two blocks in the molecule. *Table 1* shows the bound atom coherent scattering length densities and contrast factors for the polymer-solvent combinations used in this study. The data show that a polyperdeuterostyrene-*b*-poly(methyl methacrylate) block copolymer in combination with hydrogenous *p*-xylene (XYL) and deuterated *p*-xylene-d10 (XYL-d10) satisfies the above condition. Particularly, the contrast difference between the blocks is 120 fold in favour of the poly(methyl methacrylate) block when the copolymer is dissolved in XYL-d10, whilst the contrast factor is 1800 fold in favour of the polydeuterostyrene block when it is dissolved in XYL.

EXPERIMENTAL

Copolymer preparation

Two copolymers were prepared, both having a styrene/methyl methacrylate nominal mole ratio of 1:1. One copolymer (SMMA) was synthesized from totally hydrogenous monomers whilst the second copolymer (DSMMA) was synthesized using deuterated styrene-d8 obtained from Aldrich Chemical Co. Both polymerizations were carried out using high vacuum techniques and anionic initiation in previously described apparatus³⁵ and, in accordance with the findings of Freyss, Rempp and Benoit³⁶, 1,1-diphenyl ethylene was added at the end of the styrene polymerization prior to the addition of methyl methacrylate, thereby reducing the activity of the styryl anion. Analysis of the resultant copolymers by gel permeation chromatography (g.p.c.) showed small traces of homopolystyrene (presumably from termination reactions with impurities in the 1,1-diphenyl ethylene). Consequently, both SMMA and DSMMA were extracted with cyclohexane for 24 h to remove homopolymer. Subsequent re-analysis (by g.p.c.) showed no trace of contaminating homopolymer.

Copolymer characterization

Copolymer compositions were determined by combustion analysis, infra-red spectroscopy and for

Table 1 Scattering length densities

Scattering unit	$10^{-10} \rho$ (cm cm ⁻³)
MMA	0.899
S	1.472
TOL	0.944
XYL	0.766
DS	6.30
TOL d8	5.69
XYL d10	5.85

Contrast factors

Combination	$10^{-20} K^2$ (cm ⁻⁴)
S/XYL d10	19.18
MMA/XYL d10	24.56
DS/XYL d10	0.2
MMA/XYL	0.017
DS/XYL	30.66
S/TOL d8	17.78
MMA/TOL d8	22.9
DS/TOL d8	0.38

Abbreviations: MMA—methyl methacrylate; S—styrene; TOL—toluene; XYL—*p*-xylene; DS—deuterostyrene-d8; TOL d8—deuterotoluene; XYL d10—deutero-*p*-xylene

Table 2 Characterization data for copolymers

Copolymer	w_s	g.p.c. (in THF) (kg mol ⁻¹)	Light scattering M_w /kg mol ⁻¹			
			TOL	MEK	THF	XYL
SMMA*	0.49	160	230.5	265.2	204.9	468.0
DSMMA	0.43	196				

* Specific refractive index increments for SMMA at 298 K are TOL 0.055, MEK 0.160, THF 0.136, XYL 0.058 cm³ g⁻¹
 w_s = weight fraction of styrene in the block copolymer from combustion analysis and proton n.m.r.

SMMA alone, proton n.m.r. Results from different techniques were in agreement to within $\pm 5\%$. Weight-average molecular weight determination for SMMA was undertaken by g.p.c. and low-angle laser light scattering measurements from solutions of the copolymer in toluene (TOL) butan-2-one (MEK), tetrahydrofuran (THF) and *p*-xylene (XYL) at 298 K. Specific refractive index increments were determined at 632.8 nm using a modified Brice-Phoenix differential refractometer. Copolymer stereochemistry was investigated using ¹³C n.m.r. The polystyrene blocks were predominantly atactic with a Bernoullian distribution of meso and racemic diads, whilst the polymethyl methacrylate block was circa 90% syndiotactic. *Table 2* summarizes the molecular weight determinations for each copolymer. Since the part deuterated copolymer, DSMMA, was only synthesized in a very small amount ($\sim 1 \times 10^{-3}$ kg), a detailed characterization could not be carried out.

