

# Influence of temperature and composition on the small-angle neutron scattering from polydiene star diblock copolymers and mixtures with homopolymers

A.S. Brunacci<sup>a</sup>, F.T. Kiff<sup>a</sup>, R.W. Richards<sup>a,\*</sup>, R.L. Thompson<sup>a</sup>, S.M. King<sup>b</sup>

<sup>a</sup>Interdisciplinary Research Centre in Polymer Science and Technology, University of Durham, Durham DH1 3LE, UK

<sup>b</sup>ISIS Science Division, Rutherford-Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK

Received 1 March 1999; received in revised form 6 June 1999; accepted 14 June 1999

## Abstract

The small-angle scattering from star diblock copolymers (SDCs) has been calculated using the incompressible random phase approximation (RPA) and methodologies recently developed. The influence of the interaction parameter and incorporation of homopolymer has been explored theoretically for SDCs of deuteriopolybutadiene and polymethylpentadiene with four arms. For the copolymer where the polybutadiene was the outer block of the arm, the scattering over a temperature range from 298 to 418 K has been explored. Fits to the data have been obtained using the random phase expressions providing values of the interaction parameter and radius of gyration of the inner block. The dimensions of the inner block are unaltered from the unperturbed dimensions of the linear polymer of the same degree of polymerisation. The temperature variation of scattered intensity suggests a spinodal temperature for microphase separation of 196 K. Although the scattering of the mixtures of the SDC with either of the homopolymer exhibited features predicted by the random phase approximation theory, data could only be fitted by using unrealistic values of intermolecular and intramolecular interaction parameters or using radius of gyration values of the homopolymer that indicated phase separation between SDC and homopolymer. SDC data provide support for phase separation being the pertinent explanation for these phenomena. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** Small-angle neutron scattering; Polydiene; Diblock

## 1. Introduction

Mixtures of homopolymers of different species generally exist as separate phases. This well-known phenomenon is due to the fact that the enthalpy of mixing is often positive, favouring demixing, and the entropy of mixing of large macromolecules is generally too small to overcome the enthalpic term and thus favour mixing. This incompatibility of different homopolymers poses problems for applications such as recycling, or the development of new materials where mixing of polymers is required, because incompatible polymers are prone to fracture along the internal interfaces.

Adding copolymers of the two homopolymers forming a mixture may enhance the compatibility by adsorbing to the interface in a manner analogous to the emulsification of oil and water by a surfactant. Recent theoretical advances [1–3] have led to predictions of the influence of molecular architecture and composition on the effectiveness of copolymers as compatibilising agents in mixtures. Balazs et al. used

self-consistent mean field theory to predict the effectiveness of various architectures of A – B copolymers adsorbing to the interface of an A + B homopolymer mixture [1]. For fixed total degree of polymerisation, they found that the ability of copolymers to lower interfacial tension was diblock  $\gg$  alternating  $>$  random. Using Monte Carlo simulations, Dadmun [3] also predicted that a random copolymer would not be as good at compatibilising an interface as either an alternating or diblock copolymer, but concluded that the alternating copolymer would be superior to the diblock due to its ability to weave between the immiscible phases causing them to be entangled. Lyatskaya and Balazs [2] examined mixtures of copolymers of different structures in homopolymer mixtures, and found that mixtures of diblock and comb copolymers could achieve a greater degree of interfacial tension lowering than either individual component.

To make processing of a polymer mixture feasible, a compatibilising agent must not only lower the interfacial tension of the immiscible homopolymers, but also be capable of migrating to the interface sufficiently quickly

\* Corresponding author.

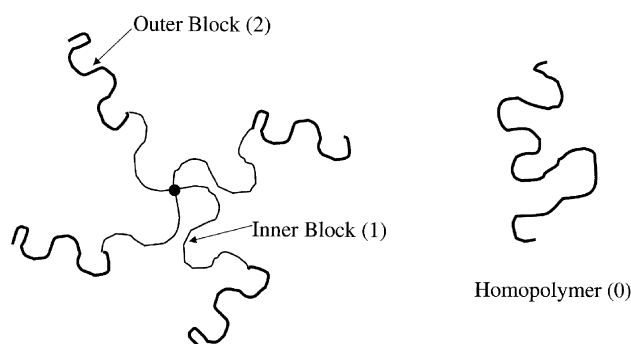


Fig. 1. Sketch of four-armed SDC and homopolymer, 0. The inner and outer blocks of the copolymer have been labelled as components 1 and 2, respectively.

to facilitate this interfacial tension reduction on a reasonable time scale. This last factor is important when the practicalities of incorporating a diblock copolymer compatibiliser are considered. The copolymer will usually have to be mixed with one of the homopolymers and will thus generally form micelles. To be effective the micelles must migrate to any polymer–polymer interface in the system, disassemble and re-organise across the interface thus reducing the interfacial tension. A possible way of overcoming this disassembly step is to use a star diblock copolymer (SDC), a schematic sketch of which is shown in Fig. 1. Such copolymers can be viewed as monomolecular micelles and have no disassembly step at the interface. Moreover, knowledge of the behaviour and properties of well-defined star polymers is relevant to understanding the aspects of molecular architecture that may be influential in branched polymers. With the development of metallocene initiated polyolefins such knowledge is increasingly pertinent. A third aspect of star copolymers which engenders our interest is the expansion and application of the random phase approximation (RPA) to the interpretation of scattering laws for structures that are more complex than the homopolymer mixtures and linear diblocks to which they were first applied. Although scattering laws for complex structures and mixtures have been written down by others [4,5], their derivation is not transparent. More recently, Read [6] has developed a simpler approach that allows the scattering law for any polymer molecular architecture (except cyclic molecules) or mixture to be rapidly set out. Combination of this method with the proper incorporation of contrast factors gives a powerful means of determining interaction parameters and the radii of gyration of component blocks.

We report here the results of a small-angle neutron scattering (SANS) study on a four-arm SDC and mixtures with each of the constituent homopolymers. Each arm of the SDC is a linear diblock copolymer of polybutadiene and polymethyl pentadiene. The influence of temperature on the SANS from one of the pure diblock copolymers is reported and for a fixed temperature we have investigated the SANS as a function of SDC–homopolymer composition.

## 2. Theory

The (incompressible) RPA [7] was originally applied to the interpretation of small-angle scattering data from non-crystalline single-phase mixtures of polymers. In recent years, the theory has been extended to include an arbitrary number of components [8] and copolymers of different architecture [6,9,10]. These various aspects are combined here to obtain RPA expressions for mixtures containing SDCs. For such complex systems the scattering laws are dependent on the interactions between all of the species present, whether deuterium labelled or not. Moreover, these interactions and hence the total scattering law are modulated by the architecture of the copolymer molecule. Consequently, a model that includes all of the interaction parameters and partial structure factors explicitly is necessary to make a meaningful interpretation of SANS data. The scattering laws for systems containing multiple components, and complex polymer architectures have been derived quite generally in previous papers [11]. In the following section, these equations are outlined using a format similar to that of Lin et al. [12].

