

Optical properties of styrene-isoprene two-block copolymers

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Four styrene-isoprene two-block copolymers of high molecular weight (M_w 5×10^5 – 2.5×10^6) containing ~50% polystyrene have been prepared in a high state of purity. Their optical properties were studied in solution by transmission and diffraction techniques. It is shown that these properties can be related to the sizes of the domains present due to phase separation.

INTRODUCTION

The formation of ordered structures in block copolymer gels¹ and in the solid state^{2–4} is a well established phenomenon which has attracted a great deal of experimental work. Investigation of domain sizes has usually been made by X-ray diffraction or by transmission electron microscopy of their films. The molecular weights of the block copolymers studied have generally been less than 10^5 because of difficulties in preparation of pure samples uncontaminated by homopolymer when the initiator concentration is very low. If samples can be made in the range of molecular weight around 10^6 , then the domain size will become comparable to the wavelength of visible light and hence optical interference effects will be produced. The observation of iridescent colouring in concentrated solutions of block copolymers of high molecular weight was described in early experiments with these materials⁵ but no systematic investigation was made at the time possibly because of difficulty in producing pure samples. In earlier studies of dilute solution properties of styrene-isoprene block copolymers⁶ rigorous vacuum techniques and initiator washed vessels were used to produce block copolymers with little homopolymer contamination. These techniques have been used to prepare a new set of block copolymers of molecular weights between 5×10^5 and 2.5×10^6 in order to investigate their optical properties.

EXPERIMENTAL

Four styrene-isoprene two-block copolymers were made in benzene solution with sec-butyl lithium as initiator using procedures described previously^{6,7}. Their composition was close to 50 wt % of styrene.

Analysis by density gradient ultracentrifugation⁷ showed that despite the precautions taken to minimize accidental impurity termination, some polystyrene was present (2–5% increasing with molecular weight). This was found to be easily removed by a simple fractionation from benzene/methanol. The supernatant liquid contained the polystyrene after a major centre cut was made. The characteristics of the final products are shown in Table 1. The styrene content of the copolymers was determined from their u.v. spectra and the molecular weights by conventional light-scattering methods using techniques described earlier⁸.

Solutions of the block copolymers were examined in a standard Fica-50 light scattering photometer using incident wavelengths of 365, 436, and 546 nm. As the diffracted light was considerably greater than that observed in normal light scattering experiments a neutral density filter (transmission ~1%) was inserted before the photomultiplier. Light transmission measurements were made in 1 cm quartz optical cells in a Cary-14 spectrophotometer. A 100 ml stoppered flask was sealed to the top of the cell so that the whole assembly could be rotated slowly for 30–40 h to dissolve the polymer before measurements were made. Benzene was used as solvent. The wavelength of light in the medium was calculated using the refractive index and its dispersion for benzene given in International Critical Tables. Similar data exist for polystyrene⁹ and polyisoprene¹⁰, enabling the refractive index of polymer films to be calculated.

RESULTS

Benzene solutions of the block copolymers were visibly coloured above a critical concentration which was lower the higher the molecular weight of the polymer (e.g. ~10 wt % for SI-a-8 and ~4.5% for SI-a-11). The polymer of lowest molecular weight was uniformly blue, the others showed a fairly random multicoloured fibrous structure. On pouring the viscous solution this oriented noticeably. All except polymer SI-a-8 showed strong diffraction effects in the range of angles $2\theta = 20$ – 160° to the main beam available in the instrument (Figure 1). In all cases they showed strong absorption at $2\theta = 180^\circ$ (Figure 2).

Characteristic spacings (d) were obtained from the diffraction experiments using the Bragg relation $m\lambda = 2d \sin \theta$. λ in the medium was calculated from the refractive index of benzene. The refractive index increment of the polymer in this solvent is low (~0.07) so

Table 1 Characterization of styrene-isoprene block copolymers

Polymer	Wt. fraction styrene	$10^{-6} \bar{M}_w^a$
SI-a-8	0.54	0.47
SI-a-9	0.48	0.86
SI-a-10	0.49	1.24
SI-a-11	0.45	2.62

^a Measured by light scattering in tetrahydrofuran

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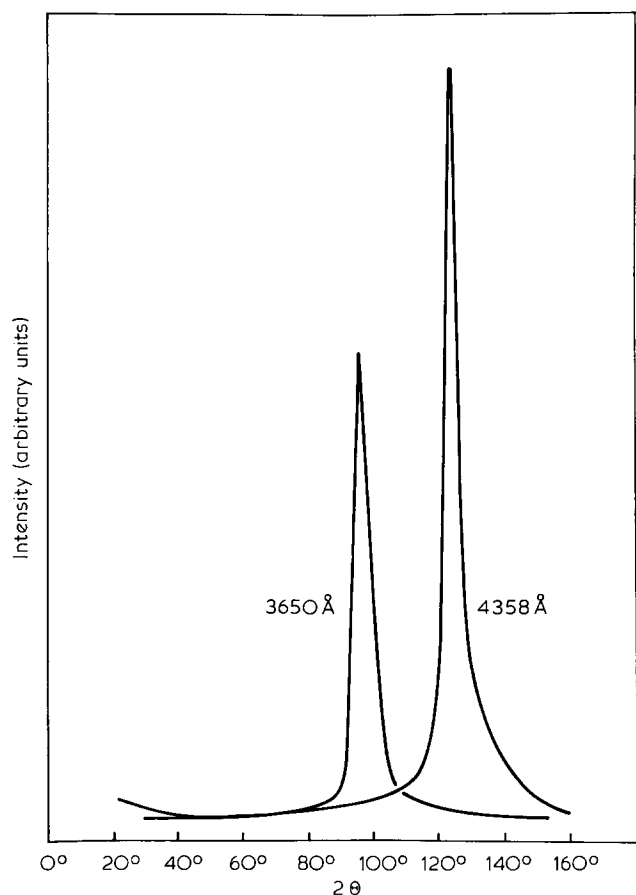


