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Nuclear Instruments and Methods in Physics Research B 208 (2003) 58–65

NIM B
Beam Interactions with Materials & Atoms

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Small angle neutron scattering and transmission electron microscopy studies of interpenetrating polymer networks from thermoplastic elastomers

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Abstract

The formation of interpenetrating polymer networks (IPNs) may allow the production of materials with controlled morphologies and greater probability of synergistic property enhancement. IPNs were made by the in situ polymerisation/crosslinking of styrene in the dispersed styrene-rich phase of block copolymers with a crosslinked elastomeric matrix. Such networks when optimally prepared can combine stiffness with toughness. In this work the ratio of stiff and hard segments (controlled by styrene/isoprene or butadiene ratio) and morphology have been altered, and two families of block copolymers, with linear and radial structures are compared.

The morphology of a brittle IPN is compared with a tough analogue, using small angle neutron scattering (SANS) and transmission electron microscopy (TEM). The former reveals substantial orientation in the drawn material, whereas the TEM shows similar structures for both.

When radial thermoplastic elastomer IPNs are prepared, the structure is found to be isometric by SANS, as shown by intensity versus scattering vector, *q*, data for sample sections cut in two directions. The linear thermoplastic elastomer IPNs show quite different scattering, consistent with the rod-like dispersed phases previously established by TEM.

The size of the hard, dispersed domains appears to be comparable using TEM and SANS, the latter giving a more sensitive indication of orientation. This possibly reflects the advantages of strong signal generation from a bulk sample, which has undergone little alteration during characterization.

PACS: 61.41.+e; 81.05.Ys; 61.12.−q; 61.16.Bg
Keywords: Interpenetrating polymer networks; SANS; Thermoplastic elastomers; Gamma irradiation; Block copolymers

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1. Introduction

Polymers can be simply blended to improve properties, as occurs in the rubber toughening of brittle thermoplastics. Blending can allow the products to have good mechanical, chemical resistance and ageing behaviour. Methods for combining the advantages of crosslinking (chemical resistance and thermal behaviour) with the ease of processing have also been researched over the past few decades, leading to dynamic vulcanisates and

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0168-583X/03/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0168-583X(03)00883-8

IPNs [1,2]. In the latter case the crosslinked polymer component may exist as dispersions derived from latex precursors (latex IPNs) or may be separated as high glass transition domains within a crosslinked elastomer matrix (thermoplastic elastomer IPNs).

Interpenetrating polymer networks (IPNs) using thermoplastic elastomers (TPEs) as starting materials can form tough and strong composites when nanostructure is controlled. At room temperature TPEs including poly(styrene–butadiene–styrene) (SBS) and poly(styrene–isoprene–styrene) (SIS) behave like crosslinked elastomers, but when heated can be processed like thermoplastics. These styrenic block copolymers undergo microphase separation giving highly ordered microstructures which lead to unique thermal and mechanical properties. The properties of block copolymers are notably different from the constituent homopolymers and random copolymers with the same composition [3]. Block copolymers based on butadiene and styrene with styrene contents of 25–30% such as SB and SBS thermoplastic elastomers are widely used in blends to toughen polystyrene (PS) [4].

Forming IPNs also enables compatibilization between the polystyrene and SBS/SIS, and can impart excellent engineering properties and chemical resistance to the material. IPNs may be considered as two or more polymers in network form, with one network polymerised and/or crosslinked in the immediate presence of the other(s) [5] to give polymer networks with controlled morphologies. If both polymeric components of an IPN are crosslinked then the material is considered to be a full-IPN, however if only one of the two component polymers is crosslinked then this is known as a semi-IPN. IPNs of TPEs exploit the nanoscale phase separation inherent in block copolymers.

Jones et al. reported PS/SBS IPNs [6] with styrene-rich domain diameters of around 20–30 nm. These materials showed good mechanical properties with relatively high fracture toughness which depended on semi- or full-IPN formation and on crosslinking levels in the first step [7]. However some samples embrittled, due to thermal oxidative degradation of the butadiene regions.

