viscometer. The intrinsic viscosities $[\eta]$ were obtained by extrapolating η_{sp}/C vs C to zero concentration. The values of $[\eta]$ were further checked from the curve of Δ/C^2 vs. C^2 (where $\Delta = \eta_{sp} - \ln \eta_r$) following the procedure of Maron *et al.*[3]. The $\bar{M}_w$ of each fraction was also determined by light scattering.

Table 2 Comparison of values of average molecular weights of SAN samples by derived relationship and the light scattering method

Sample no.	ACN content by N_2 estimation (%)	$[\eta]$	Average $\bar{M}_w$ by light scattering method	Average $\bar{M}_w$ viscosity method using derived relationship	Average $\bar{M}_w$ by viscosity method using relationship recommended for 24% ACN[1]
1	27.0	0.79	190 000	177 000	245 000
2	27.0	1.26	364 000	372 000	520 000
3	27.0	1.14	325 000	317 000	443 000
4	27.0	0.725	160 000	154 500	214 000
5	27.0	0.79	182 000	177 000	245 000

RESULTS AND DISCUSSION

Table 1 shows the results of intrinsic viscosities $[\eta]$ and weight-average molecular weights ($\bar{M}_w$) of the seven fractions. From a plot of $[\eta]$ in log–log scales the following values of K (intercept) and α (slope) were obtained: $K = 3.9 \times 10^{-4}$; $\alpha = 0.63$.

These values were further checked by applying the least square method which gave identical results. For general application, therefore, $K = 3.9 \times 10^{-4}$ and $\alpha = 0.63$ may be taken to be acceptable. The validity of these parameters was confirmed by determining the $\bar{M}_w$ of five different samples of SAN containing about 27% AN by viscometry and by light scattering. The results are given in *Table 2.* For comparison, the $\bar{M}_w$ obtained by the K and α values reported in literature earlier are also given in column 6 of *Table 2.* It can be seen that the molecular weights in column 6 vary widely from $\bar{M}_w$ obtained from the light scattering method column 4 while those of column 5 and column 4 are in close agreement.

ACKNOWLEDGEMENT

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Oriented macrolattice in a polystrene–polybutadiene block copolymer of high polystyrene content

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INTRODUCTION

In recent years there has been extensive interest in the morphology and associated physical properties of block copolymers. The two phase nature of these materials has been primarily established by means of the techniques of low-angle X-ray diffraction and transmission electron microscopy, initially on solvent cast films and later on samples prepared from the melt. For a review of this work see ref 1. One of the latest developments has been concerned with the application of a special extrusion technique to the preparation of samples possessing an oriented macrolattice formed from the segregated phase in a matrix of the other phase and giving rise to a 'single-crystal'[2]. This was first applied to a polystyrene–polybutadiene–polystyrene three-block copolymer, Kraton 102, containing 25% wt fraction of polystyrene. A morphological examination showed that samples removed from the extruded rod consisted of a hexagonal array of polystyrene cylinders whose axes were parallel to the extrusion direction and embedded in a polybutadiene matrix[3,4]. The existence of such 'single-crystals' not only provided an exceptional opportunity for detailed morphological studies but enabled their anisotropic physical properties to be measured and interpreted to a high degree of precision.

It was with these advantages in mind that similar studies were later carried out on oriented samples of a polystyrene–polybutadiene–polystyrene three-block copolymer having a polystyrene weight fraction of 48.2% and exhibiting a lamellar morphology[5,6].

In this Note we report some observations which extend the above work to a block copolymer in which the matrix phase is glassy and the dispersed phase is rubbery.