If we consider an SDC with  $f$  identical arms, we must calculate the scattering law for each component, where a component is a block of the copolymer species. A four-armed SDC thus has eight components: four outer blocks (OBs), and four inner blocks (IBs). The scattering law can become extremely complex if polydispersity in molecular weight and composition are incorporated. However, for the experiments reported here considerable simplification is enabled because the components are effectively monodisperse in molecular weight, the architecture is well defined, and all of the arms of the star are identical. This symmetry enables the pure SDC to be described by two distinct components, or if the SDC is in a mixture with a homopolymer then there are three distinct components.

For a mixture of  $n + 1$  components, the coherent differential scattering cross-section of the mixture,  $d\Sigma/d\Omega$ , is given by the following equation:

$$\frac{d\Sigma}{d\Omega}(Q) = \mathbf{B}_{i0}^T \mathbf{S} \mathbf{B}_{i0} \quad (1)$$

where  $Q$  is the scattering vector defined as  $Q = (4\pi/\lambda) \sin \theta$ , for neutrons of wavelength  $\lambda$  and a scattering angle  $2\theta$ .  $\mathbf{S}$  is an  $(n \times n)$  matrix containing the scattering laws for each component of the system. Assuming incompressibility, a mixture of  $n + 1$  components can be regarded as  $n$  components that are dispersed in a ‘solvent’ component. Hereafter, the solvent component will be labelled with a zero.  $\mathbf{B}_{i0}$  (and  $\mathbf{B}_{i0}^T$ ) is the  $(1 \times n)$  matrix (and its transpose) containing the scattering length density contrast factors between each component and the ‘solvent’

$$\mathbf{B}_{i0} = \left( \frac{b_1}{v_1} - \frac{b_0}{v_0}, \frac{b_2}{v_2} - \frac{b_0}{v_0}, \dots, \frac{b_n}{v_n} - \frac{b_0}{v_0} \right) \quad (2)$$

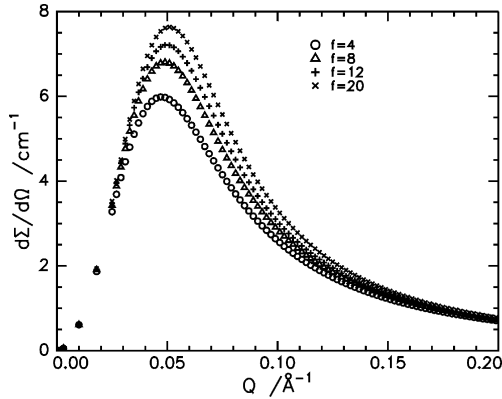


Fig. 2. Scattering cross-section calculated using RPA expressions for SDCs with different arm numbers  $f$  and deuteriopolybutadiene–polymethyl pentadiene diblock arms with a PBD volume fraction of 0.5.

where  $b_i$  and  $v_i$  are the scattering length and volume element of a repeat unit of component  $i$  in the system.

In Eq. (1),  $\mathbf{S}$  is the total scattering law and contains the structure factors,  $\mathbf{S}^o$  (describing the connectivity and dimensions of the various blocks and the interactions between them

$$\mathbf{S} = \left[ \mathbf{S}^{o-1} + \frac{(\mathbf{S}^{o-1} \cdot \mathbf{S}_{i0}^o + \mathbf{I})(\mathbf{S}^{o-1} \cdot \mathbf{S}_{i0}^o + \mathbf{I})^T}{\mathbf{S}_{00}^o - \mathbf{S}_{i0}^o \mathbf{S}^{o-1} \mathbf{S}_{i0}^{oT}} + \frac{\chi}{v_E} \right]^{-1} \quad (3)$$

$\mathbf{I}$  is the  $(n \times 1)$  identity vector (all components = 1), and  $\chi$  contains the Flory interaction parameters between different components, defined in Eq. (4) over an arbitrary reference volume,  $v_E$ . The latter is usually defined as the geometric mean of the monomer unit volumes in the polymer mixture.

$$\chi = \chi_{ij} - \chi_{i0} - \chi_{j0} \quad (4)$$

The terms of the matrix  $\mathbf{S}^o$  may be divided into ‘self-terms’ of the individual components, and the off-diagonal ‘co-terms’ relating the correlations between different ( $i \neq j$ ) components, respectively

$$\mathbf{S}_{ii}^o = N_i \phi_i v_i P_{ii} \quad (5)$$

$$\mathbf{S}_{ij}^o = S_{ji}^o = \sqrt{N_i \phi_i v_i N_j \phi_j v_j} P_{ij} \quad (6)$$

$\mathbf{S}_{i0}^o$  is the  $(1 \times n)$  matrix containing the co-terms for the correlations between each of the  $n$  components and the ‘solvent’

$$\mathbf{S}_{i0}^o = \{ \sqrt{N_1 \phi_1 v_1 N_0 \phi_0 v_0} P_{10}, \sqrt{N_2 \phi_2 v_2 N_0 \phi_0 v_0} P_{20}, \dots, \sqrt{N_n \phi_n v_n N_0 \phi_0 v_0} P_{n0} \} \quad (7)$$

$N_i$  is the degree of polymerisation of the  $i$ th component, and  $\phi_i$  is its volume fraction within the entire mixture. The  $P_{ii}$ ,  $P_{ij}$  and  $P_{i0}$  functions combine to give the structure factor of the SDC and any homopolymers that may be present. The  $P_{ij}$  ( $i \neq j$ ) and  $P_{i0}$  co-terms are zero unless they refer to blocks which are part of the same macromolecule, since in the

absence of any interactions, their respective locations would not be correlated. Within each SDC the form factors,  $P$ , are defined below. Defining the inner block of the SDC as component 1, and the outer block as component 2 (see Fig. 1), the structure factors are

$$P_{11} = f(G_1 + (f-1)F_{11}) \quad (8)$$

$$P_{22} = f(G_2 + (f-1) \exp(-2Q^2 R_{g1}^2) F_{22}) \quad (9)$$

$$P_{12} = P_{21} = f(F_1 F_2 + (f-1) \exp(-Q^2 R_{g1}^2) F_1 F_2) \quad (10)$$

$R_{g1}$  is the radius of gyration of an inner block of the star. The initial terms in  $f$  arise from the fact that each star possesses  $f$  arms. Each of the  $f$  arms is connected to  $f-1$  other arms, which is the factor for the co-terms. Where blocks are not directly linked but are connected via one or more other blocks, the co-terms are multiplied by a ‘propagator’ term that decays exponentially as the radius of gyration of the propagating block increases. The propagator term is absent in the case of the  $P_{11}$  form factor because the inner blocks are connected at a ‘point’, which is negligible in size compared to the blocks.