Temperature dependence of copolymer molecular weight and intrinsic viscosity in *p*-xylene

Number-average molecular weights were measured between the temperatures of 303 K and 323 K using a Knauer membrane osmometer and SMMA solutions in XYL. Straight line plots of reduced osmotic pressure (π/c) as a function of copolymer concentration over the range $1 < c(\text{kg m}^{-3}) < 10$ were obtained at all temperatures investigated.

An Ubbelohde suspended level viscometer was used to determine the intrinsic viscosity of SMMA in *p*-xylene between 293 K and 323 K. Straight line Huggins plots were obtained at all temperatures.

Small-angle neutron scattering

All SANS experiments reported here were performed at the Institute Laue-Langevin, Grenoble, France, using the D11 diffractometer. Each data set was normalized for monitor counts and corrected for detector efficiency. Subsequent background subtraction and evaluation of intensity as a function of scattering vector were carried out using the suite of computer programs developed for this purpose³⁷. Background scattering was obtained from experiments on mixtures of hydrogenous and deuterated solvent, the compositions of which were adjusted to account for the additional hydrogen or deuterium atoms due to the presence of the copolymer in the solution. The block copolymer DSMMA was investigated in XYL and XYL d10 at 303 K and 313 K. Additionally, solutions of poly(methyl methacrylate) (PMMA) in XYL d10 at 303 K and 313 K, were investigated by SANS. The PMMA was fractionated from a large batch and its molecular weight

was similar to that of the poly(methyl methacrylate) block in the copolymer.

RESULTS AND DISCUSSION

G.p.c. and light scattering

The molecular weight data obtained from g.p.c. and low angle laser light scattering are given in Table 2. Both components of the SMMA copolymer have reasonably large specific refractive index increments in MEK and THF, consequently the weight average molecular weight of the copolymer was taken as the mean of the two values, i.e. 235 kg mol^{-1} . Poly(methyl methacrylate) is isorefractive with toluene³⁸ and thus from the light scattering equivalent of equation (6) we obtain

$$M_{\text{App}} = M_w/w_s$$

Applying this equation to light scattering data obtained for the solution of SMMA in TOL gives M_{App} as $230.5 \text{ kg mol}^{-1}$ and the polystyrene block molecular weight as $112.9 \text{ kg mol}^{-1}$. Poly(methyl methacrylate) is also isorefractive with XYL³⁸, however calculation of the polystyrene block molecular weight from light scattering data in XYL gives a value of $229.3 \text{ kg mol}^{-1}$ at 298 K. Such a large increase in molecular weight is a clear indication of a multimerization process taking place and from the two values of the molecular weight, there appear to be 2 copolymer molecules per multimer at 298 K.

Temperature dependence of number-average molecular weight and intrinsic viscosity

Figure 1 displays the temperature variation of the apparent number average molecular weight of SMMA in XYL. The increase in molecular weight for temperatures below 313 K confirms the hypothesis of copolymer multimerization at temperatures approaching ambient. At temperatures above 313 K a constant value for the molecular weight is obtained which is identified with unassociated molecules. Comparison of molecular weights at temperatures above 313 K with that at 303 K suggests that there are approximately two copolymer molecules per aggregate whilst extrapolating the curve in Figure 1 to 298 K indicates an aggregation number of three. The apparent intrinsic viscosity data (Figure 2) shows little change until the temperature falls below 313 K, thereafter a decrease is observed over the temperature range investigated. Since this decrease is accompanied by an increase in molecular weight of the

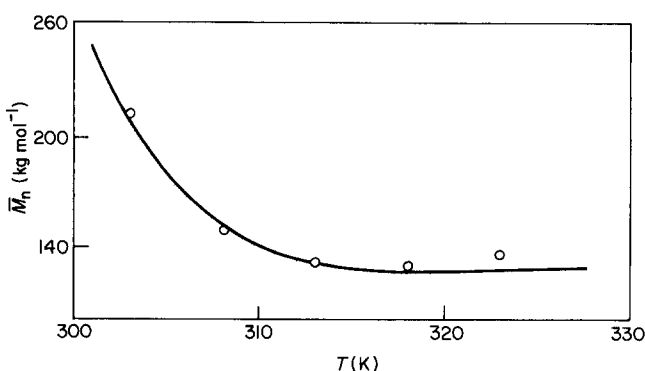


Figure 1 Dependence of number-average molecular weight on temperature for block copolymer SMMA in *p*-xylene solution

