Figure 7 Scanning electron micrograph (10 000 X) of fracture surface (cross-section) of desiccated bottle of *Figure 3*

to be resolved optically; and secondly, in transparent media in the absence of objects in the plane of focus, out-of-focus objects from other planes assume unwarranted prominence. Scanning electron micrographs do not pose these problems, because of greater resolution of the instrument, and because only surfaces can be observed.]

It is interesting to note (*Figures 4* and *5*) that there does not seem to be any great difference in the number of voids present before and after treatment, except where small voids, during growth, may have fused to form large elongated voids. Thus, the opacification seems to have resulted essentially entirely from the growth of pre-existing voids in the transparent bottle walls, with no evidence of the formation of new voids.

It was shown originally by Zimm and Lundberg[4], and since then by many others[5–12], that the diffusion of water in many polymers is not Fickian, but that the water molecules tend to be immobilized in clusters, rather than to diffuse individually through the polymer. In such systems, water–water interactions tend to be favoured over water–polymer interactions, and thus water molecules tend to cluster. Clustering could well be facilitated by the existence of voids such as those observed here; growth of the voids in the presence of moisture could then occur by accretion of more water molecules to the nascent clusters. In any case, it is clear that the voids are related to the presence of water, since opacification of the bottle wall occurred only after the bottle had been emptied of its aqueous contents and allowed to dry out.

This leaves the question of how the original voids were formed, a question which the observations described above were not intended to answer. It may be noted, however, that on being informed of the problem, the material supplier was able to modify its procedures in such a way as to essentially eliminate the whitening problem in bottles produced subsequently.

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Molecular weight of SAN copolymers: values of the constants for viscometric determination

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Determination of molecular weights of polymers by viscometry applying the formula $[\eta] = KM^{\alpha}$ offer an easy, quick and fairly accurate method.

K and α values for SAN polymers containing 24 wt % and 54 wt % of acrylonitrile (AN) using methyl ethyl ketone (MEK) as solvent are known in literature[1]. We have found that the reported K and α values ($K = 3.6 \times 10^{-4}$ and $\alpha = 0.62$) for SAN containing 24% AN are not applicable for SAN containing 27% AN which conforms to Type III of the ASTM specifications[2]. The values of K and α for SAN containing 27% AN were therefore determined and are reported here.

EXPERIMENTAL

SAN, prepared by suspension polymerization was first purified by dissolving in MEK followed by precipitation with excess methanol and drying *in vacuo* at 45°–50°C. This purified SAN was analysed and found to contain 27% AN; the weight-average molecular weight ($\bar{M}_w$), as determined by light scattering was found to be 230 000. The sample was then fractionated by precipitation using MEK (solvent) and methanol (non-solvent) at 30°C. The fractions were isolated by centrifuging (15 000 r.p.m.) and vacuum dried at 45°–50°C. Each fraction was separately dissolved in purified MEK to prepare a 0.6 to 0.7% solution and the viscosity determined at 30°C at different dilutions using an Ubbelohde

Table 1 Intrinsic viscosities and molecular weights of SAN fractions

Sample fraction	Fraction (wt %)	ACN content (wt %)	$[\eta]$	Average $\bar{M}_w$ by light scattering method
Unfractionated Sample		27.0	–	230 000
I	7.20	27.2	1.74	549 000
II	14.26	26.9	1.22	357 000
III	9.56	27.0	1.12	312 000
IV	21.54	26.95	0.84	208 000
V	20.05	26.5	0.724	166 000
VI	13.04	26.95	0.66	129 000
VII	14.35	27.5	0.437	80 000

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.

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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.

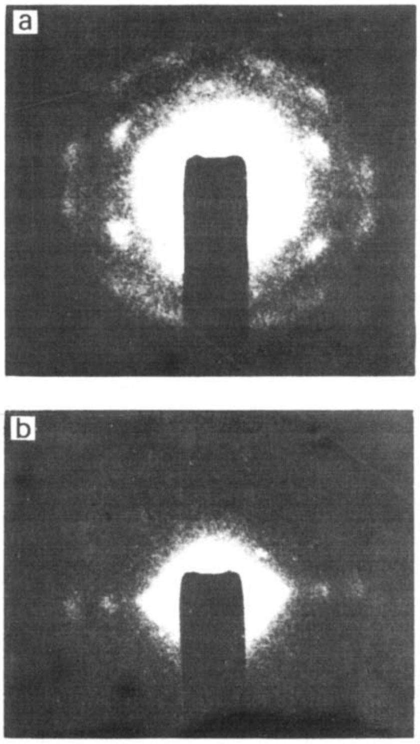

Figure 1 **Low angle X-ray diffraction patterns from an extruded sample of polystyrene rich S–B block copolymer.** (a) Beam parallel to the extrusion direction (plug axis). (b) Beam perpendicular to the extrusion direction

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