For the flexible polymer chains with which we are concerned,  $G_i(Q)$  and  $F_i(Q)$  are Debye and Leibler functions for the  $i$ th species, respectively

$$G_i(Q) = \frac{2(R_{gi}^2 Q^2 - \exp(-R_{gi}^2 Q^2) - 1)}{(R_{gi}^2 Q^2)^2} \quad (11)$$

$$F_i(Q) = \frac{1 - \exp(-R_{gi}^2 Q^2)}{R_{gi}^2 Q^2} \quad (12)$$

For diblock copolymers, the usual expressions can be obtained by substituting  $f=1$  into Eqs. (8)–(10) and the result for homopolymer mixtures can be obtained with  $f=1$  after eliminating all terms for component 2.

For the systems that are of interest in the following discussion, Eq. (3) can be simplified in two ways. Firstly by taking advantage of the symmetry of the stars, it is possible to use the more complex structure factors, and reduce the problem to a simple two component system, in which either the inner or outer block species can be identified as the ‘solvent’ component. The matrices become simple  $(1 \times 1)$  scalar quantities. Secondly, for the mixtures of star–homopolymer, Eq. (3) is simplified by defining the homopolymer as the ‘solvent’ so that the terms in  $\mathbf{S}_{i0}^o$  are zero [12]. This simplification notwithstanding, the expressions obtained are still complex. The small-angle neutron scattering cross-section predicted by these RPA expressions has been calculated and some of the theoretical scattering profiles are given here. Absolute scattering cross-sections have been calculated using monomer unit volumes, coherent scattering lengths and radii of gyration, which pertain to the polymers of direct interest here, i.e. polybutadiene (per-deuteriated) and polymethyl pentadiene. For these illustrative calculations we have used degrees of polymerisation of

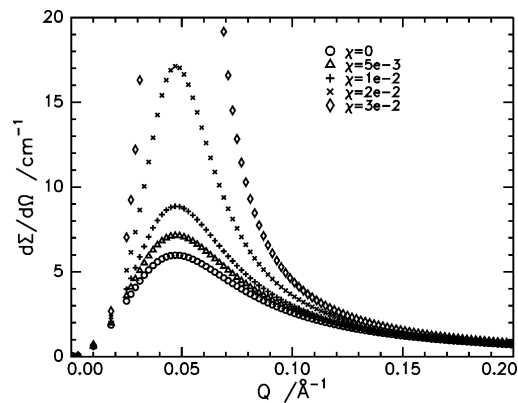


Fig. 3. Influence of the interaction parameter,  $\chi$ , on the RPA calculated SANS data for an SDC with  $f = 4$  and DPBD volume fraction of 0.5.

the homopolymers and SDC components approximately equal to those used in the experiments discussed subsequently.

Fig. 2 shows the SANS calculated for an SDC with polybutadiene outer blocks (all theoretical data shown here are for this architecture) and with an increasing number of arms with the interaction parameter between the two blocks set at zero. As expected for RPA models of block copolymers (of whatever type), a maximum in the scattering cross-section is observed at a finite value of  $Q$ . Although the number of arms increases, the overall composition is the same at a volume fraction of deuteriopolybutadiene of 0.5, however there is clearly a shift to higher values in the  $Q$  position of this maximum as the functionality,  $f$ , of the stars increases. Since the radii of gyration and the degrees of polymerisation have been kept constant for each value of  $f$ , this shift must be an intrinsic property of the RPA calculation. Fig. 3 shows the influence of the interaction parameter,  $\chi$  between polybutadiene and polymethyl pentadiene blocks. As  $\chi$  becomes increasingly positive (i.e. unfavourable to mixing), the amplitude of the scattering cross-section increases and becomes infinite when  $\chi$  reaches its spinodal value and the two components of the SDC are no longer homogeneous.

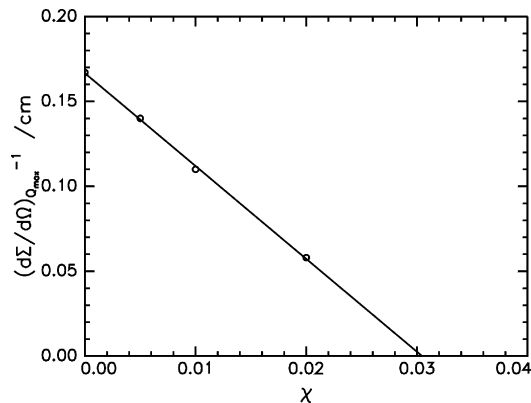


Fig. 4. Reciprocal of the RPA calculated maximum scattering cross-section plotted as a function of the values of  $\chi$  used in the calculations. The least squares fit to the points intersects the abscissa at the spinodal value of  $\chi$ .

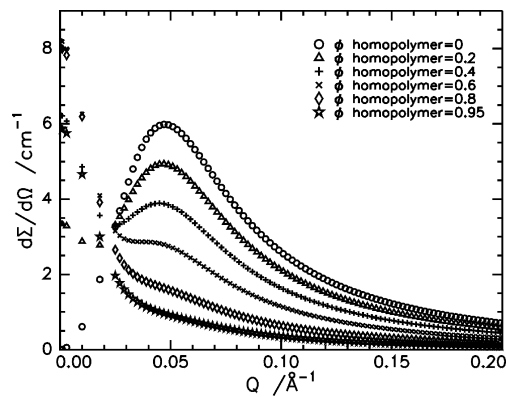


Fig. 5. RPA calculated SANS for mixtures of SDC with PMP at different mixture compositions. The interaction parameters were set equal to zero for all combinations of monomer units in the mixture for the purposes of this calculation.

The reciprocal of the maximum calculated scattering cross-section is plotted as a function of  $\chi$  values used in the calculations in Fig. 4. Extrapolating these data to  $(d\Sigma/d\Omega)_{Q_{\max}}^{-1} = 0$  suggests a spinodal value for  $\chi$  of 0.03 using a value for  $v_E$  appropriate for the two polymers investigated by SANS here.

Adding one of the homopolymers to the SDC (setting all  $\chi$  values to zero) produces a radical change in the scattering cross-section (Fig. 5). The amplitude of the maximum at finite  $Q$  decreases and a positive intercept at  $Q = 0$  becomes evident. As the volume fraction of homopolymer increases, the magnitude of this intercept increases to an asymptotic limit. The contribution of the SDC is evident as an undulation in the general decrease in scattering cross-section for increasing  $Q$ . However, when the content of homopolymer becomes very large, both the intercept at  $Q = 0$  and the general level of the cross-section decreases as anticipated due to the decline in scattering contrast in the mixture.