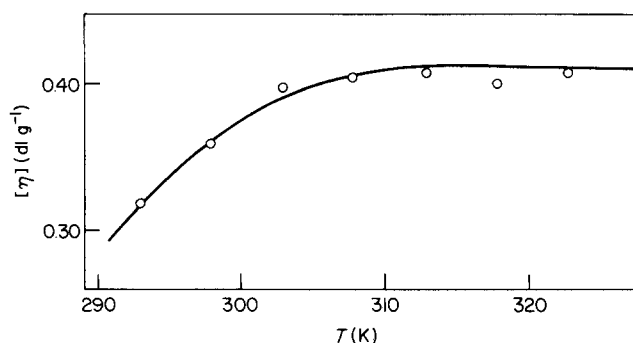


Figure 2 Dependence of apparent intrinsic viscosity on temperature for block copolymer SMMA in *p*-xylene solution

multimer, a structure of increasing compactness is indicated. It has been suggested³ that the theta temperature for poly(methyl methacrylate) in xylene solutions is 308 K. Thus the most probable structure for the multimer would be a central core of poly(methyl methacrylate) blocks in an unperturbed or collapsed state, stabilized by the solvated polystyrene blocks which extend into the solvent. Additionally, a preliminary investigation of the kinetics of multimerization and unimerization of SMMA in XYL has been carried out. To investigate multimerization a 1% (w/v) solution of the copolymer was equilibrated at 323 K for two days, an aliquot was then quickly transferred to a viscometer at 298 K and the flow time immediately recorded. Subsequent measurement of the decreased flow time showed no change over a 48 h period. For unimerization, the reverse procedure was carried out, i.e. a solution was equilibrated at 298 K for two days and an aliquot quickly transferred to a viscometer at 313 K. Again no dependence of the increased flow time on time after transfer could be detected. For each case described above, the flow time obtained was the same as that obtained in the investigation of intrinsic viscosity as a function of temperature. The structure of the multimer was explored in more detail by SANS, the results of which are discussed below.

Small-angle neutron scattering

Prior to examining the block copolymers in XYL solutions, investigations on the behaviour and conformation of PMMA and XYL were undertaken. Figures 3a and 3b show that conventional Zimm plots were obtained at both 303 K and 313 K with distinctly positive second virial coefficients. Molecular weights calculated from the intercepts at $Q=0$, $c=0$, given in Table 3 are in excellent agreement with the values determined by g.p.c., indicating no multimerization of the poly(methyl methacrylate) homopolymer. Comparison of the radii of gyration obtained from the Zimm plots with the unperturbed root mean square radius of gyration calculated for this molecular weight using the characteristic ratio, C_∞ ³⁹, indicates that the expansion factors (α^2) are ca. 1.4 and 1.7 at 303 K and 313 K respectively. These data contradict previous assertions³ that poly(methyl methacrylate) has a theta temperature of about 313 K in XYL. Our data, which are admittedly limited, suggest that the theta temperature is much lower. Solutions of DSMMA in XYL d10 at 303 K and 313 K also displayed no anomalous scattering, with linear Zimm plots being obtained at 303 K and 313 K (Figures 4 and 5). Extrapolation to $Q=0$, and $c=0$ was not complicated by

any gross distortions in the data, and apparent radii of gyration were easily calculable from the $c=0$ line. Evaluation of apparent molecular weights and second virial coefficients requires a value for the contrast factor of the DSMMA/XYL d10 combination. This factor has been calculated as the volume fraction weighted sum of the contrast factors for the two homopolymers in XYL d10⁴⁷. Apparent molecular weights and radii of gyration of DSMMA and XYL d10 at the two temperatures investigated are given in Table 3. Since the contrast factor for deuterated styrene in XYL d10 is vanishingly small

then we can write

$$M_{\text{App}} = M_{\text{MMA}}/w_{\text{MMA}}$$

whence we calculate that $M_{\text{MMA}} = 97.4 \text{ kg mol}^{-1}$ at 313 K and $M_{\text{MMA}} = 226.0 \text{ kg mol}^{-1}$ at 303 K. There is no evidence for aggregation of the copolymer in toluene and in TOL d8, the deuterated styrene portion has negligible scattering in TOL d8, consequently we can calculate the molecular weight of the molecularly dissolved methyl methacrylate block from SANS experiments on DSMMA in TOL d8⁴⁰. From measurements in TOL d8 the true molecular weight of the methyl methacrylate block is calculated as $107.0 \text{ kg mol}^{-1}$. This value is satisfactorily