In our previous studies (for example [6,7]) we have examined the morphology by TEM of semi- and full-IPNs formed by the in situ polymerisation of styrene in a range of TPEs with varying chemical composition. In that work we found that the overall structure of the constituent TPE was preserved, but the dimensions of the dispersed styrene domains were increased. That work showed increases in fracture toughness as the crosslink density in the butadiene component of the SB and SBS copolymers was increased. In those studies the proportion of hard to soft segments was kept constant, so that changes in morphology were considered important. However increases in miscibility were detected by dynamic mechanical analysis when full-IPNs were compared with semi-IPNs.

Shirodkar et al. made similar IPNs of Solprene™ 475 with polystyrene using γ-radiation at room temperature [8], but the products were confined to that 50 phr oil-extended SBS grade, where the influence of the naphthenic oil was not known. That study demonstrated that highly extendable products could be formed at doses around 20 kGy without yellowing.

The morphology of IPNs is generally complex because they show varying degrees of phase separation, with the phases varying in size, shape and definition at interfaces and degree of continuity [1,9]. Whilst the ultimate performance of any polymeric composite is affected by many variables including composition, crosslink density, interfacial tension, and inter-network grafting, we focus in this work on IPNs in which several variables including crosslink density are controlled and in which the range of starting material TPEs is also limited.

Previously [6,7] we kept total styrene content at approximately 70% but variations are known to be important not only for IPNs [10], but in blends generally [11]. Therefore here in the first part of this study the final total PS content was deliberately varied in a single Kraton™ SIS styrenic block copolymer to give thermally formed semi-I and full-IPNs with styrene contents ranging from 58–87 wt.%.

In the second part of this study, IPNs of SBS and PS were prepared using sequential polymerisation

Table 1
Calculated neutron scattering length densities for the polymer systems involved

Polymer	Density	Neutron (SLD)
Polystyrene	1.04	1.40
Polystyrene (d8)	1.10	6.29
Polybutadiene	1.00	0.46
Poly(styrene-butadiene-styrene)	1.01	0.86

with the primary SBS network being thermally crosslinked and the PS phase formed and crosslinked using γ-radiation, to avoid possible thermal degradation. A total final styrene content of 70% was used, this being the optimum ratio determined in the first section. The structure of the resultant IPNs was then again measured by SANS and TEM. We initially found that enough contrast exists between the polybutadiene/polyisoprene matrix and the polystyrene domains (Table 1) for good SANS patterns, without the need for deuteration.

Whilst we have previously used TEM extensively to characterise TPE IPNs of fixed composition, this is the first time the morphology of these systems has been investigated using both TEM and SANS [12].

2. Role of total styrene content

Kraton™ D 1107, a linear SIS block copolymer stated by manufacturer Shell to contain 14% styrene was crosslinked with different levels of dicumyl-peroxide (Dicup™) and divinyl-benzene (DVB) for full-IPNs. All of the samples were prepared by sequential thermal polymerisation. Various levels of styrene monomer (with or without DVB added) were allowed to diffuse into the crosslinked SIS before thermal polymerisation (and crosslinking) of the styrene. In a separate extensive study of 12 different semi- and full-IPNs Tan [13] showed that the breaking strain becomes very low at total styrene contents ⩾70%, as shown in Fig. 1.

Although a detailed analysis of the mechanical mechanism is beyond the scope of the present paper, we have selected two distinctive IPNs to

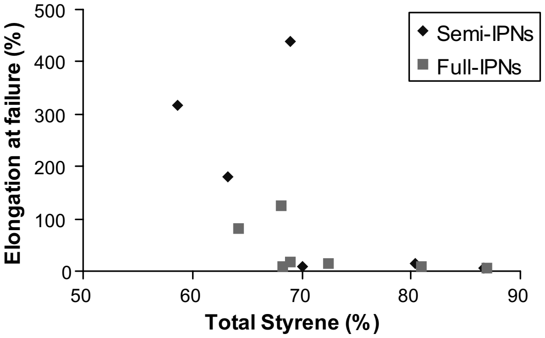


Fig. 1. Change in breaking strain with increasing total polystyrene content. Note the dramatic change in behaviour at 70% total polystyrene.