Hence like linear diblock copolymers, SDCs can undergo microphase separation if the interactions between the different polymer species become sufficiently repulsive [12–15]. The literature on SDCs has been dominated by styrene–isoprene (SI) diblock systems. Thomas et al. [13] described the ordered phases of such SDCs and their dependence on the number of arms, and the ratio of styrene to isoprene within each arm [14]. More recently, Uchida et al. [15] obtained ordered lamellar phases of SI stars with up to 77 arms by copolymerising SI diblocks with divinyl benzene. The order–disorder transition differs between SDCs and linear copolymers in that the ordering occurs more readily for SDCs than for linear diblock copolymers. This difference can be quantified using the mean field theory [16,17], and the spinodal transition for symmetric diblocks decreases from  $\chi N = 10.5$  (linear) to  $\chi N = 7.07$  (four-armed SDC), these values being calculated for diblock copolymer arms which were symmetrical. For SDCs, the ordering is a first-order transition, which manifests itself as a discontinuous

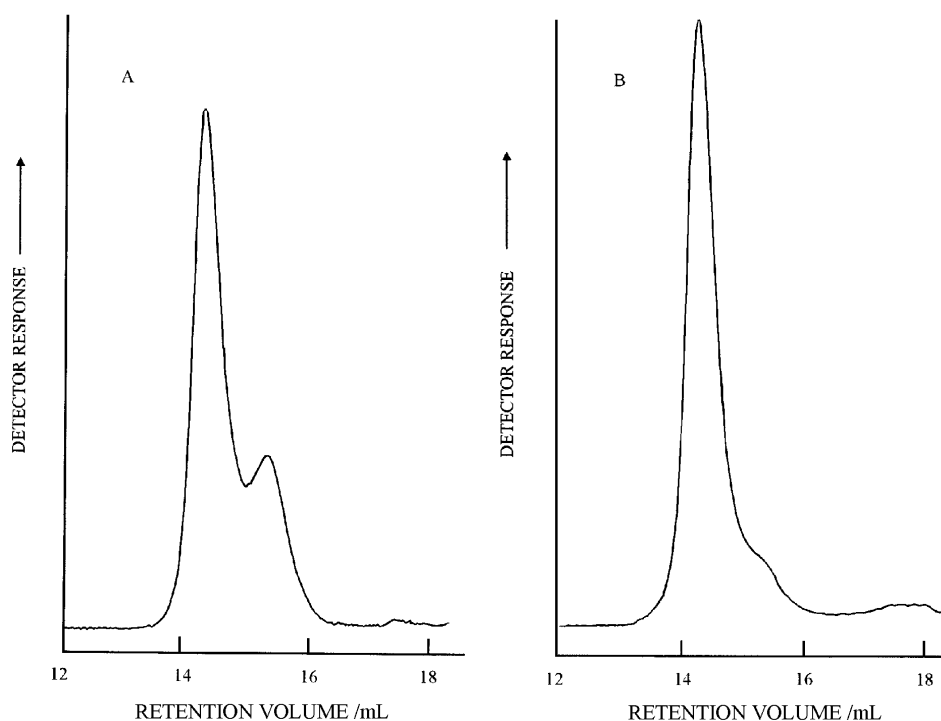


Fig. 6. Size-exclusion chromatograms of the OB SDC: (A) before; and (B) after fractional precipitation to separate it from linear diblock copolymer.

increase in the maximum intensity of a small-angle scattering spectrum [16].

### 3. Experimental

Poly(2-methyl-1,3-pentadiene) (PMP) was synthesised from 2-methyl-1,3-pentadiene (Janssen Chimica, 99%, 30/70 cis/trans) following the method of Fetters et al. [18] using secondary butyl lithium as an initiator. The polymerisation reaction was terminated after 6 days at 40°C by adding N<sub>2</sub> sparged methanol. Similarly, polybutadiene (PB) was prepared by anionic polymerisation initiated with secondary butyl lithium. This process results in PB chains for which the ratio of trans–cis–vinyl content is approximately 0.46:0.46:0.08 and is discussed in more detail by Rochefort

et al. [19]. Linear diblock copolymers of PMP and deuteriopolybutadiene (DPB) were prepared by the sequential addition of monomers and linked by adding 1,6-bis(methyl-dichlorosilyl)hexane, (Fluorochem, 97%) to the solution of living diblock copolymers to give the four-armed SDC.

The polymers were precipitated from solution by adding the solutions to methanol. To separate the SDC from linear diblock copolymer, the precipitated polymer was dissolved in toluene and the SDC fractionally precipitated by adding methanol. Fig. 6 shows size-exclusion chromatographs of the polymer before and after this fractional precipitation procedure. The SDC was re-dissolved in a small volume of toluene containing 2,6-ditertiary butyl-4-methylphenol antioxidant and the toluene allowed to evaporate off before final drying under vacuum after which the SDC was kept in a freezer until required. Our attention here is restricted to

Table 1

Weight-average molecular weight ( $M_w$ ), polydispersity ( $M_w/M_n$ ), calculated radius of gyration  $R_{gc}$ , repeat unit volume ( $v$ ) and scattering length ( $b$ ) for the SDCs and their constituents

Component		$M_w$ ( $10^3$ g mol <sup>-1</sup> )	$M_w/M_n$	$R_{gc}$ (Å)	$v$ (Å <sup>3</sup> )	$10^4 b$ (Å <sup>-2</sup> )
<i>SDC</i>						
IB	DPB (inner)	6.800	1.03	30	107	6.66
	HPMP (outer)	5.800	1.05	24	156	0.25
OB	DPB (outer)	7.130	1.03	31	107	6.66
	HPMP (inner)	6.570	1.03	25	156	0.25
<i>Homopolymers</i>						
PB2	HPB	82.2	1.03	109.5	100.9	0.42
PMP2	HPMP	91.4	1.19	94.3	155.7	0.25
PB1	HPB	78.1	1.06	106.8	100.9	0.42
PMP1	HPMP	94.0	1.11	95.8	155.7	0.25

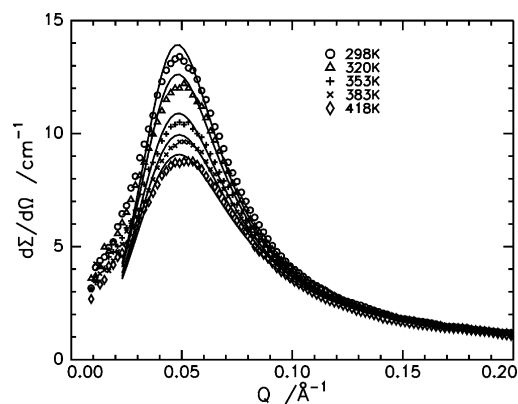


Fig. 7. SANS data for the OB SDC as a function of temperature.

two SDCs, both are four-armed DPB–PMP SDCs, namely OB and IB, where the outer blocks and inner blocks are composed of DPB. The volume fraction of DPB was 0.51 and 0.52 in OB and IB, respectively.

The molecular weights, polydispersities and neutron scattering length densities of the SDCs and homopolymers are summarised in Table 1. The molecular weights and polydispersity were obtained using size-exclusion chromatography (SEC) calibrated with polystyrene standards. The unperturbed radii of gyration anticipated for each block or homopolymer were calculated from the weight-average molecular weights using the relation

$$\langle R_{gc} \rangle = \sqrt{kM_w/6} \quad (13)$$

where  $k = 0.585 \text{ \AA}^2 \text{ mol g}^{-1}$  for PMP, and  $0.876 \text{ \AA}^2 \text{ mol g}^{-1}$  for PB [20] and we presume that the same value for  $k$  applies to DPB as for PB.