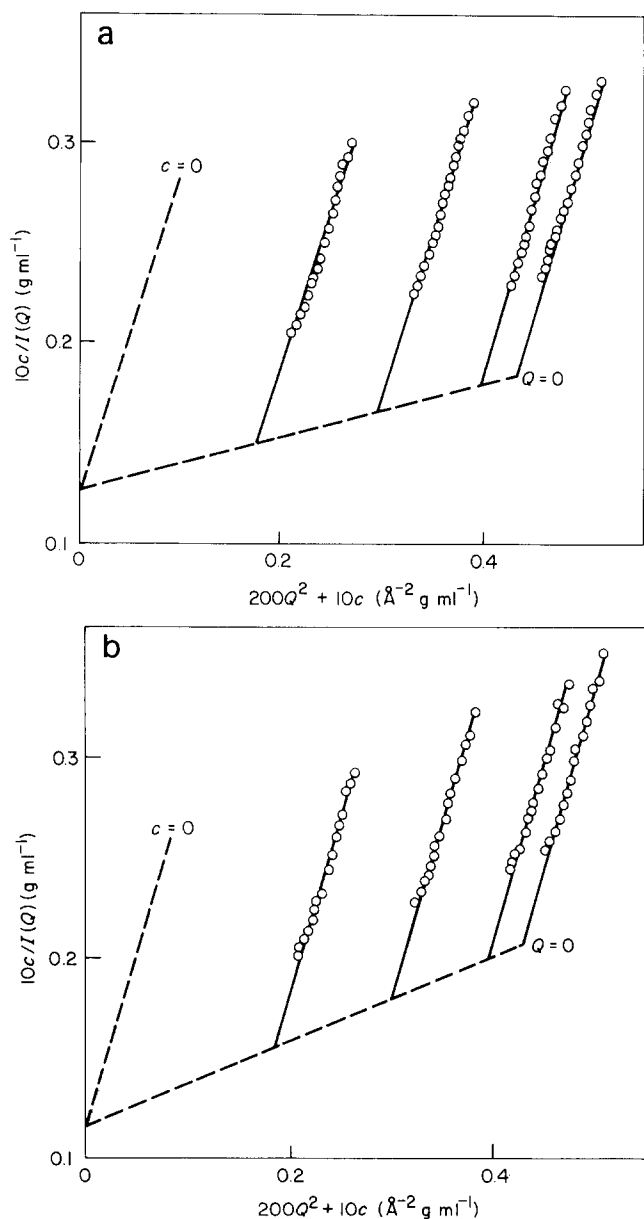


Figure 3 Zimm plots constructed from small-angle neutron scattering data for PMMA in XYL-d10 solution: (a) at 303 K; (b) at 313 K

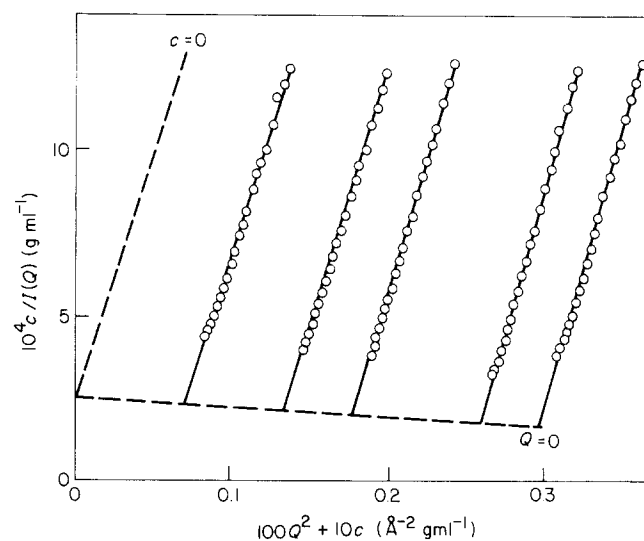


Figure 4 Zimm plot from small-angle neutron scattering of copolymer DSMMA in XYL-d10 at 303 K

