PCCP

www.rsc.org/pccp

PAPER

Shear ordered diblock copolymers with tuneable optical properties†‡

Andrew J. Parnell,[a] Nadejda Tzokova,[b] Andrew Pryke,[c] Jonathan R. Howse,[d]
Oleksandr O. Mykhaylyk,[b] Anthony J. Ryan,[b] Pierre Panine§[e] and
J. Patrick A. Fairclough*[b]

A series of high molecular weight poly(styrene-*b*-isoprene) block copolymers with optical properties defined by composition in a non-selective solvent were studied using simultaneous ultra small angle X-ray scattering (USAXS) and optical spectrometry. A small magnitude shear produces ordered and oriented states in the copolymer solutions that persist for extended periods of time, and also have superior optical properties that are directly attributable to the mesoscopic block copolymer (BCP) morphology. We have demonstrated that the optical transmission of these materials can be tuned by the addition of low molecular weight poly(isoprene) and poly(styrene) to swell their respective domains within the diblock copolymer. The optical transmission peak for the diblocks could be tuned; from 380 nm–440 nm for the 670k diblock, 425 nm–540 nm for the 850k diblock and 541 nm–625 nm for the 1 million diblock by altering the solution concentration and composition. The full width at half maximum that can be achieved for the optical transmission peaks is as small as 15 nm at 473 nm with a $\Delta\lambda/\lambda$ of 0.03, highlighting the high quality ordering in these systems. Also a small shift in the transmission peak wavelength was observed across a wide angle of view (15 nm at 30°) suggesting that these materials could be used for large area narrow band optical filters.

Introduction

Block copolymers have generated a great deal of interest as materials for photonic crystals due to their ability to self-assemble into a variety of 1D, 2D, and 3D periodic structures.[1–5] The principal advantages of block copolymer systems over colloidal systems (considered as prime candidates for photonic applications) are their large area fabrication potential and low overall cost. Colloidal systems have inherent problems and are troublesome in many ways; normally a face-centered cubic (fcc) lattice is built up from monodisperse polymer or silica spheres with diameters in the submicron range. Methods such as sedimentation and drying of these dispersions usually lead to small, thin specimens, which can contain defects and stacking faults due to the competition between fcc and hcp ordering. Also the long range ordering is difficult to control resulting in polycrystalline domains.[6]

In contrast, well ordered block copolymers structures can be made *via* self-assembly with a number of possible morphologies. Many authors have reported the use of block copolymers with solvent or metal particulate diluents to increase the reflected wavelength into the optical region, by increasing the refractive index difference between the layers.[7,8] In the Maxwell–Garnett theory, particles much smaller than the wavelength of light can be used to increase the refractive index of a phase, as the total refractive index is an average of the particles and the matrix. A major issue with this work is the difficulty in assembling the particles in just a single phase.[7,9] In the final application for a photonic structure solid films are generally preferred, as a result most workers have concentrated on the solid state properties of these systems where the film is first cast from a solvent and the solvent is then removed. In general this leads to a broadening of the transmission window as the structures dry (see ESI†, Fig. S1). This is primarily because the drying process is difficult to control, particularly for large areas, and small differences in solvent gradients make the production of uniform films challenging, consequently

[a] *Department of Physics and Astronomy, University of Sheffield, Sheffield, S3 7RH, UK*
[b] *Department of Chemistry, University of Sheffield, Brookhill, Sheffield, S3 7HF, UK. E-mail: p.fairclough@sheffield.ac.uk*
[c] *The Polymer Centre, Dainton Building, University of Sheffield, Brookhill, S3 7HF, UK*
[d] *Department of Chemical and Process Engineering, University of Sheffield, Sheffield, S1 3JD, UK*
[e] *European Synchrotron Radiation Facility, F38043, Grenoble, France*

This journal is © the Owner Societies 2011

Phys. Chem. Chem. Phys., 2011, **13**, 3179–3186 | 3179

non-uniform drying leads to buckling of layers and defects in the final dry film structure. The casting of these films can also be a lengthy process taking hours to days depending on the solvent used, less volatile solvents such as Cumene giving the best results.[10] In practice processing stages such as these would prohibit their use on a commercial basis. The principal challenges that remain to be overcome with these materials are: firstly the ability to easily control the length scale over a wide wavelength range, in the optical region, with narrow transmission peaks and secondly optimising these materials for displays and photonics over large areas.

The simplest example of a photonic structure is that of a dielectric multilayer stack often called a Bragg mirror. The reflected wavelength depends upon the optical thickness of each layer and is given by the following equation:

$$\lambda = 2 \sum_{i=1}^{N} n_i d_i \qquad (1)$$

where λ is the first order reflected wavelength, N is the number of sublayers in each layer and n_i and d_i are the refractive index and the thickness of sublayer i, respectively. In polymer systems the refractive index difference between each layer is normally small compared to that which can be achieved by inorganic materials and metals. However, the intensity of the reflected wavelength can be raised by increasing the overall number of layers.[11] For the diblock polystyrene–polyisoprene (PS–PI) copolymer system used in this study; poly(isoprene) has a refractive index (RI) of 1.50 and poly(styrene) has an RI of 1.59. This small refractive index difference becomes optically significant as the number of layers is increased.