### 3.1. Small-angle neutron scattering

Mixtures of copolymer–homopolymers obtained by co-dissolution in toluene and precipitation in an excess of cold methanol followed by drying at approximately 313 K under vacuum for several days. Each mixture was then enclosed between two quartz windows separated by a

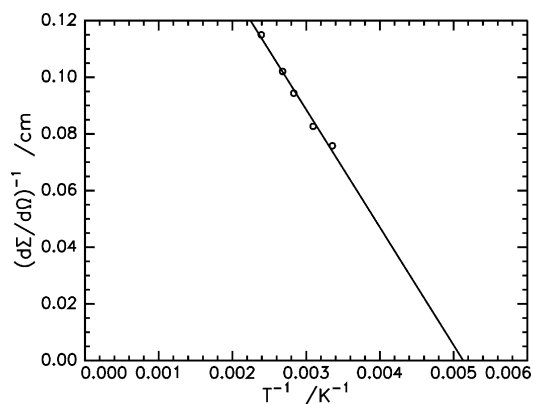


Fig. 8. Reciprocal scattering cross-section at  $Q_{\max}$  plotted as a function of reciprocal temperature. The line is a linear least squares fit to the data.

Table 2

Fitting parameters for RPA expressions for SDCs

SDC	Temperature (K)	$R_{g1(\text{fit})}$ ( $\text{\AA}$ )	$\chi_{\text{PB-PMP}}$
OB	298	25.7	0.021
	320	25.4	0.019
	353	25.0	0.015
	383	24.6	0.014
	418	24.5	0.012
IB	323	30.4	0.019

1 mm thick spacer to produce a bubble free specimen. Each of the samples was placed in brass cell, which fitted closely into a thermostatted holder in the neutron beam. Small-angle neutron scattering data were obtained using the LOQ diffractometer at the UK pulsed neutron source, ISIS, at the Rutherford-Appleton Laboratory.

SANS data were obtained over the scattering vector range of  $0.01\text{--}0.25 \text{ \AA}^{-1}$  for the pure OB SDC in the temperature range of 298–418 K and for the pure IB at the single temperature of 323 K. Approximately 50% (by volume) mixtures of OB in PB and PMP were investigated over the temperature range 298–418 K, whereas mixtures of IB in PB and PMP were investigated at one temperature only but the range of compositions was from  $\sim 10$  to 40%. The upper temperature was defined by the stability of the polymers at elevated temperatures. Intensity data were corrected for sample thickness and transmission and placed on an absolute scale by comparison with the scattering of the secondary standard, a blend of deuteriopolystyrene in hydrogenous polystyrene.

## 4. Results and discussion

### 4.1. Pure SDCs

SANS data for the pure OB SDC are shown in Fig. 7, as the temperature increases the scattering cross-section decreases and the  $Q$  position of the maximum appears not to alter. The value of the cross-section at  $Q_{\max}$  is plotted in a reciprocal form in Fig. 8, and the extrapolated linear least squares line through the data suggests that the spinodal temperature for the pure OB SDC is  $\sim 196$  K. Since this temperature is less than the  $T_g$  of PMP, such an intramolecular spinodal decomposition is unlikely to be observed. Moreover, an abrupt transition to an ordered phase is more likely to take place before the spinodal temperature is reached. We note that no abrupt change in the dependence of reciprocal intensity was observed over the temperature range investigated, suggesting that the SDC is in the disordered phase at all temperatures. The SANS data of Fig. 7 were non-linearly least squares fitted using the RPA expressions discussed earlier. For this fitting procedure, we utilised the theoretical predictions that the arms in a star polymer are likely to be stretched to

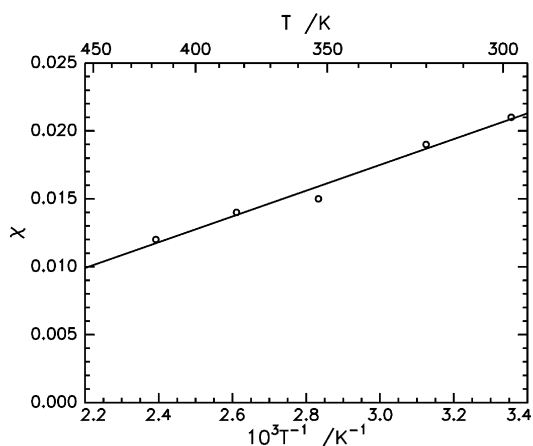


Fig. 9. Interaction parameters obtained from fitting RPA expression to the scattering cross-sections of Fig. 7 plotted as a function of reciprocal temperature. The line is the linear least squares fit to the data.

dimensions greater than those of the equivalent linear chain. Furthermore, our earlier work on star polymers with a single labelled arm [21] showed that this concept was valid experimentally. This stretching is proposed to be more evident in the *inner* portion of the arms, i.e. near the core [22]. In view of this, the radius of gyration of the outer block of the SDCs was fixed at its unperturbed value and the best fit obtained by using the radius of gyration of the outer block and the interaction parameter as the fitting variables. Included in Fig. 7 are the lines that are the best fits to the data and Table 2 reports the radii of gyration and  $\chi$  values obtained. For these latter values the fitting parameter was actually  $\chi/v_E$ , see Eq. (3), and the value of  $v_E$  used was the geometric mean of the two monomer unit volumes, i.e.  $129.1 \text{ \AA}^3$ . Included in Table 2 are the value of  $\chi$  and the radius of gyration obtained in fitting the data for the pure IB SDC at the single temperature investigated.

The fits in Fig. 7 are acceptable over the majority of the  $Q$  range but discrepancies are evident as  $Q$  approaches zero. The experimental data in the low  $Q$  region are tending to a finite intercept at  $Q = 0$ , rather than the theoretically predicted value of zero. Such excess scattering at  $Q = 0$  is a feature of many block copolymer systems, indeed it is much more evident in simple linear diblock copolymers. Evidently long range correlations are present in the systems and although some attempts to incorporate compressibility

effects [23] have been made no satisfactory explanation has yet been forthcoming to our knowledge.

The position in  $Q$  of the maximum is determined chiefly by the radius of gyration of the constituent blocks. Over the temperature range investigated, the radius of gyration of the inner PMP block of the OB SDC was essentially constant, the small decrease observed being well within experimental errors. Interaction parameters for the OB SDC are plotted as a function of reciprocal temperature in Fig. 9. A linear least squares fit to the data gave the values of  $A$  and  $B$  in the empirical equation [24]

$$\chi = A + B/T \quad (14)$$

and these values are set out in Table 3 together with values for other polymer blends and copolymers published by others. Together with the value of the spinodal temperature estimated earlier, these values of  $A$  and  $B$  suggest that at the spinodal temperature the value of  $\chi$  for this SDC is 0.037.