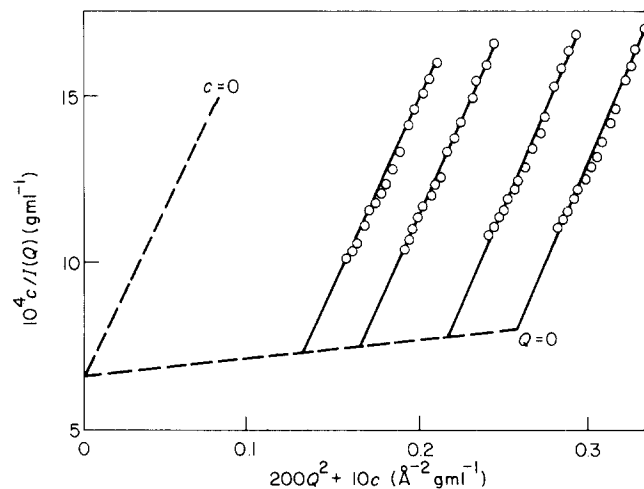


Figure 5 Zimm plot from small-angle neutron scattering of copolymer DSMMA in XYL-d10 at 313 K

Table 3 Results from small-angle neutron scattering experiment

Polymer	M_w (g.p.c.) (kg mol^{-1})	Solvent	T (K)	M_w (kg mol^{-1})	$10^4 A_2$ ($\text{kg}^{-2} \text{ m}^3 \text{ mol}$)	R_g (nm)
PMMA	81	XYL d10	313	89.6	1.06	9.6
PMMA	81	XYL d10	303	84.0	0.64	8.6
DSMMA	196	XYL d10	313	97.4	0.43	9.9
DSMMA	196	XYL d10	303	226.0	-0.27	13.4
DSMMA	196	TOL d8	303	107.0	2.9	10.1

close enough to the value obtained for solution in XYL d10 at 313 K for us to conclude that at 313 K in xylene the styrene-methyl methacrylate copolymer is molecularly dissolved. Comparisons with the molecular weight obtained at 303 K in XYL d10 again suggests that there are *ca.* 2 molecules per multimer at 303 K, a result which is in agreement with the earlier determinations of number-average molecular weight. For the MMA block in DSMMA the expansion factor at 313 K, α^2 , is calculated as *ca.* 1.5, consequently the block appears to have much the same conformation as PMMA under the same conditions. At 303 K the expansion factor calculated for the MMA multimer is 1.2, smaller than would be anticipated for PMMA of the same molecular weight. Together with the negative second virial coefficient these data suggest that the MMA blocks in the multimers associate to form a relatively compact structure. Further insight into the multimer structure was provided by the SANS data for DSMMA in hydrogenous *p*-xylene; for this combination, the scattered intensities as a function of Q for different concentrations of DSMMA are shown in Figure 6. The interesting observation is the broad maximum centred at a Q value of *ca.* 0.014 \AA^{-1} , a feature which does not move as the concentration is increased. Consequently, it cannot be associated with structure factor, or interference function, scattering typical of dense particle dispersions⁴¹. Therefore, the maximum must characterize the isolated block copolymer multimer structure. On the basis of the relatively low expansion factor for the MMA block and the observation that XYL is a poorer solvent for poly(methyl methacrylate) than polystyrene together with the evidence for a compact structure from intrinsic viscosity-temperature measurements, it appears that the simplest model to satisfy these facts is a micelle with a spherical core of PMMA. Calculated scattering functions using this model are explored further below.

Conceivably, two different, but related scattering functions are applicable to the block copolymer multimer at 303 K depending on the contrast factor. For the case of DSMMA in XYL d10, the MMA core may be viewed as a