The interactions between the blocks of a block copolymer are characterized by the Flory–Huggins interaction parameter, χ_{AB}, and the total number of segments $N = N_A + N_B$. In practice the degree of polymerization is normalized to the volume of a given monomer and this is often represented as r_v, a volume normalized degree of polymerization.[12] Depending on the composition of the block copolymer (the volume fraction of each block), microphase-separated block copolymers can form various morphologies; primary amongst these are hexagonal rod phase, lamellar and gyroid.[13,14] The simplest type of block copolymer is a linear A–B diblock made up of two distinct immiscible polymer chains. These form microphase-separated structures in which domains consisting of one block are separated by domains of the second block from a narrow interfacial region of the order of a few Ångstroms. For a symmetric diblock with a 50 : 50 volume fraction, the system will self-assemble into a periodic lamellar structure in the strong segregation limit. Recently work has also looked at the synthesis and tailoring of bottle brush polymers, where a linear chain with dense branches will also self-assemble into lamellar domains with tunable optical properties depending on the backbone length and density of combs along the chain.[15–17]

In this work, regions of the phase diagram, along with the optical properties, for two high molecular weight symmetric diblock copolymers of poly(styrene-b-isoprene) are explored (670k M_w and 850k M_w). The copolymers were studied using ultra small-angle X-ray scattering (USAXS) and optical transmission measurements. USAXS was employed to detect large domains of structural organization, which cannot be resolved by conventional SAXS measurements. This work has focused on exploring a section of phase space for two symmetric high molecular weight diblock copolymers. Oscillatory shear was used to order the systems, as it is a well-established means of aligning block copolymers in the bulk.[18] Shear induces order into the polymer solutions over large areas (10 cm^2), which facilitates structural analysis of the polymers.

Experimental section

The PS–PI polymers were synthesized using vacuum anionic techniques.[19,20] Reactions were carried out in benzene (Aldrich) purified by degassing and stirring over living polystyryllithium for 24 h, and initiated with known quantities of *tert*-butyl-lithium in cyclohexane. Monomers were purified as follows: Styrene (Aldrich) by degassing and stirring over di-n-butyl-magnesium for 24 h, isoprene by degassing and stirring over n-butyllithium. Each block was polymerized at room temperature with a 24 h reaction time for the styrene block and 72 h for the isoprene block. The final living polymer was terminated with an excess of degassed methanol added *via* an ampoule fitted with a glass dome type breakseal. The reaction mixture was then allowed to stand with periodic agitation for 2 days to ensure complete termination before the polymer was isolated by pouring into methanol containing a small amount of antioxidant. Purified polymers were then dried under vacuum at room temperature to constant weight before further analysis by GPC and ^{1}H NMR was carried out. Table 1 lists the materials used in the study along with molecular weight and polystyrene volume fractions for the diblocks. The block copolymer solutions were prepared by dissolving the appropriate amount of block copolymer in *o*-xylene and allowing the polymer to dissolve for an extended period of a week, periodic agitation was performed until the solutions were homogeneous. For some of the blends, homopolymer was added following the protocol above.

Table 1 Weight and number averaged masses of the block copolymers and homopolymers used in this study

Sample	M_w/g mol^{-1}	M_n/g mol^{-1}	PDI	PS^a weight fraction, W_{PS}	PS volume fraction, f_{PS}	Molar volume/cm^3
BCP670	676k	517k	1.31	52	0.49	87.9
BCP850	852k	657k	1.30	47	0.44	86.6
BCP1M	1174k	844k	1.39	52	0.49	87.9
I1	10.6k	10.4k	1.02	0	0	74.0
S1	10.5k	9.3k	1.13	100	100	99.0
o-Xylene	—	—	—	—	—	122.0

^{a} Polystyrene is abbreviated to PS in the table.

The USAXS experiments were performed at the European Synchrotron Radiation Facility (Grenoble, France) at the station ID02 (energy $E = 12.5$ keV, cross-section of the beam 200×200 μm^2, image intensified FreLoN CCD detector).[16] The USAXS experiment was carried out in order to study the structures of the shear ordered high molecular weight block copolymers. The samples were confined between two flat glass slides separated by a spacer of 0.1 mm thickness and an oscillatory shear was applied before being mounted on the beamline with the shear direction oriented vertically. The action of shearing the samples was performed manually and as such the magnitude of the shear required to order the solutions was low, the frequency of shear was 1–3 Hz with an amplitude of approximately 10 mm. The sample surface was either at $30°$ or $90°$ in relation to the X-ray beam and the data were acquired for 0.3–0.5 s. The raw data were subjected to detector flat field, dark current, flux and sample transmission correction. The peak positions were determined from 1D scattering curves obtained by sector integration of 2D USAXS patterns using Fit2D software.[21]

The USAXS experiment was performed simultaneously with the optical transmission measurements. The spectro-photometer used was a UCB 2000, from Ocean Optics Inc., equipped with an FO-6000 fibre optics light source. Two fibre optic cables, one attached to the light source and another to the spectrometer, were aligned perpendicularly to the sample surface. The light impinged on the sample at the same spot as the X-rays, although the cross section of the light beam was larger than the X-ray beam cross-section and so the spectroscopy data are in fact averages over a larger area of the sample. Background correction for the dark current of the spectrometer was acquired and a baseline correction was performed at the beginning of each measurement.

The light source for the angular transmission measurements was a collimated Tungsten lamp. The transmission spectra were measured using a Shamrock ANDOR spectrograph with a wavelength range of 400 nm to 900 nm using an air cooled CCD; the acquisition time for each measurement was 0.25 s.

Results and discussion

Ultra small angle X-ray measurements (USAXS)

The USAXS scattering patterns displayed in Fig. 1 for the 850k PS–PI diblock copolymer are a representative data set highlighting the main effects for these systems. The increase in block copolymer concentration is mapped in the vertical direction, from A to E. In the horizontal direction the addition of homopolymer is indicated; the S series being the addition of homopoly(styrene) and the I series the addition of homopoly-(isoprene). In the diagonal direction is the addition of both homopolymers with equal concentrations to a fixed amount of diblock copolymer.