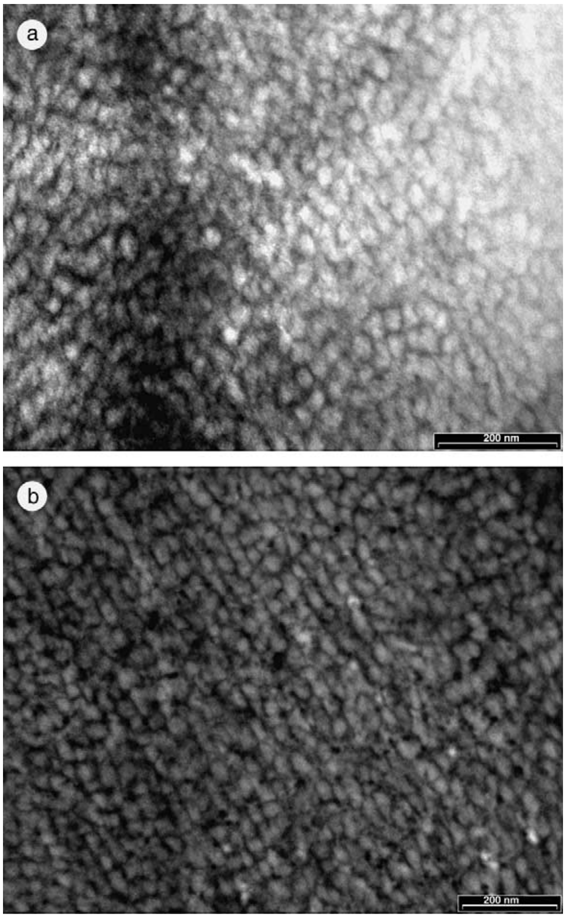


Fig. 2. Electron micrographs of (a) the tough semi-IPN and, (b) the brittle full-IPN. Bar = 200 nm.

illustrate the use of SANS and TEM. The first is a tough semi-IPN ($\sigma_b = 18$ MPa, $\varepsilon_b = 72\%$) with a high level of SIS crosslinking (1.0% Dicup™) and a total PS content of 63%, and the second is a brittle ($\sigma_b = 22.5$ MPa, $\varepsilon_b = 3.5\%$) full-IPN with high SIS crosslinking and 72% PS. During mechanical testing the tough semi-IPN fractured in a ductile manner showing stress whitening and plastic deformation, while the full-IPN showed brittle fracture behaviour with no plastic deformation evident.

Surprisingly, given the difference in total PS content, TEM (Hitachi H-7000) of these two IPNs after microtoming (Reichert Ultracut E) shows similar structures (Fig. 2). Both contain discrete polystyrene phase domains within a continuous (OsO_4 stained) polyisoprene phase. The size of the polystyrene domains ranges from about 45 nm for the tough material and 25–30 nm for the brittle IPN. Here the TEM does not reveal significant changes in structure to explain the difference in fracture behaviour.

The SANS patterns suggest that while the size of the phase domains is broadly similar, the shape of these domains differs between the two samples. Examination of the plot of intensity against the scattering vector q (Fig. 3) shows that although the gross size of the PS domains is of the same order, their structures are significantly different, with the tough IPN having two types of domains. The match in size from TEM and SANS contrasts with the differences reported by Berney et al. [14] who found that measurements of domain size by TEM usually gave smaller results than SANS results.

Results from the 8 m SANS instrument at the National Institute of Standards and Technology (NIST) facility in Gaithersburg (MD) [15] also allowed us to examine the tough semi-IPN in a section that had been elongated by tensile extension and a region that had not been elongated. TEM appeared to give little difference in morphology, although orientation would have lessened during the oven-ageing step needed to cure the embedding resin prior to sectioning. The SANS results however show a clear difference in the structure, with the elongated region of the semi-IPN having major orientation consistent with the 72% strain, as shown in the patterns in Fig. 4.

3. Radiation formed IPNs from radial and linear SBS

The TPEs used were Kraton™ D1101 linear SBS with a butadiene/styrene ratio of 69:31 and Kraton™ D1084 with a radial $(SB)_4$ structure and a B:S ratio of 70:30.