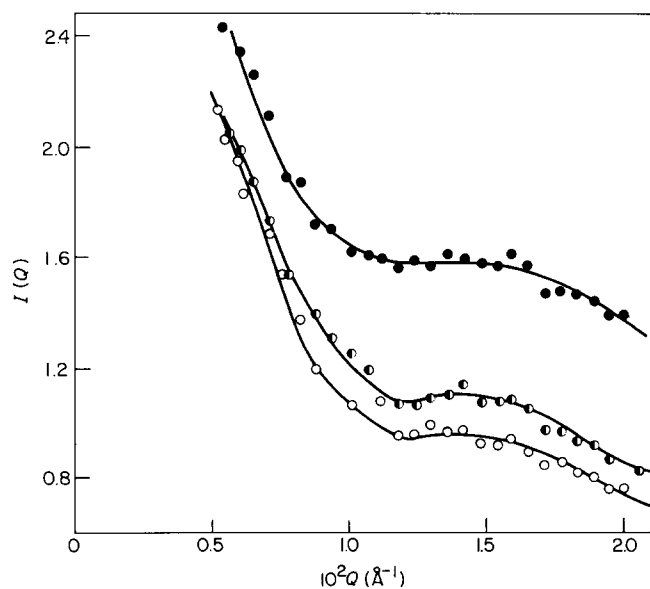


Figure 6 Neutron scattering intensity ($I(Q)$) as a function of scattering vector (Q) for copolymer DSMMA in hydrogenous *p*-xylene at 303 K: concentration = 8.62 kg m^{-3} ; concentration = 11.65 kg m^{-3} ; concentration = 20.56 kg m^{-3}

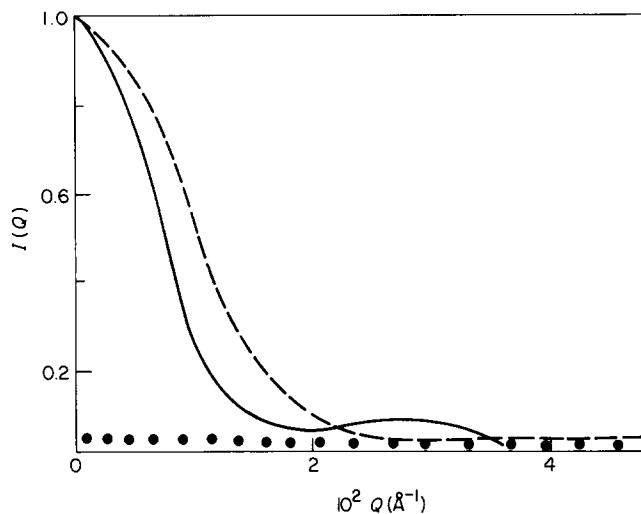


Figure 7 Calculated scattering from spherical particles with varying structures. Sphere radius in all cases = 17.3 nm, whilst thickness of finite shell = 2 nm: (—) solid; (---) thin shell; (· · ·) finite shell

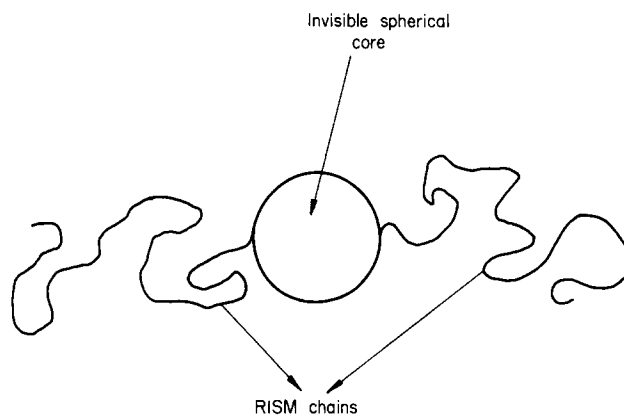


Figure 8 Schematic diagram of the model block copolymer dimer used in Monte Carlo calculation of scattering law

sphere of constant segment density with a scattering law given by⁴²:

$$I(Q) = [9\pi/2(QR)^3] J_{3/2}^2(QR)$$

where R is the sphere radius ($R^2 = 5/3R_g^2$) and $J_{3/2}(X)$ is the Bessel function of the first kind of order $3/2$.

When DSMMA is dissolved in hydrogenous xylene and only the deuterio styrene component of the multimer contributes to the scattering, one of two simple models may be applicable, both pertaining to a hollow sphere. When the DS blocks are wrapped tightly round the spherical MMA core, the model of a hollow sphere covered by an infinitely thin shell is suitable⁴³;

$$P(Q) = (\sin(QR)/QR)^2$$

If the DS layer has finite thickness then⁴⁴;

$$P(Q) = \frac{9}{2}\pi [(J_{3/2}(QR_o)/(QR_o)^{3/2}) - (R_i/R_o)^3 J_{3/2}(QR_i)/(QR_i)^{3/2}]^2$$

where R_o , R_i are respectively the outer and inner radius of the spherical annulus. Each of these scattering functions is represented schematically in Figure 8 for a sphere of inner radius 17.3 nm, which corresponds to the radius of gyration of DSMMA in XYL d10. The scattering function for a hollow sphere with an infinitely thin shell produces

the best qualitative agreement with the observed scattering of DSMMA in hydrogenous xylene. Quantitative agreement however is not obtained since least squares fitting of this scattering law to the data produces a best fit for a hollow sphere with an infinitely thin shell at a radius of 300 Å which is much larger than the value obtained from the radius of gyration of the poly(methyl methacrylate) core. Consequently, the use of simple constant density spherical models to describe the multimers formed by polystyrene-*b*-poly(methyl methacrylate) diblock copolymer in *p*-xylene solution was not pursued further.