The low concentration copolymer sample of 7.6 wt% copolymer in solution gives a disordered USAXS pattern labelled A, and also shows no peak in the optical spectra, therefore demonstrating that the mesoscopic ordering is the cause of the novel optical properties, these appear as the BCP concentration is increased. For the lamellar phases the
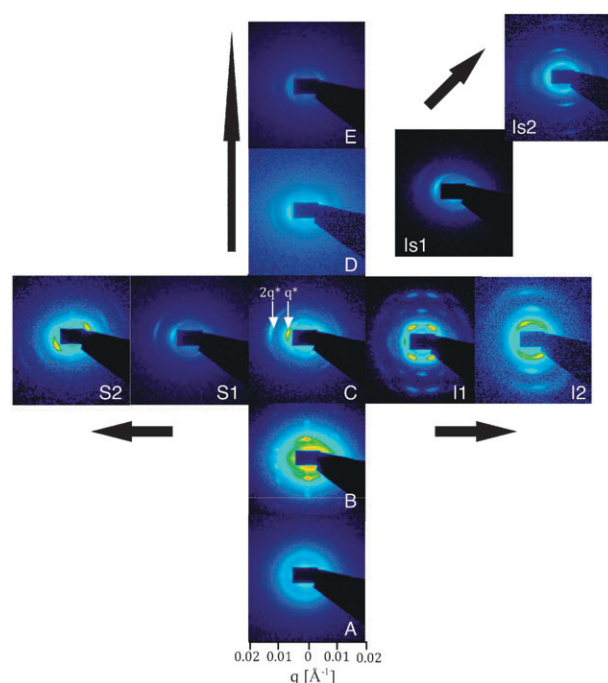

Fig. 1 Ultra small angle X-ray scattering patterns for a symmetric 850k M_w poly(styrene-b-isoprene) diblock copolymer. The series A through E is increasing weight percent of diblock copolymer: A (7.6 wt%), B (10 wt%), C (15 wt%), D (17 wt%) and E (20 wt%). The I series is the addition of low M_w poly(isoprene) and series S is the addition of low M_w poly(styrene): I1 (4 wt% PI), I2 (8 wt% PI), S1 (2 wt% PS) and S2 (6 wt% PS). The IS series is the addition of equal amounts of low M_w poly(styrene) and poly(isoprene): IS1 (2 wt% PS and PI) and IS2 (10 wt% PS and PI). All images were collected from samples with the sample surface rotated at $30°$ in relation to the beam direction.

scattering patterns (as the weight percent of polymer is increased) show peaks in intensity at $q*$ and $2q*$ from the oriented layers of the block copolymer. The small region of the phase diagram mapped out shows the effects of increasing block copolymer concentration and the addition of low molecular weight poly(styrene) and poly(isoprene) (both having an M_w of ~ 10k). The scattering patterns in series A through E (Fig. 1) show the effect of increasing diblock copolymer concentration from an initially disordered state in A (7.6 wt% solution) through to a metastable hexagonal perforated lamellar (HPL) phase in B (10 wt%). At a weight percent of 10% diblock copolymer the system has become ordered with a metastable hexagonal perforated lamellar (HPL) phase. The stretched reflections in the scattering pattern of this phase suggest the presence of stacking faults in the packing of the perforated layers.[21] Further measurements are required to confirm this; according to the well established phase diagram of PS–PS diblocks this is where this phase should be. This is followed by well ordered lamellar phases in C (15 wt%), D (17 wt%) and E (20 wt%). According to the well established phase diagram for PS–PI block copolymers and calculating the effective solution inter-action parameters for our diblocks, that is the $\phi\chi N$ for our system (where ϕ is the volume fraction of polymer),[3] the phase space between the disordered state and the HPL phase is conventionally Ia3d gyroid structure for this system, although

we did not observe this for the 850k BCP. The calculated effective interaction parameters ($\phi\chi N$) values are 91 and 116 for the 670k and 850k systems, respectively (both at 15% by weight). The lower boundary for the effective solution interaction parameter $\phi\chi N$ was 45 for the 670k polymer solutions and 58 for the 850k polymer o-xylene solutions at 7.5 weight percent. The calculated effective solution interaction parameters for the systems are listed in Table S1, ESI.†

850k Block copolymer

The domain spacings for the pure block copolymer lamellar structures in C, D and E are 169 nm, 171 nm and 178 nm, respectively. The wavelength of the optical transmission peak is approximately 3 times the domain spacing of the diblock microstructure for the lamellar systems, which is consistent with estimations made from equation (1). The increase in domain size for increasing polymer concentration reflects the enhancement of the segregation between the PS and PI chains. This has previously been seen for low molecular weight PS–PI diblock copolymers by Hashimoto *et al.*[22] This is contrary to what one would naively expect. As solvent is removed, or polymer added, the exponent in the domain length scaling increases. In the weak segregation regime, the interactions are diluted by the solvent as $d \approx N^{\frac{1}{2}}$. However as solvent is

Fig. 2 The scattering pattern for a solution of 850k M_w PS–PI diblock (15% by weight) and poly(isoprene) (4% by weight) in o-xylene. The sample surface was either rotated at 30° (A) or 90° (B) in relation to the beam direction. The USAXS pattern is indexed using hexagonal axes.

removed the system enters the strong segregation regime; the domain length now scales as $d \approx N^{\frac{2}{3}}$.

The added low molecular weight poly(styrene) 2% PS and 6% PS also exhibit lamellar structure with domain sizes of 159 nm and 169 nm respectively. The addition of low molecular weight poly(isoprene) in I1 (4wt% homo PI) and I2 (8 wt% homo PI) to a 15% solution by weight of diblock copolymer results in non-lamellae phases showing that the system is not entirely symmetric. In frame I1 of Fig. 1 the hexagonal rod phase was observed for the 850k M_w diblock system upon the addition of 4% by weight low molecular weight poly(isoprene) (10k molecular weight). This frame is also reported in Fig. 2A along with indexing to verify the structure as hexagonal rods. The USAXS measurements revealed a well-ordered structure (Fig. 2A and B) with peaks corresponding to multiples of the initial peak q^* value, $1: \sqrt{3}: \sqrt{4}: \sqrt{7}: \sqrt{9}$. The systematic absence of the 02 reflection (corresponding to $\sqrt{4}$) in the patterns for the sample oriented normal to the beam (Fig. 2B) is caused by the overlapping of the reflections with the position of the minimum in the form factor of the cylinders. The hexagonal rod phase still exhibits some optical transmission with a peak at 486 nm (data not shown).