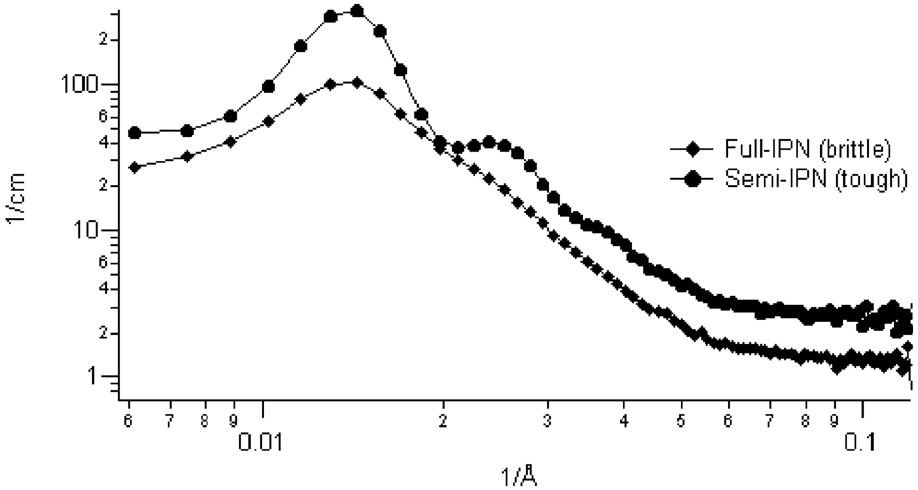


Fig. 3. Plot of intensity against scattering vector (q) for the semi-IPN and full-IPN from neutron scattering pattern collected at NIST.

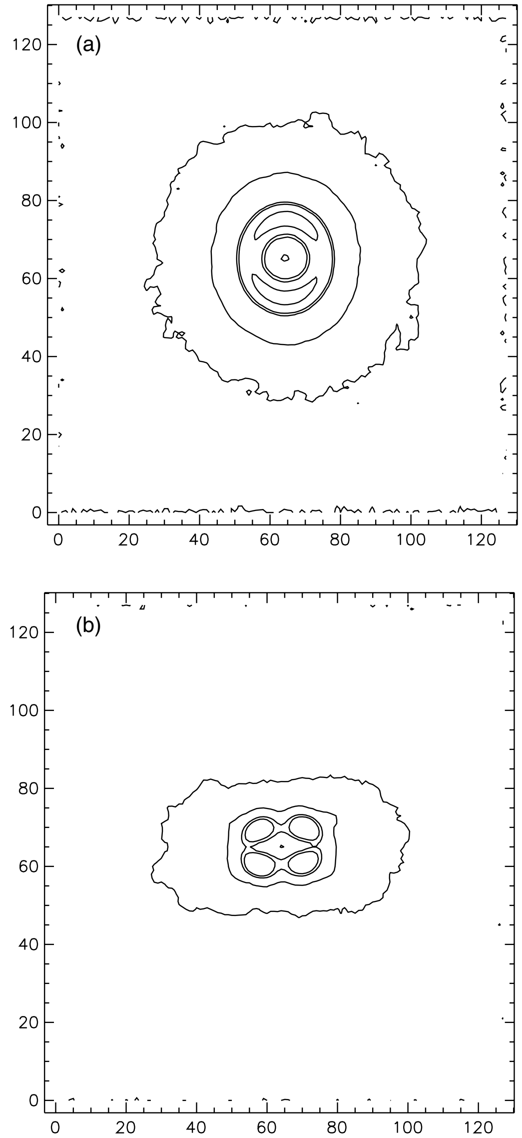


Fig. 4. Contour maps of the small angle neutron scattering from the tough semi-IPN (a) in an unstressed region and, (b) from an elongated region.

Styrene monomer and 10% trimethlolpropane triacrylate (TMPTA) were added to the thermally crosslinked SBS network before room temperature γ-radiation (500 kGy) to polymerise and crosslink the styrene to give 70% total styrene. There is no discolouration indicating that degradation of the butadiene segments has not occurred.

The size of the phase domains was examined using TEM and SANS which both show discrete 20–50 nm polystyrene domains in a polybutadiene continuous phase, as reported before [6].

TEM of the linear structure showed spherical styrene domains in one direction. However images from samples cut in a perpendicular direction show lamella indicating cylindrical domain morphology (Fig. 5).