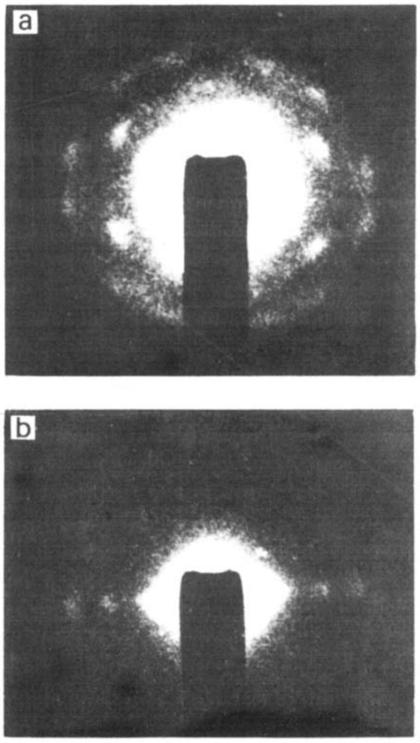

Figure 1 **Low angle X-ray diffraction patterns from an extruded sample of polystyrene rich S–B block copolymer. (a) Beam parallel to the extrusion direction (plug axis). (b) Beam perpendicular to the extrusion direction**

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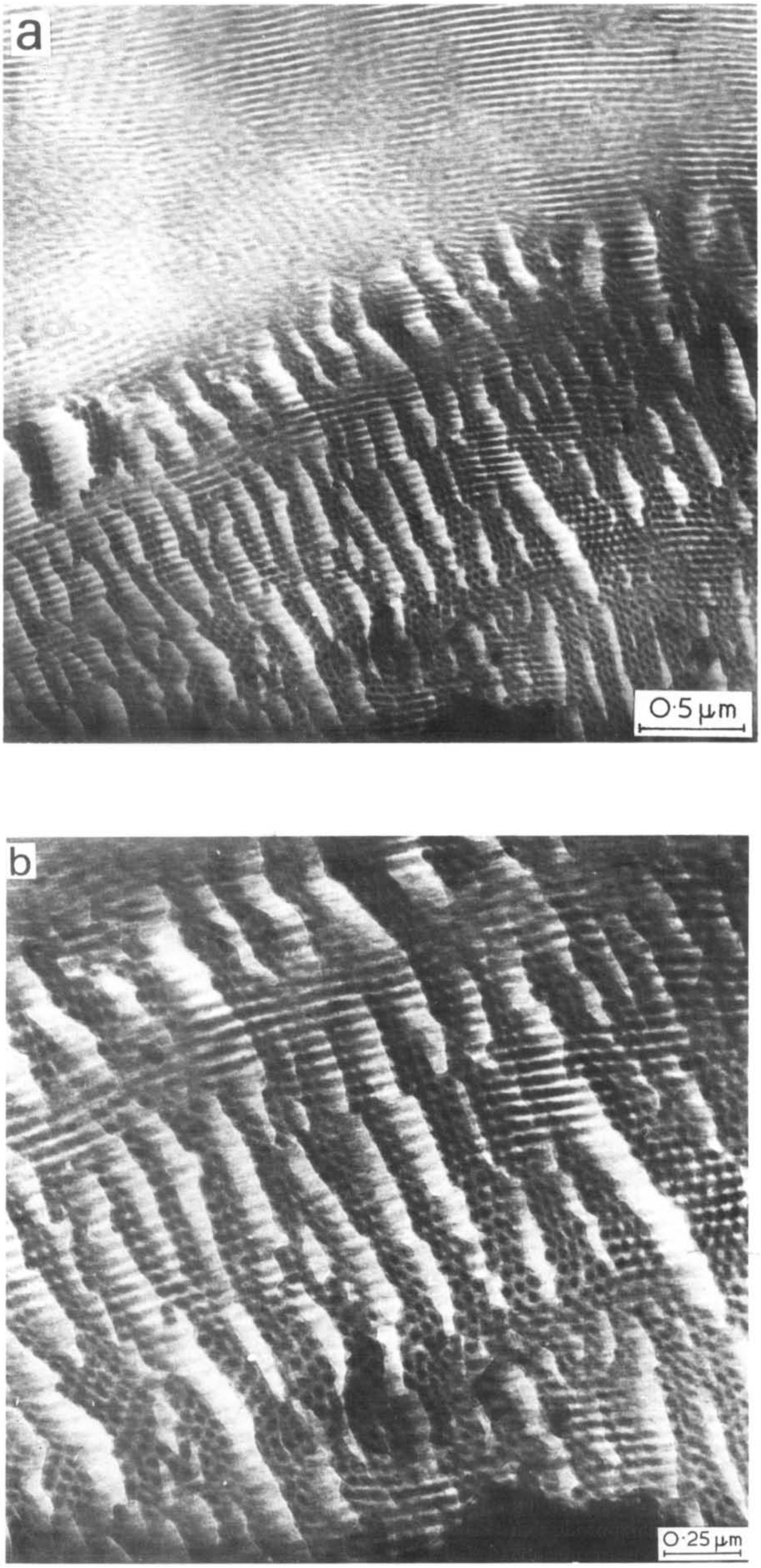