670k Block copolymer

In Fig. 3 we show an exploration of phase space for the 670k molecular weight PS–PI block copolymer. The general behaviour for this system is similar to that seen in Fig. 1. The initially disordered low concentration solutions of 7.5 weight percent block copolymer in o-xylene in frame A of Fig. 3 shows no order and so consequently has no structural effect on the optical transmission of the material. As the BCP concentration is increased the system shows ordered lamellar phases with domain sizes around 130 nm, giving a range in the peak optical transmission spectra of 380 nm–415 nm depending on diblock copolymer concentration.

The domain sizes and optical transmission values and BCP phases for the 670k solutions are listed in Table 3. The hexagonal rod phase was also observed, both for the separate addition of homopoly(styrene) and homopoly(isoprene), at 8 wt% added homopolymer, showing that there is symmetry in this region of phase space, unlike the 850k diblock, which has a larger asymmetry between the two blocks.

The USAXS pattern in Fig. 4 shows a highly ordered lamellar structure for the 15 wt% block copolymer with added poly(styrene) and poly(isoprene) homopolymers, both at 10% concentration by weight. Six orders of lamellar peaks can be seen in the integrated one dimensional data in Fig. 4C. The time between shear ordering the sample and measuring the scattering from the sample using USAXS was approximately 3–5 minutes and in this time the sample still maintains a high degree of order, as evidenced by the USAXS patterns in Fig. 4A and B. The shear-induced order is persistent and does not disappear from the sample after an hour (Fig. 4B). The change in the intensity of the peaks together with shift of their positions towards small q-values after an hour (Fig. 4C) is probably caused by some loss of solvent and increase in the segregation strength in the system. This relaxation process
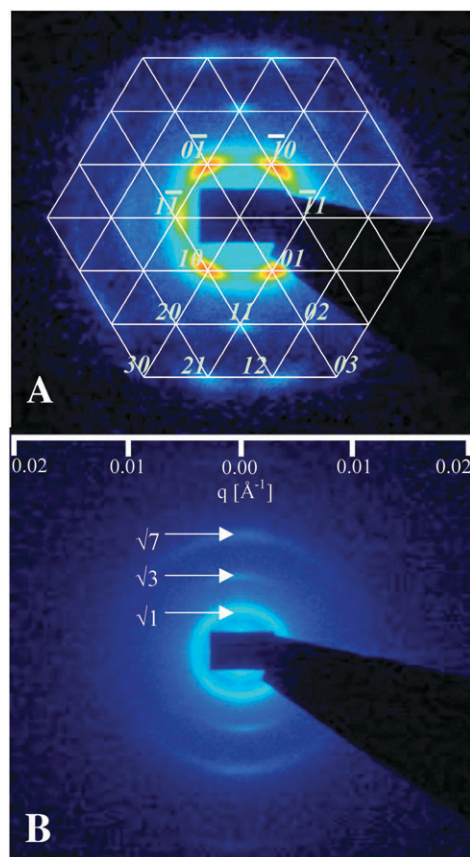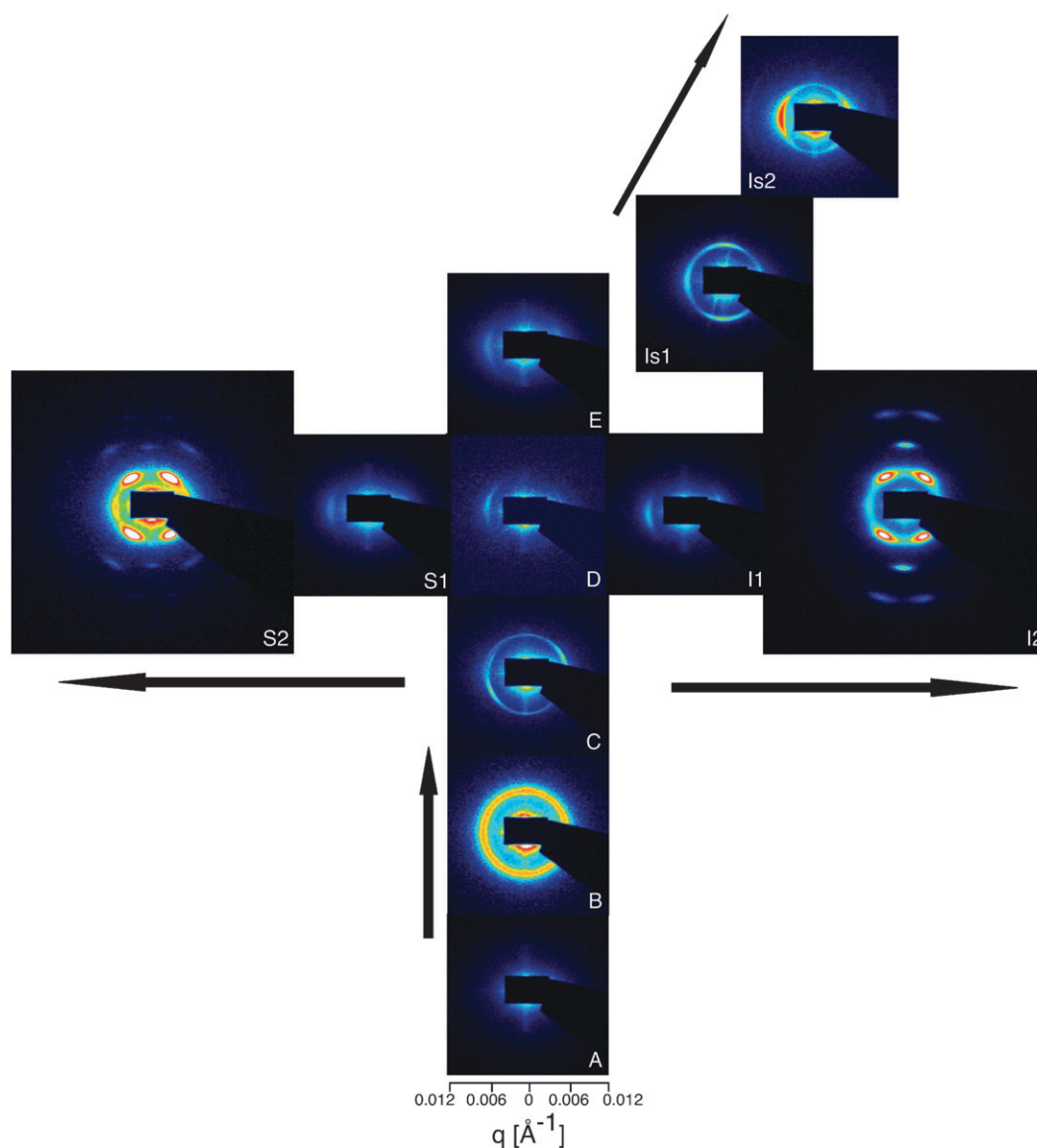
Fig. 3 Ultra small angle X-ray scattering patterns for a symmetric 670k M_w poly(styrene-*b*-isoprene) diblock copolymer in *o*-xylene. The series A through E is increasing weight percent of diblock copolymer: A (7.5wt%), B (10wt%), C (12.5wt%), D (15 wt%) and E (17.5 wt%) all in the solvent *o*-xylene. The I series is the addition of low M_w poly(Isoprene) and series S is the addition of low M_w poly(styrene): I1 (4 wt% PI), I2 (8 wt% PI), S1 (4 wt% PS) and S2 (8 wt% PS). The IS series is the addition of equal amounts of low M_w poly(styrene) and poly(isoprene): IS1 (2 wt% PS and PI) and IS2 (8 wt% PS and PI). All images were collected from samples with the sample surface rotated at 30° in relation to the X-ray beam direction.