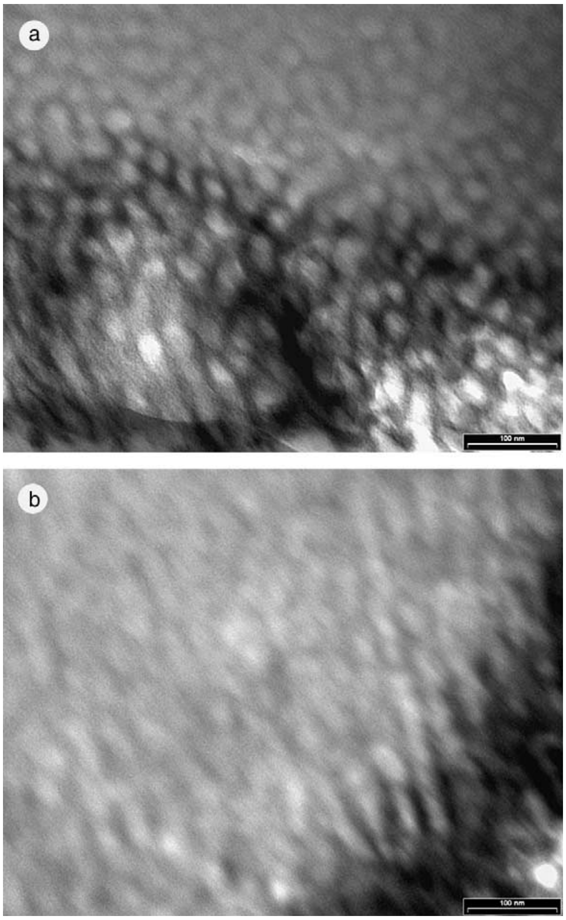
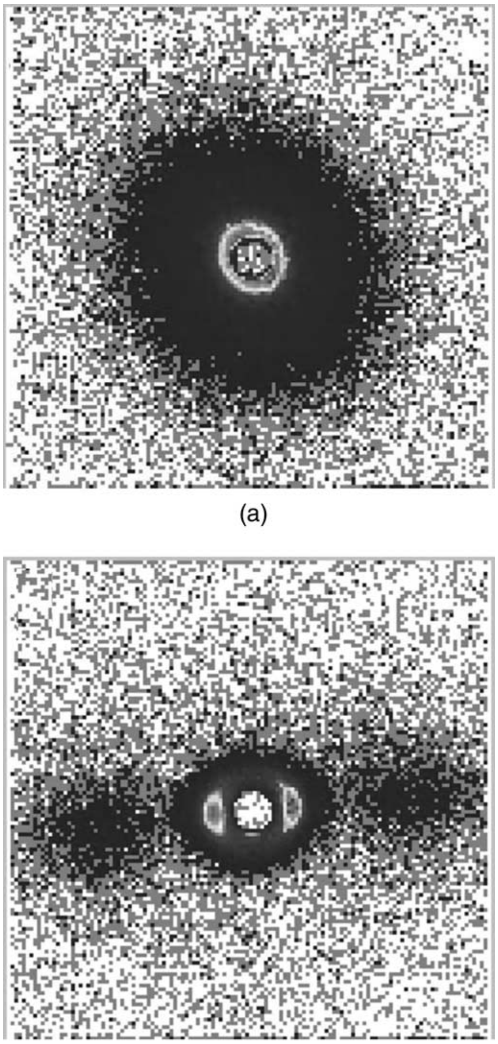


Fig. 5. TEM of a linear SBS based IPN in a (a) normal direction and, (b) in a perpendicular direction. (b) Suggests some oriented lamella, consistent with that given in Jones' work and consistent with the cylindrical space filling mechanism of Meier.


(a)

(b)

Fig. 6. SANS patterns from (a) radial SBS and, (b) linear SBS.

The neutron scattering patterns from the initial linear and radial SBS networks are markedly different as shown in Fig. 6. The IPNs formed from these two base polymers show similar trends. This is consistent with the final nanostructure of the IPN being controlled by the nanostructure of the initial SBS precursor network, as previously shown in [6,7].

The diffraction patterns from the linear SBS-based IPNs suggest lamellae. When TEM data are also included, we conclude that PS cylinders exist in the IPNs. Whilst slight orientation in the radial SBS-based IPNs appears to exist from the SANS results, it is far less evident than for the linear IPNs.