Figure 1 Diffraction of light in an 8.0 wt. % benzene solution of polymer SI-a-9

negligible error is produced in neglecting its contribution to the refractive index. This was confirmed by measurement of the refractive index of a 36.4% solution of sample SI-a-8. It was found to be only 0.02 higher than that of benzene even at this high concentration. Domain spacings were as expected independent of the incident wavelength. Because of the limited $\lambda/\sin \theta$ range available, normally only one diffracted beam was observable except for polymer SI-a-11 where at an incident $\lambda = 365$ nm, a very weak secondary maximum was observed at higher angle (Figure 3).

The sequence of angles at which diffraction occurs depends on polymer morphology¹¹. Because of the much shorter wavelength used in X-ray diffraction experiments many diffraction lines are observed. These occur at $\sin \theta$ ratios of 1, 2, 3, ... for lamellar structures and 1, $\sqrt{3}$, $\sqrt{4}$, ... for cylindrical hexagonal structures, the two most commonly observed morphologies in block-copolymers. With the much higher wavelengths used in optical studies, only the first line of the series would be observable except for the block-copolymer of highest molecular weight at the shortest incident wavelength. In this case, the two bands were observed at a $\sin \theta$ ratio of 1:1.85 which does not allow a clear cut decision to be made between the two possibilities, although cubic structures are clearly excluded. This polymer shows very strong absorption however, so that it is likely some error is caused in angular measurements because of displacement of the scattering centres from the cell centre. Lamellar structures are always found in gels and solid samples of block copolymers of this composition¹⁻⁴ so it seems likely that this is true in the present case. The transmission measurements described below confirm this.

Where strong diffraction effects occur, the transmitted beam will show light absorption. It is possible, therefore, to examine light transmission as a function of incident wavelength rather than measuring diffraction angle at a fixed wavelength. Diffraction occurs at all incident wavelengths which satisfy the Bragg relation. Moreover the diffraction experiments in the Fica-50 instrument showed that the diffracted intensity increased as the incident wavelength was increased from 365 nm to 436 and 546 nm. A parallel increase in diffraction angle occurs. When examined in transmission, therefore, as the incident wavelength is increased, transmission will decrease until the diffraction angle reaches the value π ($\sin \theta = 1$). At higher wavelengths the Bragg relation cannot be obeyed and no diffraction can occur, hence light transmission should rapidly increase.

Figure 2 shows the optical density of a 5.5 wt % solution of polymer SI-a-11. Besides the main absorption edge at 857 nm, a smaller secondary one occurs very close to one half the wavelength (432 nm) as expected for a lamellar structure. The domain spacing obtained from $d = m\lambda/2$ (290 nm) is in good agreement with that obtained from diffraction angle measurements (285 nm). The polymers of lower molecular weight showed only one strong absorption at shorter wavelength. The secondary maximum would be at too short a wavelength to be observed, due to masking by absorption of the styrene units and increased

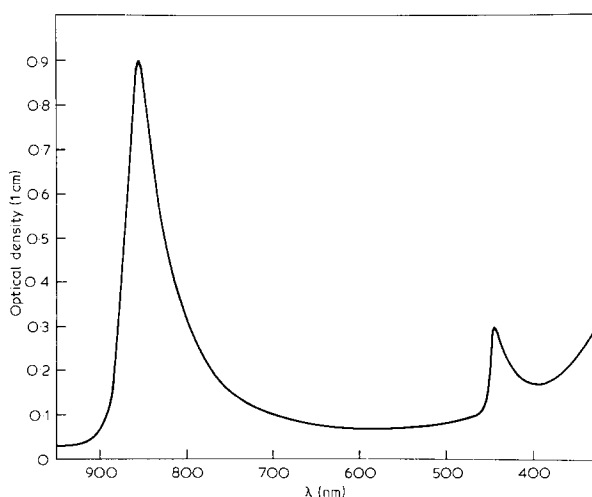


Figure 2 Light transmission in a 5.5 wt. % benzene solution of polymer SI-a-11

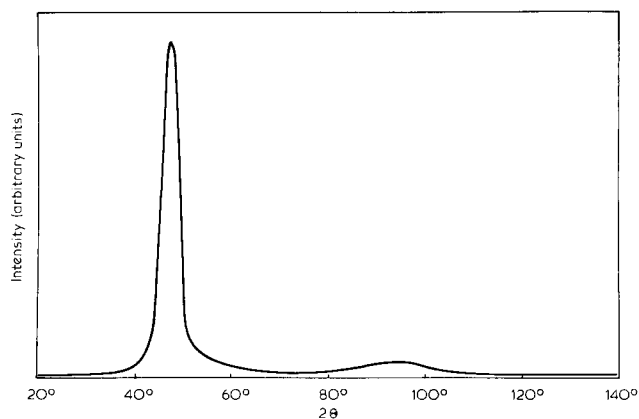


Figure 3 Diffraction of light in a 5.5 wt. % benzene solution of polymer SI-a-11. Incident wavelength 365nm