Monte Carlo model of the copolymer multimer

The model employed has a central spherical core of zero scattering power with two diametrically opposed chains which are unable to penetrate the central core. A schematic diagram of the model is shown in Figure 8. The total scattering function for such an arrangement of scattering centres has been calculated using a previously described Monte Carlo method⁴⁵ which calculates configurational averages of properties determined by the spatial distribution of segments in the molecule. For convenience the pendant chains were modelled as off lattice polymethylene chains using molecular parameters given by Flory³⁹. For a central sphere of diameter 50 Å with pendant chains between 10 and 60 segments long, Figure 9 shows the scattering function variation with Q whilst Figure 10 shows the scattering function variation as a function of QR_g , where R_g is the root mean square radius of gyration of the complete structure. The characteristic features of Figure 9 are the maxima at $QR_g = 3.7$ and $QR_g = 6.7$.

If the chains are placed randomly on the sphere surface, rather than diametrically opposite each other, the maxima are much more rapidly damped as shown in Figure 11. Random placement of chains would permit mutual interpenetration of the chains, whereas for polystyrene in a good solvent such as XYL the interactions between the polystyrene chains will be repulsive and consequently the model with the chains diametrically opposite one another should reflect the experimental conditions more accurately. This view is

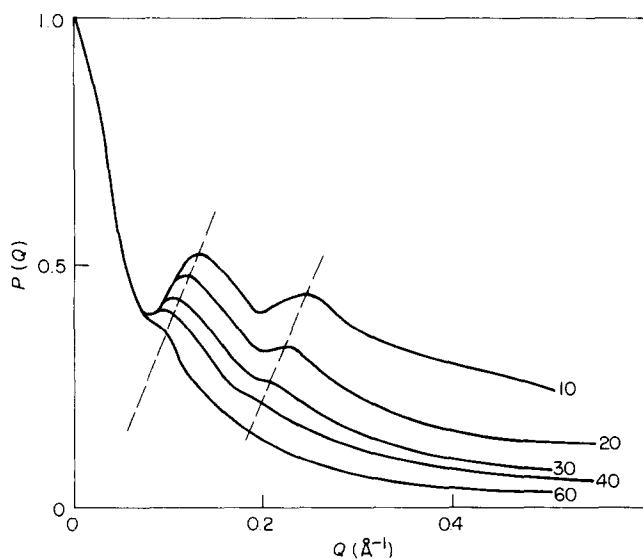


Figure 9 Calculated scattering law for two RISM chains diametrically opposite each other on a contrast matched, 5 nm diameter impenetrable sphere. The number of segments per chain is indicated on each curve

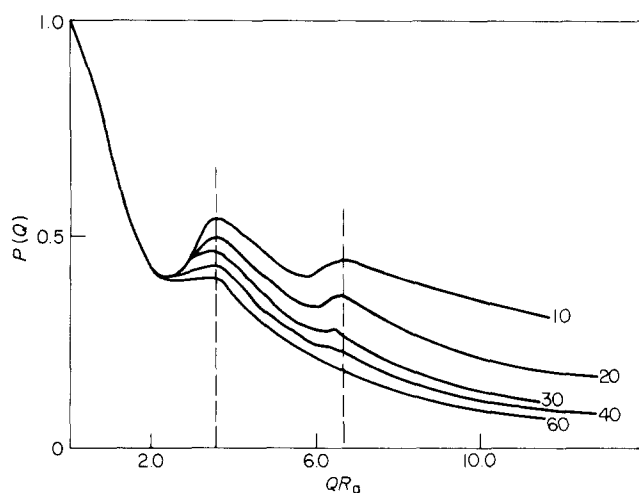


Figure 10 Data of Figure 9 plotted as a function of the dimensionless variable QR_g