could be overcome by using suitable encapsulation methods or by crosslinking of the solvent matrix, immediately after shear ordering.[23] The sample setup used for collecting the USAXS data was not sealed and as such there will be some amount of evaporation/drying of the sample on this longer timescale.

Optical properties

The ordered structures of the 850k M_w PS–PI block copolymer shown in Fig. 1 and listed in Table 2 show the effect of increasing the block copolymer concentration on the mesoscopic structure. The optical properties of ordered pure BCP lamellar structures are displayed in Fig. 5. The effect of increasing the weight percent of pure BCP on the transmission peak results in

an increase in the reflected peak optical wavelength from 425 nm to 520 nm.

The optical measurements were taken simultaneously with the USAXS data and so allow us to correlate the block copolymer domain sizes with the optical properties. At low block copolymer concentrations the system is disordered and shows no peak in the transmission. At a weight percent of 10% diblock copolymer the system has become ordered with a metastable hexagonal perforated lamellar (HPL) phase in B. However, this structure has a peak in the transmission at 425 nm, albeit with only 30% transmission. Increasing the concentration to 20% gives a domain spacing of 178 nm and a transmission peak centered on 517 nm. The disagreement in the progression between the 17% and 17.4% solution is most
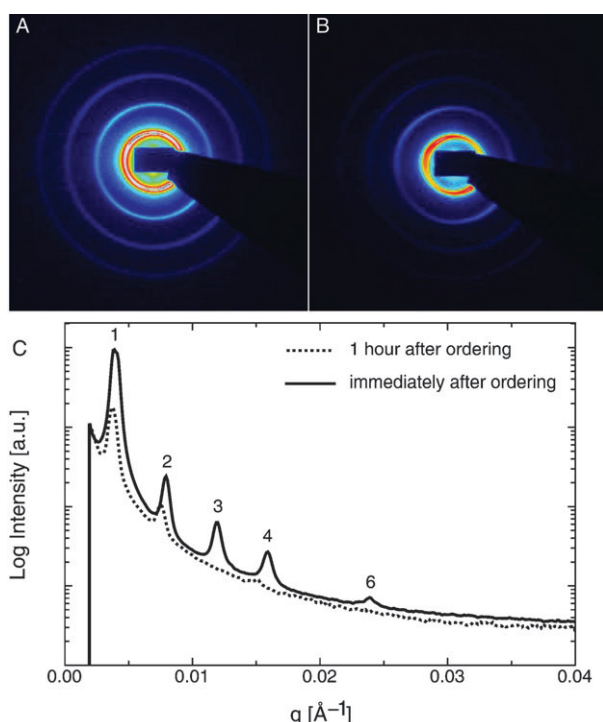
Fig. 4 Ultra small angle X-ray scattering patterns for a symmetric 670k M_w poly(styrene-b-isoprene) diblock copolymer 15% by weight in o-xylene with the addition of equal amounts of low M_w poly-(styrene) and poly(isoprene) both at 10% by weight. Making a total polymer weight percent of 35%. The data in figure (A) were taken immediately after the shear ordering and in (B) after an hour has elapsed. The integrated intensity for both scattering patterns is plotted in (C). The diffraction peaks corresponding to lamellar structure are indexed.

Fig. 5 Transmission spectra for the 850k M_w PS–PI diblock copolymer ordered lamellar layers as the diblock copolymer solution concentration is increased from 10% to 20% by weight in o-xylene.

percent solution composition of added homopolymer with a range of over 40 nm. It would be possible to select a particular wavelength over a certain range for a specific application. The transmission peak for the 10 wt% added homopolymer composition shows a very broad tail at lower wavelengths due to macrophase separation of the block copolymer and the homopolymer, which can be seen in Fig. 1 part IS2 as there are two lamellae present.

