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MACROSCOPIC « SINGLE CRYSTALS »
OF AN S-B-S THREE BLOCK COPOLYMER

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Abstract. — The structure and properties of a particular polystyrene-polybutadiene-polystyrene (SBS) three block copolymer (Kraton 102) is examined. This polymer provided an exceptional opportunity for the study of the ordering of segregated microphases and resulting properties, hopefully with some general implications. When obtained in the form of an extruded plug (first provided by the University of Genoa) it displayed single crystal type diffraction patterns at low angles, from which it could be deduced that the whole sample, or at least macroscopic portions of it, could be regarded as a « single crystal » formed by the segregated phases which themselves are amorphous. Here, the glassy S phase is in the form of cylinders arranged in a crystallographically regular manner within a rubbery B matrix. The cylinder direction is identifiable with a macroscopic sample dimension, so that the structure postulated from the diffraction patterns could be directly tested and verified in a quantitative manner by electron microscopy involving ultrathin sectioning along preselected cutting directions.

Again, the observed birefringence was quantitatively accountable by form birefringence, implying random orientation of the molecules within the individual phases themselves. This randomness has been verified lately for each phase separately by infra-red dichroism. Swelling behaviour was found to be anisotropic. In its first stages it corresponds to the correspondent dispositions cristallographiques de manière régulière au sein d'une matrice caoutchouteuse B. La direction des cylindres coïncide avec une dimension macroscopique de l'échantillon, si bien que la structure qui est postulée à l'aide des diagrammes de diffraction a pu être vérifiée, directement et de manière quantitative par microscopie électronique, ce qui a nécessité un sectionnement ultra-fin le long de directions de coupe prééliminées.

Introduction. — The subject of the studies to be reported is a three block copolymer of constitution polystyrene-polybutadiene-polystyrene (SBS). This is one example of the class of materials known as thermoelastomers consisting of incompatible amorphous phases which owing to molecular connection between the phases can only separate on a submicroscopic scale forming discrete dispersed particles. If the matrix is a rubber and the dispersed phase a glass the material will behave as a vulcanized elastomer where the glassy
particles act as cross-links. Above the glass transition temperature of the glassy phase the objects are mouldable hence the term thermoelastomers. The dispersed phases are known to be in the form of either spheres, cylinders or lamellae and as revealed by electron-microscopy, usually on cast films, or by low angle X-ray reflexions, can form surprisingly regular lattice arrays. All these objects which feature in preceding studies, however, are «polycrystalline» on a macroscopic scale, i.e. they give rise to rings in their X-ray diffraction patterns at low angles (ref. e.g. [1]-[6]).

The particular novelty of our work is that we obtained objects which are «single crystals» in the macroscopic sense, i.e. the lattice vectors are identifiable in terms of the macroscopic sample directions. The first stages of the work will be concerned with the verification of the single crystal nature of our samples which will be followed by the examination of certain anisotropic properties which follow from the existence of such macrocrystals. It is to be emphasized that we are not dealing with crystals in the conventional sense. On the molecular scale both constituents, matrix and dispersed phase are amorphous, it is the regular arrangement of these amorphous phases which gives rise to the lattice with a lattice periodicity on the scale of several 100 Å.

Samples. — The SBS polymer of our principal studies contains 25 % weight fraction of polystyrene with a molecular weight 10^6 for S and 5.5 × 10^4 for B [7] which features under the Shell trade name Kraton 102. (Studies currently in progress are extending this work to the similar SBS polymer Kraton 101 and an SIS polymer — I stands for polyisoprene — so far with similar results.) The actual samples in question were obtained from Genoa University in the form of moulded plugs involving a certain degree of extrusion. The plugs had diameters of 9 mm and were several cm long. It was these samples which exhibited the unique properties in question. Currently work is in progress with positive results, to establish the exact conditions of fabrication responsible for the features to be described [8]. This subject will be deferred to a later publication, for the present we merely report that samples with the unique features in question can be produced, and confine ourselves to the description of experiments performed on these samples.