The values of  $\chi$  obtained and plotted in Fig. 9 at first sight appear to be unexpectedly large for interactions between rather similar hydrocarbon polymers and consequently the manner by which they were obtained should be examined rather carefully. In this respect it is perhaps worthwhile pointing out that the temperature range used is significantly greater than most used hitherto in the examination of the thermodynamics of polymers using SANS [25–30]. Moreover, the range of  $Q$  over which the fit to the data has been made is also very large. Nonetheless,  $\chi$  values appear two orders of magnitude larger than most of those reported including mixtures of hydrogenated polybutadienes and polyisoprenes. However in a recent paper, Balsara and co-workers [31] reported interaction parameters between polyethylene and polypropylene obtained by SANS either on blends of the two polymers or on a linear diblock of the two. The values they report are exactly of the same order of magnitude as those reported by us here and consequently such large values seem to be symptomatic of interactions between rather similar hydrocarbon polymers.

#### 4.2. Mixtures of SDC and homopolymer

Fig. 10(a) shows the SANS data for mixtures of the OB SDC with polymethyl pentadiene PMP1. As the volume fraction of OB in the mixture decreases the amplitude of the RPA maximum, at  $Q = 0.055 \text{ \AA}^{-1}$ , decreases and is

Table 3

Fitting constants for the temperature dependence of  $\chi_{PB-PMP}$ ,  $\{\chi = A + B/T \text{ (K)}\}$  and some published values for related systems

Mixture	$v_E \text{ (\AA}^3\text{)}$	$A \text{ (10}^{-2}\text{)}$	$B \text{ (K)}$	Temperature range (K)
DPB–PMP	129.1	–1.09	9.5	298–418
PB–DPB [26]	111	–0.022	0.305	183–250
Polymethylmethacrylate–deuteriopolystyrene [27]	149, 179	–1.74	2.39	393–453
Polystyrene–polyisoprene [28]	179, 136	–0.079	17.6	373–453
Polystyrene–polyisoprene (diblock) [16]	144	3.0	10	403–423
Polystyrene–polyisoprene (SDC) [16]	144	3.4	6.6	433–453
Polyethylene–polypropylene [29]	161.5	–2.45	16.6	410–445

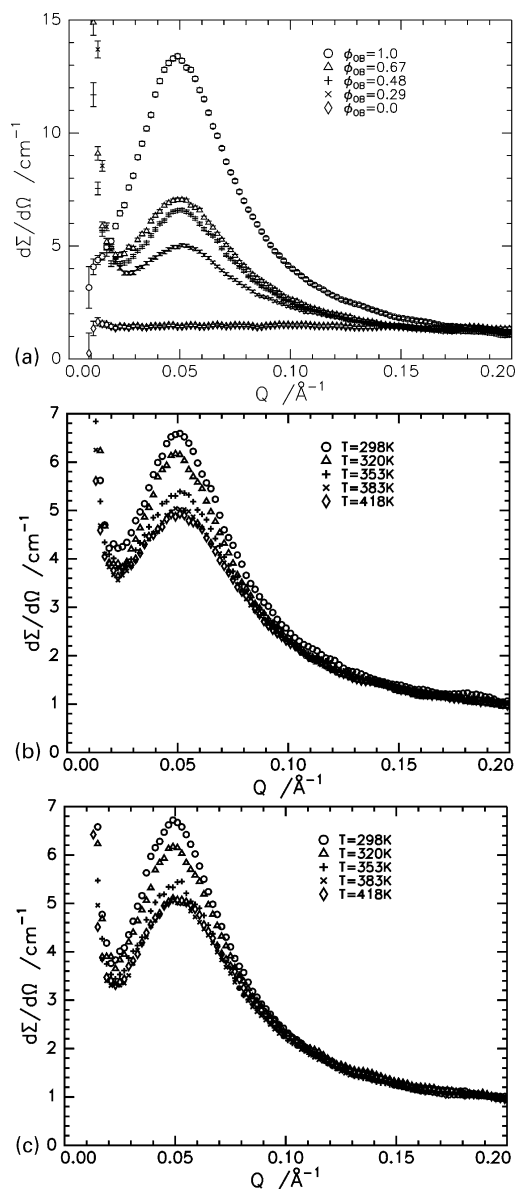


Fig. 10. (a) Scattering cross-sections for mixtures of OB SDC in PMP1 at 298 K, the volume fraction of OB in each mixture is indicated. (b) Scattering cross-sections for 0.48 volume fraction OB in PMP1 obtained at the temperatures indicated. (c) Scattering cross-sections for 0.5 volume fraction OB in PB obtained at the temperatures indicated.

accompanied by a sharp increase in the scattering cross-section for  $Q$  values less than 0.02. Included in Fig. 10(a) are the data for pure PMP1 which shows no increase in scattering over this low  $Q$  range and thus the increased scattering observed in the mixtures is not an artefact due, for example, to incident beam contamination. For a fixed composition of mixture, increasing the temperature has the same effect on the mixture scattering as on that for the pure SDC, i.e. a reduction in the amplitude of the maximum. However, the temperature has little influence on the scattering for  $Q$  less than  $\sim 0.02 \text{ \AA}^{-1}$ , as demonstrated in Fig. 10(b) and (c).

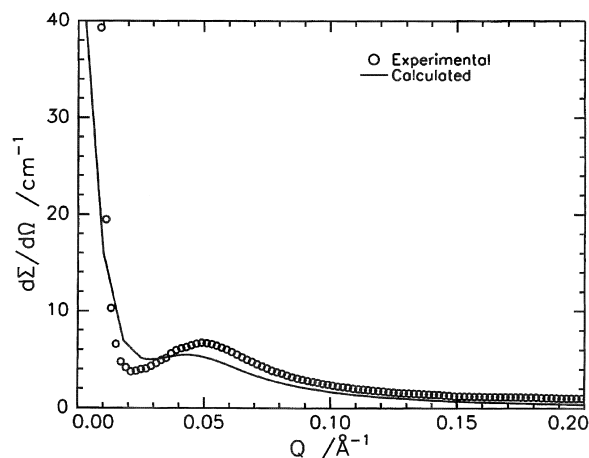


Fig. 11. Coherent scattering cross-section calculated for a mixture of OB SDC and polybutadiene homopolymer assuming all interaction parameters are zero (solid line) compared with the experimental data at 298 K (○).

A priori, we anticipate little difference if any for the values of  $\chi$  between PBD and PMP whether the PMP forms part of the SDC or is the surrounding homopolymer. However, if the value of  $\chi$  obtained earlier is incorporated into the RPA calculation for a mixture of SDC and homopolymer, the calculated scattering cross-section is divergent (i.e. below a critical  $Q$  value the scattering cross-section becomes negative) indicating that the order–disorder transition condition has been crossed.