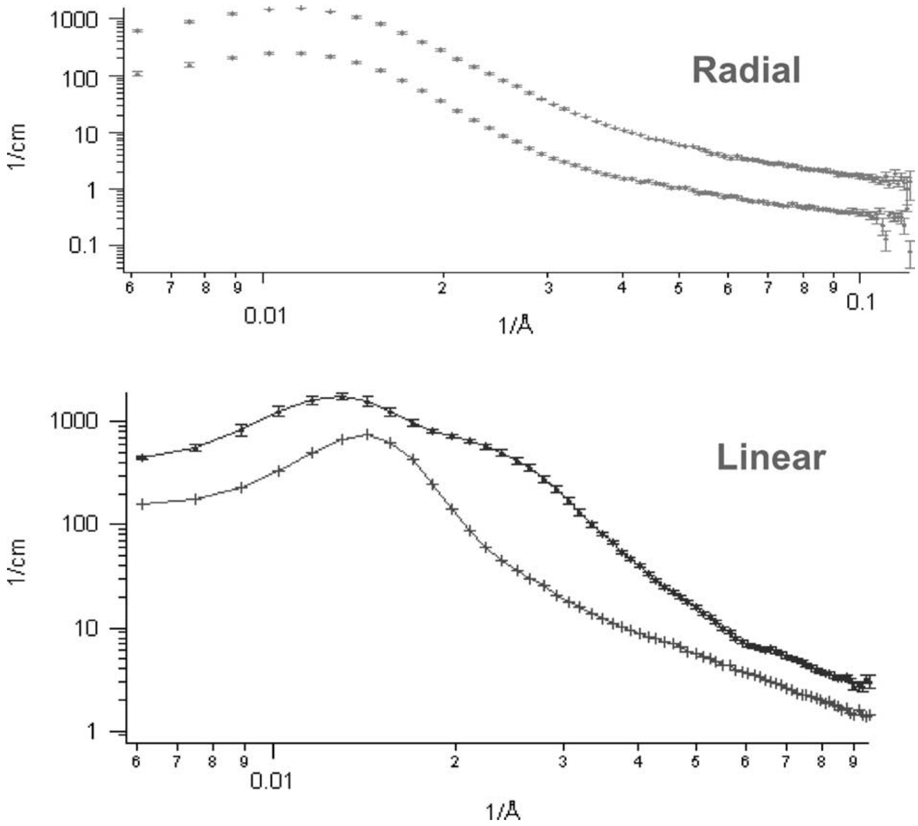
The neutron scattering in two perpendicular directions for similar SBS/PS IPNs was examined at NIST. The radial IPNs showed similar scattering in both directions, whilst the linear IPNs showed different scattering (Fig. 7), supporting a cylindrical structure in the linear IPNs and a more symmetrical structure in the radial IPNs.

Electron microscopy (TEM) provides a visual image of the morphology but is limited to small sections of the sample and requires significant sample preparation. Neutron scattering from SANS requires very little sample preparation although greater processing and interpretation may be needed.

4. Conclusions

Two types of IPNs based on TPEs were examined by TEM and SANS. In the first case, a thermally prepared brittle full-IPN with higher PS content was compared with a semi-ductile IPN with lower PS. Whilst TEM suggests that both unstrained composites have similar nanostructures, SANS indicates that the semi-IPN has two characteristic dimensions, consistent with orientation due to block copolymer rods or lamellae, compared with a single dimension in the full-IPN. The morphology of strained regions of the semi-IPN seems unaltered by TEM, but gives a dramatically altered SANS pattern.

In the second case, IPNs were prepared by irradiating two different TPEs which had been thermally crosslinked. TEM of the IPN from the linear TPE again suggests orientation, but more dramatic evidence is found using SANS. For the radial TPE IPN a similar SANS pattern is found for sections cut in two directions, consistent with the PS domains being spherical, whereas the linear



Radial

Linear

Fig. 7. Sector averaged SANS profiles in two directions for radial and linear SBS based IPNs.

TPE IPN gives two different *I* versus *q* plots, indicating anisotropy. Whilst the characteristic dimensions for each method are of the same order, SANS appears to be a more sensitive method for highlighting orientation in ordered and deformed materials.

Acknowledgements

The authors gratefully acknowledge AINSE (Australian Institute for Nuclear Science and Engineering) for financial support to use the gamma pond facilities. The NIST SANS facilities are supported by the US Department of Commerce and their use for this work is gratefully acknowledged. The valuable assistance of C.J. Glinka and M. Lin (NIST) with the SANS experiments is also acknowledged, together with the contribution of work by former students K.T. Tan, J.J. Jones and B.D. Shirodkar and the personnel in the Electron Microscopy Unit, UNSW.

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