Structure. — X-RAY DIFFRACTION. — When the extruded plugs of Kraton were examined by low angle X-ray diffraction, single crystal diffraction patterns were obtained on macroscopic sample portions, usually from the outer annuli of 2-3 mm width, and in special circumstances practically from the whole plug [9], [10]. The clearest «single crystal» patterns were obtained on heat treatment of the extruded plugs between 120° and 180° C.

The «single crystal» nature of the objects was most apparent with the beam along the plug axis (which is in the direction of the original extrusion). An example is shown by figure 1. As seen the pattern is hexagonal. With the beam perpendicular to the plug axis, patterns as in figure 2 were obtained. The most obvious conclusion [9], [10] is that we have a hexagonal lattice formed by regularly arranged cylinders, which from the point of view of our diffraction work (resolution limit ~ 1 000 Å) can be considered as infinitely long. The hexagonal cell parameter i.e. the centre to centre separation of the cylinders is 300 Å. It follows from the stochiometry and from the macroscopic densities of the individual phases that the cylinders are 150 Å in diameter. The same conclusion is reached from the intensities of the reflexions, in particular from the systematic weakening of the 2nd order of the basic hexagonal reflexions. This means that the minimum

![Fig. 1. Low angle X-ray diffraction pattern from an annealed sample of extruded SBS copolymer (Kraton 102) with the beam parallel to the extrusion direction (plug axis). (One of the six strongest reflections obscured by beamstop.) (Ref. [12]) after ref. [9] and [10].](image1)

![Fig. 2. Low angle X-ray diffraction pattern of sample as in Fig. 1 but beam perpendicular to plug axis which is vertical [9], [10].](image2)
cylinder separation is 150 A, i.e. the cylinders are separated by matrix material of thickness which is about equal to their own diameter.

In studies currently in progress the single crystal type samples have been examined also as a function of temperature, including the «annealing» temperature to which the samples were first subjected to enhance their single crystal nature [8]. It has been observed that the single crystal type hexagonal diffraction pattern such as in figure 1 was retained at all temperatures up to 200 °C, the highest examined, with only a very small spacing change. Accordingly the lattice persists beyond the glass transition temperature where the object is soft, without change in the cylindrical units.

The same basic lattice was also obtained by with uniaxially and biaxially stretched samples but in the form of more complex texture patterns. The common feature however was always the same: the hexagonal axis, which we identify with the cylinder axis, is along the direction of the orienting influence.

**Electron Microscopy.** — The possession of macroscopic «single crystal» samples provided us with the opportunity to carry out an electron microscope examination on ultrathin sections cut along preselected directions with respect to the lattice as established by X-rays [11]. The technically difficult process of cutting was carried out at low temperatures, a technique specially developed for the ultramicrotomy of polymers. The cutting was performed along two directions: transversely and longitudinally with respect to the hexagonal (hence the assumed cylinder) axis. The sections were stained with osmium which makes the polybutadiene matrix opaque but leaves the polystyrene phase transparent.

Figure 3 shows a detail of a transverse and figure 4 that of a longitudinal section. The order seen in these micrographs extends over areas as least as large as encompassed by the original negatives which was up to 10 μ.

The hexagonal arrangement of light hence S circles is immediately apparent from figure 3. This in combination with the streaks in the longitudinal sections such as in figure 4 is fully consistent with the cylindrical structure deduced from the X-ray photographs. Allowing for variations within the photographs the dimensions of both lattice periodicity and cylinder diameter are in satisfactory quantitative agreement with deductions from the X-ray diffraction patterns.

Tilting experiments were also performed both on the transverse and longitudinal sections while in the electronmicroscope with results which are in full agreement with the postulated structure. The tilting of the longitudinal sections along the striation direction is particularly interesting: the striations become visible with high contrast only at 60° tilt intervals. This is fully consistent with the hexagonal lattice arrangement of cylinders within the section which is thick compared with the lattice periodicity, and follows directly from the expected imaging conditions of lattices, both from simple geometrical and from diffraction optical considerations.