Figure 2 Electromicrograph of a cracked oblique section from a polystyrene rich S—B plug. Osmium stained, polybutadiene cylinders dark. (a) Overall view showing cylinders as continuous striations together with the cracked region. (b) Detail of cracked region displaying perspective view of cylinders adjacent to the cracks

MATERIAL AND SAMPLE PREPARATION

The raw material chosen for our studies was a polystyrene–polybutadiene two-block copolymer kindly provided by Drs M. Hoffmann and H. Krömer, Bayer AG, Leverkusen, W. Germany. This had a nominal polystyrene content of 70% by wt and the total molecular weight of both blocks was quoted as 7.5 x 10^4.

This material was then extruded using the special technique developed for Kraton 102[2]. The plug of extruded material was 8 mm in diameter and about 6 cm long and was very transparent. The plug was subsequently annealed for 18 h at 155°C.

LOW-ANGLE X-RAY DIFFRACTION

Samples for the low-angle X-ray diffraction studies were cut from the extruded and annealed plug at a point about three-quarters of a radius. From our experience in earlier studies[2], this was the region of the plug where the microphase ordering was expected to be in its most pronounced form. Even during sample cutting, the anisotropic character of the material was revealed. Cutting parallel to the extrusion direction was easily carried out by lightly inserting a razor blade into the sample surface, after which a crack propagated unimpeded parallel to the extrusion direction, leaving two plane mirror surfaces. Cutting perpendicular to the extrusion direction proved much more difficult and was accompanied by very pronounced stress whitening. It will be seen later that these observations are entirely consistent with the structure of these samples, as deduced from low-angle X-ray diffraction and electron microscopy.

With the X-ray beam along the extrusion direction, a single crystal diffraction pattern having hexagonal symmetry was obtained, as shown in *Figure 1a.* The same sample portion with the beam perpendicular to the extrusion direction gave reflections only along a line perpendicular to the plug axis (the zero layer line), as shown in *Figure 1b.* These observations, together with the quoted stoichiometry of this material are in accord with a structure consisting of a hexagonal array of polybutadiene cylinders embedded in a polystyrene matrix and with the cylinder axes parallel to the extrusion direction. The separation of the cylinder axes was evaluated from the diffraction patterns and found to be 442 Å. Using the quoted polystyrene weight fraction and bulk values of 0.86 and 1.04 as the densities of the polybutadiene and polystyrene phases, respectively, the diameter of a polybutadiene cylinder was calculated to be 236 Å. A value for the cylinder diameter can also be obtained from an analysis of the intensity distribution of the diffraction maxima. For a uniform cylinder, the intensity distribution is of the form $(J_1(x)/x)^2$ where $J_1(x)$ is a first order Bessel function. By matching the observed intensity distribution, as recorded by a microdensitometer, with this function, a value of 220 Å was obtained for the cylinder diameter, in satisfactory agreement with the value obtained using the sample stoichiometry.

Even if the diffraction patterns are not as clearly defined they are analogous to the earlier studies on Kraton 102[1,3]. On the basis of the above evidence here we also appear to have a 'single-crystal', but in this case the roles of the two phases are reversed from that in Kraton 102.

TRANSMISSION ELECTRON MICROSCOPY

Further direct evidence for this structure was sought using transmission electron microscopy. The technique used for obtaining thin sections was identical to that used in our earlier studies, namely, the sections were cut at a temperature of about −100°C with a diamond knife fitted to an LKB microtome. The sections were subsequently stained with osmium tetroxide vapour for 1 h. This provides the necessary contrast between the polybutadiene and polystyrene when viewed in transmission.