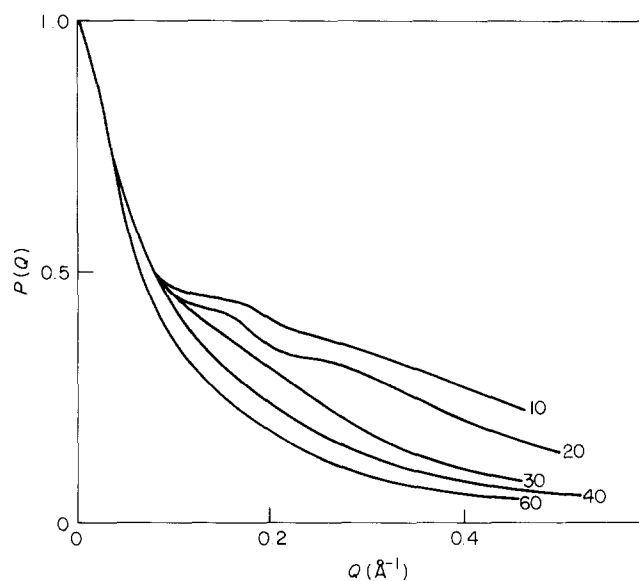


Figure 11 Calculated scattering function for two RISM chains which are allowed to be attached randomly on the surface of a 50 Å diameter impenetrable sphere

reinforced by the agreement between the experimental scattering function for DSMMA and XYL and the calculated scattering function which is shown in Figure 12. The theoretical scattering function pertains to a 50 Å diameter sphere with two 50 segment chains attached to it diametrically opposite each other. Although the model is scaled down with respect to the actual dimensions of the multimer studied where each styrene chain has *ca.* 800 repeat units, the ratio of core size to pendant chain of the block copolymer length is preserved.

CONCLUSIONS

The sociation of polystyrene-*b*-poly(methyl methacrylate) diblock copolymers in *p*-xylene at temperatures of 303 K and below has been demonstrated by light scattering, osmometry and viscometry. At 303 K the multimer formed is a dimer whilst at lower temperatures the number of molecules in the multimer increases. Such small association numbers have not previously been reported and the detailed reasons for their occurrence for this system cannot be deduced from the present limited data.

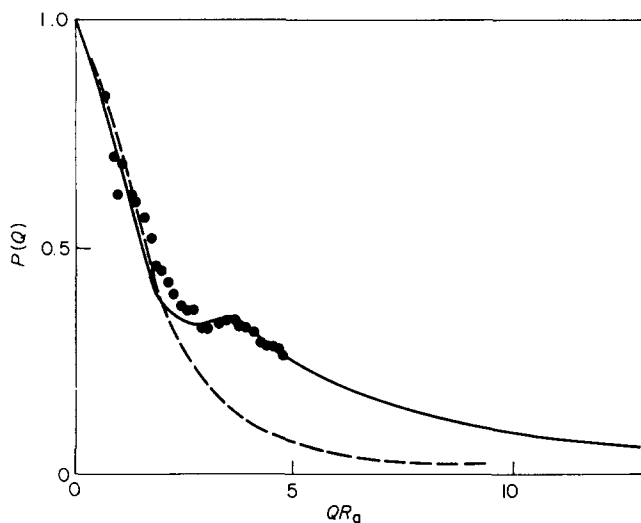


Figure 12 Calculated scattering functions ($P(Q)$) compared with experimental data for DSMMA in hydrogenous *p*-xylene at 303 K at a concentration of 20.56 kg m^{-3} : (●) experimental data; (—) scattering function obtained by Monte Carlo calculation of the model in Figure 8; (---) Gaussian approximation for a chain with the same radius of gyration of the solid curve

Small-angle neutron scattering data from copolymer solutions in *p*-xylene has confirmed the conclusions made using data from classical techniques. Furthermore they have provided results which permit a detailed description of the multimer structure to be deduced. The structure proposed is one wherein the less soluble poly(methyl methacrylate) blocks sociate to form a spherical core with the polystyrene blocks radiating from the sphere surface in such a way as to minimise contact between them. Thus for a dimer, the polystyrene blocks are diametrically opposite each other. Notwithstanding, the compactness of the sociated poly(methyl methacrylate) blocks (compared with the homopolymer of equivalent molecular weight), they are still expanded with respect to the unperturbed dimensions and consequently the spherical core must contain a significant amount of solvent.

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