Thus the regular hexagonal lattice structure (formed by cylinders of practically infinite length) and its magnitude is fully confirmed by direct visual observations.

Some faulted regions, including terminating striations are nevertheless seen in figure 4. We believe that some of the more diffuse regions seen in figure 3 correspond to cross sectional views of such faults, a subject requiring further examination.

**Properties.** — In what follows some properties expected to be associated with the anisotropic structure just established will be examined.
BIREFRINGENCE. — Samples of « single crystal » structure displayed optic uniaxial character with the plug axis as the optic axial direction which is in accordance with expectations for a hexagonal lattice [12]. The birefringence was $(4.92 \pm 1.0) \times 10^{-4}$ with the largest refractive index along the plug axis (positive birefringence). Birefringence in polymers is normally associated with molecular orientation, hence potentially it should provide information about the molecular arrangement as opposed to arrangement of the submicroscopic particles in our macro-crystal. Nevertheless an oriented arrangement of dimensionally anisotropic particles with at least one dimension smaller than the wavelength of light can give rise to birefringence in itself without the involvement of molecular anisotropy, the so called « form birefringence ». The present samples consisting of uniformly oriented cylinders embedded in a matrix of differing refractive index are expected to produce form birefringence. Consequently before any conclusion can be drawn as regards molecular orientation the effect of form birefringence has to be assessed.

Form birefringence $n_\alpha - n_\sigma$ depends solely on the volume fraction ($v_1 v_2$) and refractive indices ($n_1, n_2$) of the two phases and can be expressed as

$$n_\alpha - n_\sigma = \frac{v_1 v_2 (n_1^2 - n_2^2)^2}{2 n_\sigma (v_1 + 1) n_1^2 + v_2 n_2^2}$$

where

$$n_\sigma^2 = v_1 n_1^2 + v_2 n_2^2$$

(see ref. [12]).

Here $v_1$ and $v_2$ are given and $n_1$ and $n_2$ are taken as the values measured on homopolymers. For our best oriented samples $n_\alpha - n_\sigma = 5.15 \times 10^{-4}$ was calculated in excellent agreement with the observed birefringence. In addition to the interesting fact that the usually elusive form birefringence has been quantitatively verified this finding implies that there is no intrinsic molecular orientation in our single crystals as the observed birefringence is accounted for by form birefringence alone (other values for the birefringence could be obtained by stretching the sample; here obviously additional molecular birefringence is introduced [12]).

Form birefringence is expected to be altered in a predictable manner by introduction of selective swelling agents which will primarily affect the form birefringence by changing the refractive index difference. Decane is a swelling agent for polybutadiene only and in the present system should increase ($n_\alpha - n_\sigma$). In fact an increase in birefringence on swelling with decane has been observed [8] (see below). Quantitative evaluation is in progress.

INFRA-RED DICHOISM. — A more specific method for determining molecular orientation in the present case is infra-red dichroism. With this method the possible orientation due to the S and B phases can be assessed individually by choosing suitable dichroic absorption bands characteristic of each constituent. Longitudinal sections of our single crystal sample have shown no dichroism whatsoever for either of the two phases [13]. In fact the traces recorded with the polarizer parallel and perpendicular to the hexagonal axis (original plug axis) were coincident which within our experimental sensitivity means that dichroism if present is less than 1.08 [13]. It is difficult to define the limits on the molecular orientation set by this observation without a separate study of the infra-red dichroism of the homopolymers undertaken specially for this purpose (such work is in progress). It is clear nevertheless that molecular orientation, if present, can only be very small in either of the phases. This point is very relevant to theoretical considerations on the phase separation and size and shape of the dispersed particles [14], [15].

SWELLING BEHAVIOUR. — Swelling experiments have already been referred to above in connection with form birefringence. Here it will only be stated that in addition to optical properties changes in sample dimensions and in the diffraction patterns have also been examined [8].