The USAXS scattering patterns and the simultaneous optical data show the correlation between the domain spacing and the optical properties of these materials (Fig. 5 and 6). The narrow optical transmission peaks in Fig. 5 are due to the highly ordered state of the block copolymer morphology after shearing. The addition of low molecular weight homopolymer(s) to the block copolymer can be utilised to achieve increased length scales via the swelling of individual domains with their associated homopolymer.[24–26] Visible wavelength dielectric mirrors can be achieved using high molecular weight diblock and homopolymer blends. Although the current literature has focused on dried block copolymer films that have very broad relative peak widths, $\Delta\lambda/\lambda$, in the range of 0.15–0.25,[8,27] in our

likely due to a small error in the sample preparation, the difference between the two solutions being only ~ 3 nm in their optical spectra.

The transmission spectra for the addition of equal amounts of homopolymer to a 15 wt% solution of 850k M_w block copolymer in o-xylene is shown in Fig. 6. There is an increase in the peak wavelength going from 498 nm without homo-polymer to 550 nm with 10 wt% added homopolymer. The high degree of tunability can be seen for the 4, 6 and 8 weight
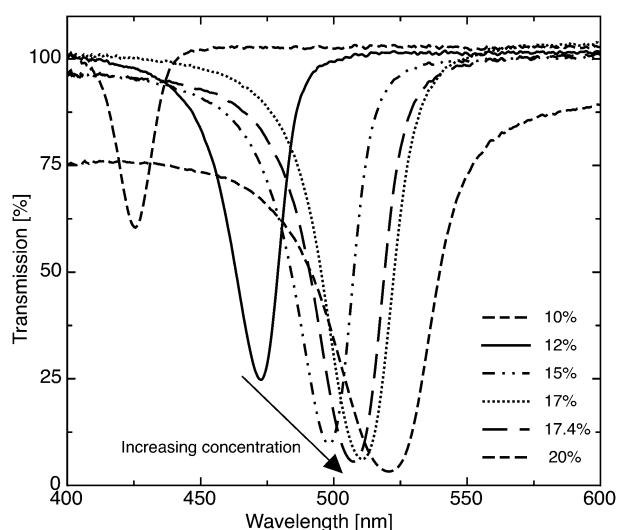
Table 2 The measured domain spacings, their corresponding peak optical wavelength and the morphology seen for the various 850k M_w block copolymer solutions

850k M_w BCP solution composition in o-xylene	Period measured by USAXS, d	Peak in the optical transmission spectra, t	BCP phase	Ratio of $\frac{t}{d}$	Polystyrene volume fraction, V_{PS}
7.6%	—	—	Disordered	—	0.44
10%	153 nm	425 nm	Perforated lamellar	2.8	0.44
15%	169 nm	496 nm	Lamellar	2.9	0.44
17%	171 nm	509 nm	Lamellar	3.0	0.44
20%	178 nm	517 nm	Lamellar	2.9	0.44
15% + 4% PI	159 nm	468 nm	Hexagonal rods	2.9	0.34
15% + 8% PI	158 nm	476 nm	Lamellar	3.0	0.28
15% + 2% PS	159 nm	480 nm	Lamellar	3.0	0.50
15% + 6% PS	169 nm	481 nm	Lamellar	2.8	0.59
15% + 2% PS and PI	168 nm	494 nm	Lamellar	2.9	0.44
15% + 10% PS and PI	181 nm	542 nm	Lamellar and phase separation	3.0	0.46

3184 | *Phys. Chem. Chem. Phys.*, 2011, **13**, 3179–3186

This journal is © the Owner Societies 2011

Table 3 A table of the measured domain spacings, their corresponding measured optical peak and the morphology seen for the various 670k M_w block copolymer solutions

| 670k M_w BCP solution composition in o-xylene	Period measured by USAXS, d	Peak in the optical transmission spectra, t	BCP phase	Ratio of $\frac{t}{d}$	Polystyrene volume fraction, V_{PS}
7.5%	—	—	Disordered	—	0.49
10%	116 nm	—	Lamellar	—	0.49
12.5%	126 nm	378 nm	Lamellar	3.0	0.49
15%	127 nm	403 nm	Lamellar	3.2	0.49
17.5%	134 nm	414 nm	Lamellar	3.1	0.49
15% + 4% PI	134 nm	414 nm	Lamellar	3.1	0.38
15% + 8% PI	139 nm	406 nm	Hexagonal rod phase	2.9	0.31
15% + 4% PS	130 nm	405 nm	Lamellar	3.1	0.59
15% + 8% PS	143 nm	414 nm	Hexagonal rod phase	2.9	0.66
15% + 2% PS and PI	133 nm	402 nm	Lamellar	3.0	0.48
15% + 8% PS and PI	144 nm	437 nm	Lamellar	3.0	0.48
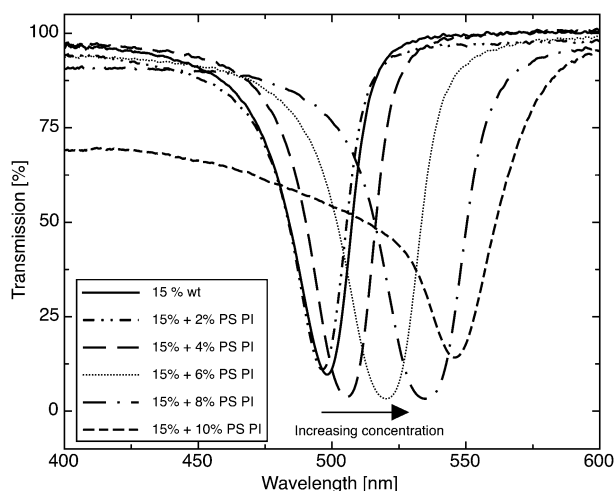
Fig. 6 Transmission spectra for the 15% by weight 850k M_w PS–PI diblock copolymer in o-xylene with the addition of equal amounts of homo poly(styrene) and homo poly(isoprene), these are also by weight.