Table 2 Domain spacings in block-copolymer solutions

SI-a-8							
Concentration (wt. %)	10.4	12.3	15.2	24.7	30.4	36.4	100
<i>d</i> (nm)	107	117	124	134	138	139	103
SI-a-9							
Concentration (wt. %)	8.15	9.25	10.2				
<i>d</i> (nm)	155 (161)	161 (164)	163				
SI-a-10							
Concentration (wt. %)	6.9	8.0	8.4	9.2	10.4		
<i>d</i> (nm)	187	191	(194)	195	20.3		
SI-a-11							
Concentration (wt. %)	4.7	5.5	6.3				
<i>d</i> (nm)	276	290 (285)	294				

Data obtained from transmission measurements. Figures in parentheses from Fica-50 measurements

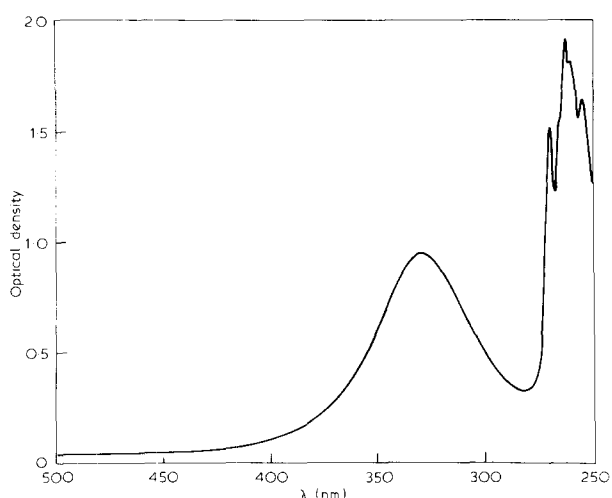


Figure 4 Light transmission of a thin film of polymer SI-a-8, (0.1 mm)

Rayleigh scattering. The summarized results are shown in Table 2. Ideally the transmission measurements should show an extremely sharp absorption edge at a given wavelength. The sharpness will depend however on the degree of perfection of the organized structures. It was noticed that when freshly poured into the cell, solutions exhibited a much broader maximum in optical density which gradually sharpened on standing.

In principle the transmission method can be used on solid polymer films if a uniform sample can be formed. Figure 4 shows the optical density of a 0.1 mm film of polymer SI-a-8 (produced by evaporation of solvent from a concentrated solution followed by evacuation). The absorption maximum is broader indicating less perfect ordering than in the gels. Fortunately the determination of domain size is not very sensitive to the estimation of λ cut-off (the point at which $\sin \theta = 1$). The difference in wavelength between the position of maximum absorption and the long wavelength tail is only 10%. A similarly produced film from SI-a-10 gave an even broader maximum. Attempts to use the standard method of transmission electron microscopy on thin films stained with OsO_4 to determine domain sizes failed. Well-defined lamellar structures were not observed even after annealing, although some phase separation was clearly present. This confirms that with block copolymers of very high molecular weight, well-ordered structures are more difficult to attain in the solid state than with the polymers of lower molecular weight normally studied.

The concentrations indicated in Table 2 were the lowest

ones at which diffraction effects were observable. In general, concentrations 0.5–1.0% lower showed no evidence of micellar structures. Theories of domain formation¹² in solvent containing systems predict as observed, that the critical concentration will decrease as the molecular weight increases at constant polymer composition. This critical concentration appears to be approximately proportional to the inverse square root of polymer molecular weight rather than simply proportional to inverse molecular weight as predicted by Meier¹².

The domain sizes in solutions immediately above the critical concentration appear to be close to those in solid films as judged by the experiment on SI-a-8 and the fact that the present results at those concentrations would fit well on a single line with the data given for solid samples of lower molecular weight by Kawai¹³ with a molecular weight dependence to the power ~ 0.56 . The domain sizes increase somewhat with polymer concentration but must level off as observed with SI-a-8 at $\sim 40\%$ concentration and then slowly de-swell to the value characteristic of solid films. X-ray diffraction experiments on gels with 70–100% polymer show this latter effect clearly¹. The overall changes in domain size with polymer concentration do not however seem to be large.

In summary it has been shown that domain sizes in solutions of very high molecular weight block copolymers can be obtained by optical measurements. These domain sizes are not very dependent on polymer concentration and are very similar to those expected in solid films.

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