The sample expansion on swelling in an atmosphere of decane, which is selectively swelling the matrix phase B, was found to be anisotropic. As a function of time the sample expanded laterally i.e. perpendicular to the hexagonal axis, while expansion along this axis was absent or very small. In the course of time the lateral dimension reached a constant value but the longitudinal direction started to increase suddenly and this increase could far exceed the initial lateral expansion. According to our interpretation in the original undisturbed structure the cylinders become first separated by the swelling of the rubber but swelling along the cylinder direction is impeded by the continuity of the cylinders. The sudden onset of dimensional increase along the cylinder direction would then be due to disruption in cylinder continuity caused by the swelling pressure. Conditions of reversibility are under examination.

The most significant information on the first stage of the above swelling behaviour comes from correlation with the X-ray diffraction pattern. The hexagonal lattice was observed to expand on swelling and the correspondence between changes in lattice spacing and sample dimension was found to be quantitative in full support of the picture of laterally separating cylinders.

MECHANICAL PROPERTIES. — The possible mechanical anisotropy of our samples is perhaps of the greatest interest, both because of its relevance to application and also because here the anisotropy is expected to be very significant. The latter will be immediately apparent if we consider our samples as consisting of parallel glass fibres embedded in a rubber matrix of a modulus lower by several magnitudes, the
two phases being molecularly connected. Clearly we expect the material to be very much stiffer in the fibre direction.

In order to examine this behaviour test pieces were cut from a well defined « single crystal » specimen with long dimension at different directions with respect to the plug axis so as to enable the stress-strain behaviour to be recorded. The stress-strain curves and modulus $E_0$ were determined as a function of angle ($\theta$) with respect to the original extrusion direction. Figure 5 shows the results for some of the most significant angles $\theta$ while in figure 6 the corresponding $E_b$ values (together with some additional ones) are plotted. The very significantly larger stiffness along the cylinder direction ($\theta = 0^\circ$) as compared with that for larger $\theta$ values is immediately obvious. (Also there is a small but definite minimum at $\theta = 55^\circ$.) Thus the sample behaves as a glass and as a rubber in two mutually perpendicular directions respectively. This very large anisotropy is in agreement with the qualitative expectations laid out above. In what follows we shall compare actual numerical values with quantitative predictions [12].

![Fig. 5. Stress strain curves for a macroscopic single crystal [12]. O stress parallel to extrusion direction; A stress at 55° to extrusion direction X stress perpendicular to extrusion direction (for definition of broken line see ref. [12]).](image)

To take the simplest model we consider the two phases as separate blocks without any interaction between them. Then the behaviour for $\theta = 0^\circ$ will correspond to the case where the two blocks taken in the appropriate volume ratio are coupled parallel with respect to the stress. For this case the moduli will add weighted with the appropriate volume fractions. Thus

$$E_0 = v_s E_s + (1 - v_s) E_b$$

(1)

where $v_s =$ volume fraction of polystyrene, $E_s$ and $E_b$ being Youngs moduli of $S$ and $B$ phases respectively.

For $E_s$ and $E_b$ we take the macroscopically measured moduli of the corresponding homopolymer which are $2 \times 10^{10}$ dyn.cm$^{-2}$ and $1 \times 10^7$ dyn.cm$^{-2}$ respectively. (As $E_b \ll E_s$ the exact value for $E_b$ which depends on the degree of cross linking in the polybutadiene homopolymer is of little consequence.) The value calculated for $E_0$ is $4.0 \times 10^9$ dyn.cm$^{-2}$ in excellent agreement with the measured $4.25 \times 10^9$ dyn.cm$^{-2}$ fully supporting the underlying model.