Fig. 7 Transmission spectra for the 670k M_w PS–PI diblock copolymer ordered lamellar layers as the diblock copolymer solution concentration is increased from 10 wt% to 20 wt% in o-xylene.

systems we have relatively narrow reflection peaks with full width at half maximum values within 15 nm ($\Delta\lambda/\lambda \approx 0.03$), indicating good ordering and constant layer thicknesses of the lamellae. This value is comparable with conventional opal systems, which are not tunable and require intricate preparation routines when compared to these block copolymer systems. Although in our system as the total amount of homopolymer content increases, the width of the reflected peak broadens and the total reflection is seen to decrease due to the phase separation of the homopolymer and the diblock. This is seen in the phase diagram as two oriented lamellae due to the onset of macrophase separation of block copolymer and homopolymer rich regions. This occurs, as the homopolymer becomes a larger constituent of the blend as seen in frame IS2 of Fig. 1. In this formulation the homopolymer is 20% by weight and 15% diblock. The degradation in the optical properties can be seen clearly in Fig. 6, the peak for the 10 wt% added PS and PI has an asymmetry with reduced transmission at low optical wavelengths.

The optical properties of the 670k M_w symmetric PS–PI diblock are shown in Fig. 7 and 8. In Fig. 7 increasing the concentration of diblock from 12 wt% up to 20 wt% moves the transmission peak from 380 nm to 430 nm for the 20 wt%
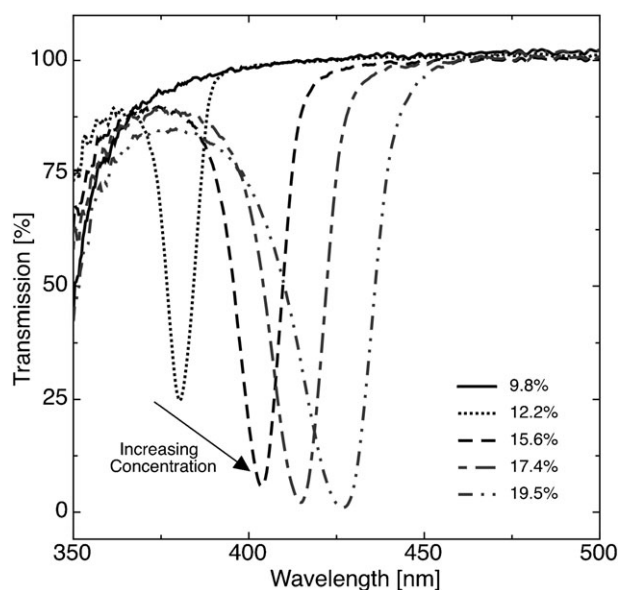
o-xylene solution. The 9.8 wt% sample shows no peak in the optical spectrum but this probably is due to the lack of intensity below 370 nm from the light source.

The equal addition of homopolymer to the 670k M_w BCP seen in Fig. 8 produces a wavelength range from 400 nm up to 475 nm before the peak broadens and there is the onset of macrophase separation. Further optical data for the addition of the two homopolymers can be found in the ESI†, in Fig. S3 the addition of homo poly(isoprene) and Fig. S4 the addition of homo poly(styrene). The angular properties of two of the pure block copolymer (670k and 850k) solutions were also studied as a function of incident angle. The data in Fig. 9 show that as the incident angle is increased the wavelength shifts to shorter wavelengths (see eqn (2)) consistent with the behaviour of a Bragg stack. Where θ is the incident angle and n_e is the effective refractive index of the medium.

$$\lambda' = \lambda \left(1 - \left(\frac{\sin\theta}{n_e} \right)^2 \right)^{\frac{1}{2}} \qquad (2)$$
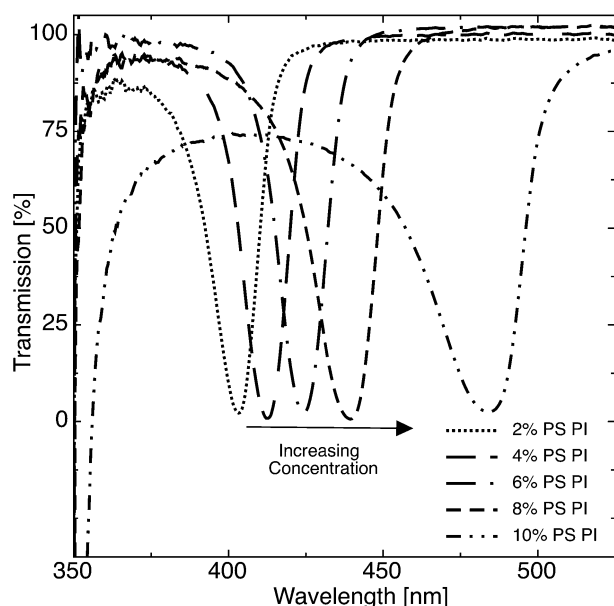
This journal is © the Owner Societies 2011

Phys. Chem. Chem. Phys., 2011, **13**, 3179–3186 | 3185

Fig. 8 Transmission spectra for the 15 wt% by weight 670k M_w PS–PI diblock copolymer solution with the addition of increasing wt% of homo poly(styrene) and homo poly(isoprene).
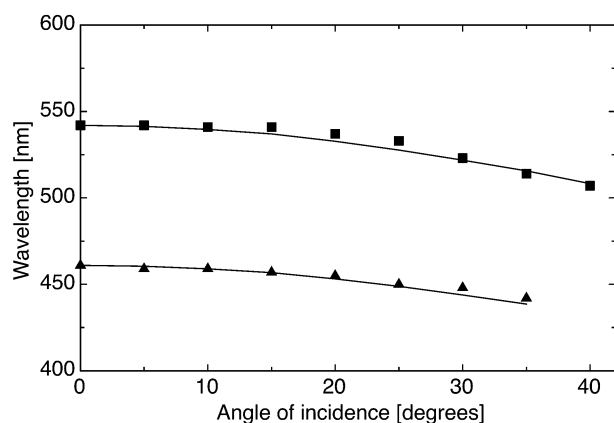

Fig. 9 The shift in transmission peak wavelength as a function of incident angle. The squares correspond to the 850k M_w diblock copolymer and the triangles to the 670k M_w diblock. The black lines are fits to the data using eqn (2).