To confirm the structure deduced from low-angle X-ray diffraction it is necessary to take sections from both parallel and perpendicular to the extrusion direction. As in earlier works in Kraton 102[4] this enables a side view and end-on view of the cylinder to be obtained in separate sections. However, unexpectedly, while attempting to cut obliquely, the section cracked during sectioning. Here a rather dramatic perspective view of the cylinders along the walls of the multiple cracks presented itself which serves to illustrate how a complete view of the cylinders was obtained in only one section as shown in *Figure 2*. Within the same micrograph, there is also a region that has not cracked, showing continuous striations (*Figure 2a*) which are off axis projections of the cylinders, which are themselves seen more clearly in the enlarged detail in *Figure 2b*.

An approximate figure only was obtained for the cylinder diameter from the electromicrograph and found to be 250 Å. It is interesting to note that where cracks have appeared, only complete polybutadiene cylinders are found adjacent to a crack i.e. the crack once propagating passes around the rubbery cylinders and is parallel to the cylinder axes.

OPTICAL ANISOTROPY

Small samples cut from the annealed extruded plug were examined between crossed polars in a Carl Zeiss Ultraphot I polarizing microscope. With the plane of polarization of the light either parallel or perpendicular to the extrusion direction, a sharp extinction was observed. Using a quartz wedge, it was confirmed that the sample exhibited positive birefringence with respect to the extrusion direction.

With the incident light along the extrusion direction, the material appeared uniformly dark for all positions of the stage showing that we have transverse isotropy about the extrusion direction.

Using an Ehringhaus quartz compensator, a value for the birefringence was obtained and found to be $(3.5 \pm 1.0) \times 10^{-4}$.

As discussed in detail in an earlier publication[7] the birefringence in such a two phase system can derive from form birefringence together with molecular birefringence due to any residual molecular orientation in either the polystyrene or polybutadiene phase or both. The former contribution can be evaluated from a knowledge of the volume fractions of the two phases together with their respective refractive indices. For a parallel array of cylinders of refractive index n_1 embedded in a medium of refractive index n_2, the form birefringence is given by:

$$n_a - n_0 = \frac{\nu_1\nu_2(n_1{}^2 - n_2{}^2)^2}{2n_a[(\nu_1 + 1)n_2{}^2 + \nu_2 n_1{}^2]}$$

where $n_a{}^2 = \nu_1 n_1{}^2 + \nu_2 n_2{}^2$ and ν_1, ν_2 are the respective volume fractions of the phases.

For the present material we have chosen:

$n_1 = 1.52 \qquad n_2 = 1.59$

$\nu_1 = 0.344 \qquad \nu_2 = 0.656$

which leads to a value of $n_a - n_0 = 6.95 \times 10^{-4}$.

The discrepancy between the measured value and the calculated form birefringence may be attributed to a small residual molecular orientation in either or both phases. The magnitude of this orientation would be difficult to assess independently.

Previously such an orientation has been observed in a lamellar two phase system[6] but not in the case of Kraton 102, exhibiting a cylindrical morphology of glassy polystyrene rods in a rubbery polybutadiene matrix. In the latter case, the measured birefringence was accountable by form birefringence alone. The presently found excess positive birefringence could be due either to the rubbery polybutadiene component having some orientation along the cylinder direction or to the molecules of the polystyrene matrix being oriented in a direction perpendicular to the plug axis. In view of the findings in the lamellar system, the latter may be plausible. Also slight orientations of this kind may be expected on theoretical grounds[8,9]. As regards the difference between the two kinds of cylindrical morphology (i.e. in ref 7 and the present one) we have no further comment to make.

CONCLUSIONS

We have reported the preparation and characterization of samples of a two-block copolymer exhibiting a uniformly oriented macrolattice of polybutadiene cylinders in a polystyrene matrix. Furthermore, the presence of cracks in the electron microscope sections provided an unexpected view of the dispersed phase. The possible application of this to other two phase systems in which cracks, even if not occurring naturally, might be induced to occur, could provide a valuable experimental technique for the perspective observation of microphase ordering. The optical anisotropy of the samples was consistent with the morphology. The anisotropy of other physical properties requires further work. In particular, the application of such a structure to fracture mechanics studies and its relationship to the mechanism of toughening in rubber modified thermoplastics, obviously presents itself in view of the analogy of our system with this commercially important class of materials for which it could serve as a model.