The experimental SANS data for mixtures of the OB SDC with either homopolymer can be fitted by the RPA expression by relaxing either of two constraints imposed on the RPA expressions used thus far here. Firstly,  $\chi$  could be allowed to differ for intramolecular interactions within the SDC from that with the ‘solvent’ homopolymer and the unlike component of the SDC. Some justification for this approach can be found in the PRISM description of star polymers [22], where the excluded volume interactions exist within sections of the arms near the core even at bulk concentration of star polymer. When the homopolymer is hydrogenous polybutadiene, there is an additional justification for relaxing the constraint on the value of  $\chi_{\text{PBMP}}$ , because from the viewpoint of absolute rigour, the mixture now has three components, hydrogenous polybutadiene, deuterated polybutadiene and polymethyl pentadiene. Although a fit to the data can be obtained by allowing this relaxation in intramolecular and intermolecular  $\chi$ , the values obtained are very different from each other. For example, the best fit to the data for the mixture of 48% OB in PMP1 at 320 K is obtained with  $\chi_{\text{intra}} = 0.044$ , and  $\chi_{\text{inter}} = -0.009$ . This difference in both magnitude and sign is far too large to be attributable to molecular architecture alone and suggests they are ‘effective’ values, i.e. they are merely values which provide a fit to the data but have no real physical meaning.

Secondly, the experimental data could be fitted by the RPA expressions by allowing the dimensions of the



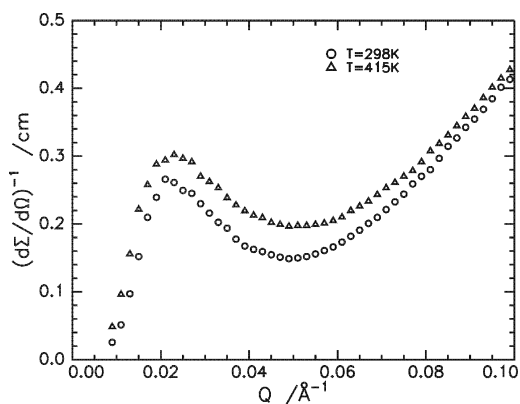


Fig. 12. Reciprocal scattering cross-section for a mixture of OB in PMP at an OB weight fraction of 48% at temperatures of 298 and 415 K.

individual polymer components to be perturbed, whilst maintaining the  $\chi_{\text{intra}} = \chi_{\text{inter}}$  constraint. However, because the  $Q$  position of the maximum in the scattered intensity does not vary greatly as the mixture composition changed, clearly the dimensions of either block in the SDC do not change significantly. We remarked earlier on the more rapid increase in the low  $Q$  scattering cross-section compared to that calculated by assuming all intramolecular and intermolecular  $\chi$  values were zero (Fig. 11). This suggests that there are increased correlations between homopolymer molecules. Allowing this parameter to become an adjustable variable in the fitting process gave homopolymer radii of gyration between two and six times the unperturbed value. Irrespective of either homopolymer, the values of  $R_{g0}$  are insensitive to temperature, but decrease systematically as  $\phi_{\text{SDC}}$  increases from  $\sim 0.3$  to  $\sim 0.7$ . The perturbation to  $R_{g0}$  is slightly larger for mixtures of OB with PMP than the corresponding mixtures with PB. One could speculate that this asymmetry arises from the PMP core of the SDC being 'screened' by a corona of the DPB outer block, and is thus less compatible with the PMP than the PB homopolymer.

Although the perturbed value of  $R_{g0}$  was still well within the contour length of the homopolymer, it is perhaps still surprising that such a large perturbation should appear for one species whilst the other species appears to retain its unperturbed dimensions. To determine what may be happening in these mixtures of ODC and homopolymer we use a suggestion made by Mori et al. [4] some years ago. In their RPA calculations of the scattering functions for binary polymer mixtures, they commented on the nature of the *minimum* in the reciprocal of the scattering cross-section. In mixtures of linear diblock copolymers and homopolymers, the minimum could be at  $Q = 0$  or at a finite  $Q$  value. The former corresponded to an eventual macrophase separation of block copolymer from homopolymer, the latter was symptomatic of microphase separation characteristic of pure block copolymers. Plotting the data obtained for the mixtures of SDC and PB as reciprocals (Fig. 12) shows that negative intercepts are indicated at  $Q = 0$ . This

indicates that the optical clarity of the SDC–homopolymer mixture notwithstanding, there is macrophase separation between the SDC and the homopolymer and over the temperature range studied there is only a small change in the direction of homogeneity.

Confirmation of this somewhat surprising finding is obtained from differential scanning calorimetry on the pure SDCs and their mixtures with the homopolymers. Fig. 13 shows the thermograms obtained. In a mixture of the two homopolymers the glass transition temperature of the polybutadiene and polymethyl pentadiene are clearly evident at 180 and 273 K, respectively (Fig. 13(A)). For the SDCs, only a single glass transition is observed for either copolymer. The OB star diblock has a very broad transition centred at ca. 210 K, whilst that of the IB copolymer is more distinctive and centred at 250 K (Fig. 13(B)). In mixtures of either copolymer with polybutadiene (0.5 weight fraction) the only transition observable is that of polybutadiene which is unmoved from the  $T_g$  value of the pure homopolymer (Fig. 13(C)). The absence of any glass transition for the SDC suggests that it is present as a dispersion of very small dimensions leading to such an extreme broadening of the transition [32] that it cannot be discerned from the general change in heat capacity as the mixture transforms from glassy to a liquid state. Under these circumstances, although the scattering cross-sections obtained have the characteristics predicted by the random phase expressions, their interpretation using them would be entirely erroneous.

## 5. Conclusions

The small-angle scattering from a four-armed poly-(deuterio-butadiene–methylpentadiene) SDC with the deuteriobutadiene blocks forming the outer part of the arms has been obtained as a function of temperature. The observed variation in scattering intensity can be quantitatively described using the incompressible random phase approximation as long as the influence of molecular architecture is accounted for. The dimensions of the inner block, which would be anticipated to be most disturbed, were unaltered from the unperturbed dimensions of the linear polymer of the same molecular weight. The temperature dependence of the interaction parameter between polybutadiene and polymethyl pentadiene was determined from the SANS data over a temperature range of 298–418 K. From the temperature dependence of the scattering intensity at the value of the scattering vector where a maximum intensity is observed, the spinodal temperature for microphase separation of this SDC was estimated to be 196 K.

Although the RPA expressions could be fitted to the small-angle neutron scattering data for mixtures of the SDC with homopolybutadiene, this could only be achieved by incorporating one of the two factors: either (i) using different values for the intermolecular and intramolecular