The 670k M_w diblock has a shift from 461 nm to 442 nm at an incident angle of 35°. The 850k M_w diblock has a shift from 542 nm to 507 nm at 40°. At low angles of around 10° both copolymers exhibit small shifts of only 10 nm. This could make them useful in displays where viewing angle is important.

Conclusions

In this study we have examined optically significant regions of the phase diagram for a series of high molecular weight symmetric block copolymers of poly(styrene-b-isoprene) using USAXS and optical spectroscopy. A number of well ordered phases were observed for various weight percent solutions with and without added homopolymer, which displayed narrow peaks in the optical transmission (up to $\Delta\lambda/\lambda \approx 0.03$). The link

between the domain structure and the optical properties was confirmed. The most useful region of the phase diagram was the lamellar region as here it was possible to selectively swell the respective lamellae over a large range and achieve tunability of the structure, whilst maintaining high quality ordering and consequently produce efficient Bragg mirrors with small relative widths that are comparable to opal structures. Encapsulation or cross linking of these shear ordered layers would provide an inexpensive method to produce large area narrow transmission filters.

Acknowledgements

References

1 J. Y. Cheng, C. A. Ross, H. I. Smith and E. L. Thomas, *Adv. Mater.*, 2006, **18**, 2505.
2 T. Deng, C. Chen, C. Honeker and E. L. Thomas, *Polymer*, 2003, **44**, 6549.
3 A. Khandpur, S. Förster, F. S. Bates, I. W. Hamley, A. J. Ryan, W. Bras, K. Almdal and K. Mortensen, *Macromolecules*, 1995, **28**, 8796.
4 E. L. Thomas, R. L. Lescanec, F. C. Frank, J. S. Higgins, A. Klug and I. W. Hamley, *Philos. Trans. R. Soc. London, Ser. A*, 1994, **348**, 149.
5 Y. Fink, A. M. Urbas, M. G. Bawendi, J. D. Joannopoulos and E. L. Thomas, *J. Lightwave Technol.*, 1999, **17**, 1963.
6 J. H. Moon and S. Yang, *Chem. Rev.*, 2010, **110**, 547.
7 M. Bockstaller, R. Kolb and E. L. Thomas, *Adv. Mater.*, 2001, **13**, 1783–1786.
8 M. R. Bockstaller and E. L. Thomas, *J. Phys. Chem. B*, 2003, **107**, 10017.
9 R. B. Thompson, V. V. Ginzburg, M. W. Matsen and A. C. Balazs, *Macromolecules*, 2002, **35**, 1060.
10 J. Yoon, W. Lee and E. L. Thomas, *Macromolecules*, 2008, **41**, 4582.
11 A. B. Port, J. P. A. Fairclough, A. J. Ryan and C. J. Salou, *US 6,720,061*, U. S. P. Office, United States of America, 2004.
12 S. M. Mai, W. Mingvanish, S. C. Turner, C. Chaibundit, J. P. A. Fairclough, F. Heatley, M. W. Matsen, A. J. Ryan and C. Booth, *Macromolecules*, 2000, **33**, 5124.
13 F. S. Bates and G. H. Fredrickson, *Phys. Today*, 1999, **52**, 32.
14 I. W. Hamley, *The Physics of Block Copolymers*, Oxford University Press, 1998.
15 M. B. Runge and N. B. Bowden, *J. Am. Chem. Soc.*, 2007, **129**, 10551.
16 J. Rzayev, *Macromolecules*, 2009, **42**, 2135.
17 Y. Xia, B. D. Olsen, J. A. Kornfield and R. H. Grubbs, *J. Am. Chem. Soc.*, 2009, **131**, 18525.
18 A. Keller, E. Pedemont and F. M. Willmouth, *Nature*, 1970, **225**, 538.
19 H. Iatrou and N. Hadjichristidis, *Macromolecules*, 1992, **25**, 4649.
20 M. Morton and L. J. Fetters, *Rubber Chem. Technol.*, 1975, **48**, 359.
21 L. Zhu, P. Huang, W. Y. Chen, X. Weng, S. Z. D. Cheng, Q. Ge, R. P. Quirk, T. Senador, M. T. Shaw, E. L. Thomas, B. Lotz, B. S. Hsiao, F. Yeh and L. Liu, *Macromolecules*, 2003, **36**, 3180.
22 T. Hashimoto, M. Shibayama and H. Kawai, *Macromolecules*, 1983, **16**, 1093.
23 J. P. A. Fairclough, C. Ferneyhough and N. Tzokova, *GB 2,424,647A*, U. K. P. Office, United Kingdom, 2006.
24 T. Alfrey, E. F. Gurnee and W. J. Schrenk, *Polym. Eng. Sci.*, 1969, **9**, 400.
25 A. Urbas, Y. Fink and E. L. Thomas, *Macromolecules*, 1999, **32**, 4748.
26 A. Urbas, R. Sharp, Y. Fink, E. L. Thomas, M. Xenidou and L. J. Fetters, *Adv. Mater.*, 2004, **12**, 812.
27 J. Yoon, R. T. Mathers, G. W. Coates and E. L. Thomas, *Macromolecules*, 2006, **39**, 1913.