Extension of the previous consideration to $\theta = 90^\circ$ (i.e. stress perpendicular to the plug direction) would require a series coupling of the phases, i.e. here it is the compliances of the two phases weighted according to their volume fractions which should add. Bearing in mind that $E_b \ll E_s$ this gives

$$E_{90} = \frac{E_b}{1 - v_s}.$$  

However, it is apparent by simple considerations that here the independence of the two phases cannot be assumed even as a first approximation because the rubber matrix stretched along $\theta = 90^\circ$ will be prevented from contracting along the direction $\theta = 0^\circ$ by the polystyrene cylinders. In fact the rubber will not be under uniaxial tension but pure shear which will make it stiffer. The true modulus along $\theta = 90^\circ$ will be given by

$$E_{90} = \frac{4}{3} E_{90}' = \frac{4}{3} \times \frac{E_b}{1 - v_s}.$$  

(3)

From the observed $E_{90}$ eq. (3) gives a value of $2.79 \times 10^7$ dyn.cm$^{-2}$ for $E_b$ which is reasonable in
view of the uncertainty of the degree of cross linking to which our sample corresponds when comparing with a standard homopolymer. Significantly a further check can be performed based on the simple model. It can be easily shown [12] that the restriction on the contraction of the rubber due to the cylinders will be removed when $\theta = 55^\circ$, thus for this case eq. (2) should pertain:

$$E_{55} = \frac{E_0}{(1 - e_0)} = \frac{3}{4} E_{90}. \quad (4)$$

Consequently $E_{55}$ should be lower than $E_{90}$, in fact it should be a minimum which is immediately apparent from figures 4 and 5. Further, the numerical relation between $E_{55}$ and $E_{90}$ can be tested. For $E_{90} = 4.65 \times 10^7$ a value for $E_{55} = 3.48 \times 10^7$ dyn. cm$^{-2}$ is expected by eq. (4) in practically complete agreement with the experimental value of $3.50 \times 10^7$ dyn. cm$^{-2}$.

In general the angular dependence of the modulus of a uniaxially oriented sample should obey the tensor transformation formula

$$\frac{1}{E_\theta} = S_{33} \cos^4 \theta + (2 S_{13} + S_{44}) \sin^2 \theta \cos^2 \theta + S_{11} \sin^4 \theta \quad (5)$$

where $S_{ij}$ are the compliances (index 3 refers to the direction of axial symmetry, i.e. to $\theta = \pi/2$ and 2 to any of the equivalent transverse directions (see e.g. ref. [16])). With six points of measurement and three unknown coefficients ($S_{33}$, $2 S_{13} + S_{44}$ and $S_{11}$) a least square test could be performed and complete fit with experiment was obtained [16] (Fig. 6). Thus internal consistency of the data is verified.

In what follows we attempted to account for the observed behaviour by a simple model in which the first approximation considered the cylinders as completely rigid. This gave for the Young's modulus [12].

$$\frac{1}{E_\theta} = \frac{1}{E_{90}} (\sin^4 \theta + 4 \sin^2 \theta \cos^2 \theta) \quad (6)$$

Figure 5 compares this relation with measurement. Except for $\theta = 0$ where $E_\theta$ should be infinite owing to the assumption of rigid cylinders the curve follows closely the experiment including the minimum at $\theta = 55^\circ$ [12].

In current work a more sophisticated theoretical approach is being adopted and the compliances $S_{ij}$ in eq. (5) are being individually determined from those of the homopolymer by the theory of fibrous composites [17].

We see that the basic «crystal» unit of this type of material is mechanically extremely anisotropic. We have just mapped out this anisotropy and practically fully accounted for it by an extremely simple model. It will be apparent that these considerations will have to be taken into account when attempting to interpret the mechanical behaviour of a copolymer sample of a more complex polycrystalline texture — as it may be more usual in practice — of which the present crystal is the basic texture unit.

Apart from its significance for the polymer itself the present «single crystal» samples provide an exceptionally good model substance for theoretical work on fibrous composites due to the perfection of the order, the large differences between constituents, hence the large resulting anisotropy, and to the perfect connection between the phases. This potential of the present samples is being currently exploited [17].

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