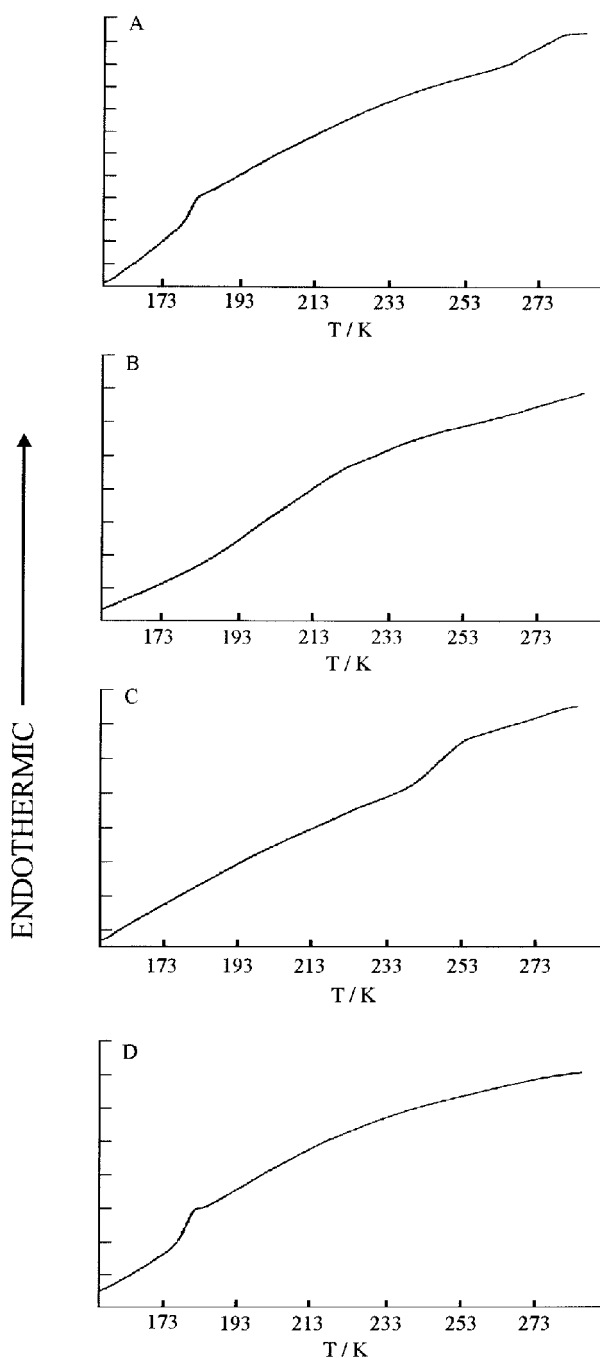


Fig. 13. DSC thermograms for: (A) a mixture of polybutadiene and polymethylpentadiene with a weight fraction of 0.5; (B) pure OB SDC; (C) pure IB SDC; (D) OB SDC mixed with polybutadiene at a weight fraction of 0.5.

interaction parameters; or (ii) allowing the homopolymer radius of gyration to become very large, i.e. suggesting phase separation. Evidence from differential scanning calorimetry supports the latter case because the glass transition of the homopolymer in the mixture was unaltered from that of the pure homopolymer rather than observing a single glass transition temperature that was somewhere between the values for the SDC and the homopolybutadiene. Although this behaviour is consistent with the theoretical

expectation derived by calculating the inverse scattering intensity for such mixtures at large length scales, this finding undermines the quantitative nature of the analysis. The RPA analysis of the scattering data is not valid for these phase-separated systems, and therefore interaction parameters and polymer dimensions determined are not true descriptions of the thermodynamic state of the components in the mixture. Nevertheless, the position of the peak in intensity due to the copolymer did not vary significantly for any of the mixtures as a function of either composition or temperature, and this leads us to conclude that the components within the system are close to their unperturbed dimensions.

### Acknowledgements

We thank the EPSRC for the financial support of the research programme of which this work forms part. CCLRC are also thanked for the provision of the neutron scattering facilities at the Rutherford Appleton Laboratory.

### References

- [1] Lyatskaya Y, Gersappe D, Gross NA, Balazs AC. *J Phys Chem* 1996;100:1449.
- [2] Lyatskaya Y, Balazs AC. *Macromolecules* 1996;29:7581.
- [3] Dadmun M. *Macromolecules* 1996;29:3868.
- [4] Mori K, Tanaka H, Hashimoto T. *Macromolecules* 1987;20:381.
- [5] Balsara NP, Jonnalagadda SV, Lin CC, Han CC, Krishnamoorti R. *J Chem Phys* 1993;99:10011.
- [6] Read DJ. *Macromolecules* 1998;31:899.
- [7] de Gennes PG. *Scaling concepts in polymer physics*. Ithaca, NY: Cornell University Press, 1979.
- [8] Benoit H, Benmouna M, Wu WL. *Macromolecules* 1990;23:1511.
- [9] Benoit H, Hadziiaonnou G. *Macromolecules* 1988;21:1449.
- [10] Read D. PhD Thesis. University of Leeds, 1997.
- [11] Akcasu AZ, Tombaklogu T. *Macromolecules* 1990;23:607.
- [12] Lin CC, Jonnalagadda SV, Balsara NP, Han CC, Krishnamoorti R. *Macromolecules* 1996;29:661.
- [13] Thomas EL, Alward DB, Kinning DJ, Martin DC, Handlin Jr. DL, Fetters LJ. *Macromolecules* 1986;19:2197.
- [14] Herman DS, Kinning DJ, Thomas EL, Fetters LJ. *Macromolecules* 1987;20:2940.
- [15] Uchida S, Ichimura A, Ishizu K. *Polymer* 1999;40:1019.
- [16] Floudas G, Pispas S, Hadjichristidis N, Pakula T, Erukhimovich I. *Macromolecules* 1996;29:4142.
- [17] de la Cruz MO, Sanchez IC. *Macromolecules* 1986;19:2501.
- [18] Zhongde X, Mays J, Xuexin C, Hadjichristidis N, Schilling FC, Bair HE, Pearson DS, Fetters LJ. *Macromolecules* 1985;18:2560.
- [19] Rochefort WE, Smith GG, Rachapudy H, Raju VR, Graessley WW. *J Polym Sci, Polym Phys Ed* 1979;17:1197.
- [20] Fetters LJ, Lohse DJ, Colby RH. In: Mark JE, editor. *Physical properties of polymers handbook*. Woodbury, NY: American Institute of Physics, 1996. p. 336.
- [21] Hutchings LR, Richards RW. *Macromolecules* 1999;32:880.
- [22] Grayce CJ, Schweizer KS. *Macromolecules* 1995;28:7461.
- [23] McMullen WE, Freed KF. *Macromolecules* 1990;23:255.
- [24] Balsara NP. In: Mark JE, editor. *Physical properties of polymers handbook*. Woodbury, NY: American Institute of Physics, 1996. p. 264.
- [25] Bates FS, Wignall GD. *Phys Rev Lett* 1986;57:1429.
- [26] Russell TP. *Macromolecules* 1993;26:5819.

- [27] Lin CC, Jonnalagadda SV, Kesani, Dai HJ, Balsara NP. *Macromolecules* 1994;27:7769.
- [28] Krishnamoorti R, Graessley WW, Fetters LJ, Garner RT, Lohse DJ. *Macromolecules* 1995;28:1252.
- [29] Reichart GC, Graessley WW, Register RA, Krishnamoorti R, Lohse DJ. *Macromolecules* 1997;30:3036.
- [30] Taylor-Maranas JK, Debenedetti PG, Graessley WW, Kumar SK. *Macromolecules* 1997;30:6943.
- [31] Jeon HS, Lee JH, Balsara NP. *Phys Rev Lett* 1997;79:3274.
- [32] Wunderlich B. In: Turi EA, editor. *Thermal characterization of polymeric materials*, 2nd edn. New York: Academic Press, 1997. p. 205 Chapter 2.