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Kinetics of copolymerizations: 1. Dilatometric investigation of the copolymerizations of benzyl methacrylate, styrene and methyl methacrylate

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INTRODUCTION

Dilatometry is a well known method for determination of conversions and polymerization rates. The necessary condition is a volume change during the polymerization and a correlation between shrinkage and conversion (U) yields the equation[1]:

$$U = \frac{1}{K} \times \frac{\Delta V}{V} \times 100 \qquad (1)$$

where V is the initial volume, ΔV is the decrease in volume and K the so-called conversion factor. K can be evaluated from equation (1) by direct gravimetric determination of the conversion for a polymerization of known shrinkage.

A second method is based on the densities of monomer (ρ_m) and polymer (ρ_p):

$$K = \frac{\rho_p - \rho_m}{\rho_p} \qquad (2)$$

The two equations are valid for homo- as well as copolymerizations, although it must be noted that for any particular composition of monomers there must be a corresponding conversion factor Bevington *et al.*[2] used the relation:

$$K = K_1 x_1 + K_2 x_2 \qquad (3)$$

which is a linear interpolation between the conversion factors K_1 and K_2 of the two homopolymerizations x_1 and x_2 are the mole fractions of the two components in the copolymer. Most experimental data[3,4] do not obey equation (3) and Wittmer[4] suggested that:

$$K = K_{11}B_{11} + K_{22}B_{22} + K_{12}B_{12} \qquad (4)$$

involving binary bonding frequencies B_{ij} and conversion factors. The B_{ij} values can be easily calculated[4] from the reactivity ratios of a binary system and the composition of the actual monomer mixture. K_{11} and K_{22} are the conversion factors of the respective homopolymerizations and K_{12} that of the alternating copolymerization step. Apart from K_{12}, all quantities in equation (4) are easily accessible.

For the system ethyl acrylate/styrene, Wittmer confirmed the constancy of K_{12}. Accordingly it is possible to predict the behaviour of any possible monomer mixture of a copolymerization system by measuring the shrinkage for only one monomer mixture and hence calculating K_{12}.

The purpose of the present investigation was to test Wittmer's theory for the three binary copolymerizations of benzyl methacrylate (BMA), styrene and methyl methacrylate (MMA). Discussion of the kinetics of the copolymerizations will be given in another paper. The volume changes during polymerization have been followed in a specially designed dilatometer which has the advantage over others described in the literature[5–7] in that it is of relatively large volume, and allows the reaction mixture to be stirred vigorously; a temperature gradient in the vessel can thus be avoided and the large volume can lead to substantial yields of polymer even for low conversions. The second and greater advantage of the dilatometer is the possibility of regulating and recording the temperature of the polymerizing mixture. The heat of polymerization can be dissipated so that the reaction proceeds isothermally. A temperature rise due to the Trommsdorff-effect at higher conversions cannot be controlled because of the inertia of the cooling system.

EXPERIMENTAL

Materials

Benzyl methacrylate was prepared by esterification of methacrylic acid with benzyl alcohol. Immediately before use, it was vacuum distilled under nitrogen and run over a basic aluminium oxide column. Boiling point: 85°C/1.7 Torr.

Styrene and methyl methacrylate was distilled under nitrogen after removing the stabilizer.

Azoisobutyronitrile (AIBN) was recrystallized twice from ethanol.

Polymerizations

Polymerizations were carried out in bulk at 60°C with AIBN as initiator.

For determining reactivity ratios, monomer mixtures were polymerized under nitrogen. The resulting polymers were precipitated in methanol and dried *in vacuo* at 50°C to constant weight for determination of conversion. The compositions were found by n.m.r.-spectroscopy and elemental analysis.

The polymerizations for kinetic measurements were followed dilatometrically. Because of the complicated design of the dilatometer these experiments could not be carried out in the absence of oxygen. The polymer samples have been treated as described above.