Transverse Screw Dislocations: A Source of Twist in Crystalline Polymer Ribbons

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A new model to explain the twisting of ribbonlike crystals within spherulites is proposed. The model is based on the inherent twisting perpendicular to the axis of a screw dislocation. In the proposed model a sequence of transverse screw dislocations of the same sign are spaced along the ribbon axis. The magnitude of the twist given by such a string of dislocations is calculated, and the mean dislocation spacings needed to give the measured degrees of twist are noted and found to be not unreasonable. The model also predicts the correct form of the temperature dependence of the degree of twist. An interpretation of the extant model of polymer ribbons is presented, whereby the nature of the orientation of the polymer chains within the crystals and the folding of chains at the ribbon surfaces cause the sign of the dislocations to be maintained and control the sign of the twist throughout the spherulite.

IN THE last several years, our understanding of the microstructure of bulk semi-crystalline polymers has increased enormously. The use of the electron microscope and X-ray small angle scattering as tools for morphological investigation has led to the concept of spherulitic polymeric systems composed on the finest scale of very thin ribbonlike crystals within which the polymer chains must re-enter the crystal many times*. In addition, it is known that the speed with which such ribbons grow increases markedly as the undercooling is increased[2]. The inability of the polymeric material to crystallize neatly at high rates of growth is reflected in the irregular features observed in single crystals grown from solution at large undercooling[1] and in the higher values of specific volume associated with crystallization at large undercoolings in bulk polyethylene[3]. Among the types of defect associated with rapidly crystallized material, we think of loose folds, tie chains, point defects, and dislocations. The incorporation of dislocations into polymer crystals could occur by growth accidents[4] or by thermal nucleation[5]. It has further been postulated that observed bundles of crystalline ribbons are generated by growth centred on transverse screw dislocations[1].

At the higher undercoolings, the spherulites of many polymers exhibit a radial banding. Fischer has shown that this banding is due to the twisting of the lamellar ribbons[6]. The pitch of this helical twisting of ribbons about their axes decreases as the undercooling or the molecular weight is increased[7]. Previous attempts to explain the twist were based on stresses associated with fold packing in the lamellae[8], the accumulation of impurity material at lamellar surfaces[9], and axial screw dislocations[9].

*For a review, see ref. 1.

Lindenmeyer and Holland measured the dependence of the degree of lamellar twist on crystallization temperature and concluded that none of the above mechanisms in its simplest form can account for the observed temperature dependence[7]. It appears that a nucleation event must be involved in the generation of the twist.

It is interesting to note that lamellar twisting has not been observed in isolated crystals. The twisting is not observed in solution-grown single crystals. Further, published photographs of crystalline fragments isolated from melt-crystallized polyethylene and polypropylene by selective oxidation also do not show twisting[10–12]. However, twisting is seen in stacks of crystallites interconnected in the direction of stacking (the thin dimension)[10, 11]. A theory which purports to describe lamellar twisting should predict these observations.

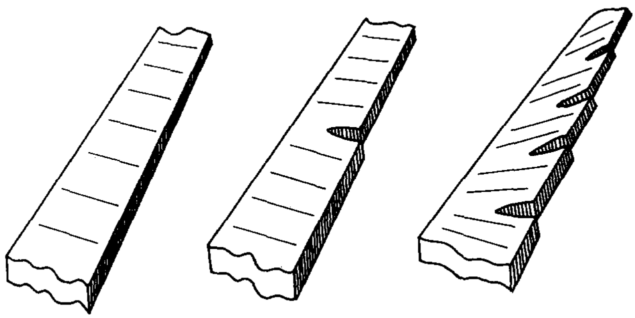

Figure 1—Effect of a sequence of transverse screw dislocations of the same sign on the morphology of a crystalline ribbon

The model of lamellar twisting presented here is centred on the necessity of a screw dislocation to produce twisting normal to its axis. The twist is effected by the presence of crystal boundaries normal to the axis of the dislocation. This twist is illustrated in Figures 2.2 and 2.3 of ref. 13, which show dislocations in bounded and unbounded media. *Figure 1* illustrates the effect of a sequence of transverse screw dislocations of the same sign lined up along the axis of a ribbon. The magnitude of the twist produced by such a sequence of dislocations is treated in the next section. The ability of dislocations of the same sign to become aligned and the correlation of these predictions with experimental results are treated in the final section.

METHOD AND RESULTS

We first calculate the magnitude of the twist due to one transverse screw dislocation in a crystalline ribbon. To do so we must calculate certain elastic displacements and some of their derivatives. Specifically, we need the quantities in the expression for the elastic twist

$$\varphi = \partial u_x / \partial z - \partial u_z / \partial x \tag{1}$$

where u_x is the displacement in the widthwise direction (x) and u_z is the displacement in the thickness direction (z). These displacements are obtained by using a dislocation imaging method to extend the results previously given by Eshelby and Stroh (E–S) for thin plates of infinite diameter[14]. *Figure 2* depicts the problem to be solved. The dislocated disc represents the case solved by E–S. Indicated also in the figure are the additional cuts to be made to remove a ribbon from the disc. In doing this, two new surfaces are formed. If the E–S solution is to be extended to this case, additional terms must be included to remove the stresses acting on the new surfaces. The shears shown in *Figure 2* are oppositely directed on the two new surfaces and constitute a torque about the ribbon axis. In addition to the depicted shear stresses there are normal stresses operating on these surfaces.

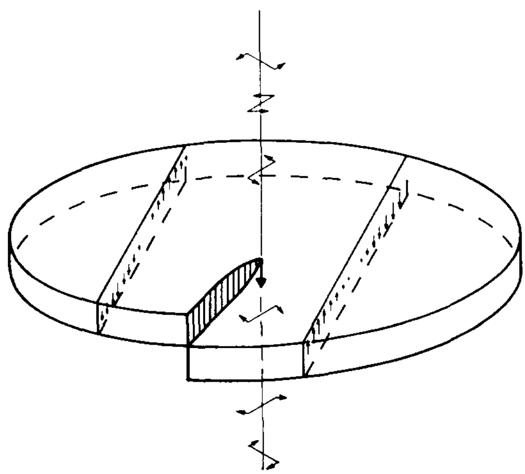

Figure 2—Transverse screw dislocation in a disc and in a ribbon cut from the disc. Double arrows represent sequences of point torques necessary to eliminate surface tractions when extending solution for an infinite body to a disc of infinite radius. Single arrows represent shear stresses in new surfaces created by cutting a ribbon out of the infinite radius disc

In this work, we consider the case of a dislocation lying on the y axis—that is, centred between the two new surfaces. We further consider in the calculation only those elementary blocks of material lying along the y axis. The normal stresses on the new surfaces will contribute no net moment to these blocks. This is a useful idea because it permits us to use a simple image dislocation model which treats the shears only.

The image model used to calculate the needed displacements is depicted in *Figure 3*. Here the shear field of the screw dislocation in the ribbon is nullified at the new surfaces by image dislocations of alternating sign, located at distances $\pm 2na$ from the y axis. This queue of dislocations was constructed in the following way. The first image dislocation (ID) on the right just nullifies the shear field of the real dislocation (RD) on the surface to the RD's right. Similarly, the first ID to the left nullifies the shear of the RD on the surface to the RD's left. However, the first ID to the right has added to the shear field on the left and the ID on the left has added a stress to the right boundary. Thus the second ID to the right is added to nullify the effect on the right hand boundary of the first ID to the left. But this new ID has contributed a new stress on the left boundary, which stress is just cancelled by the third ID to the left. In this manner the dislocation queue is constructed.

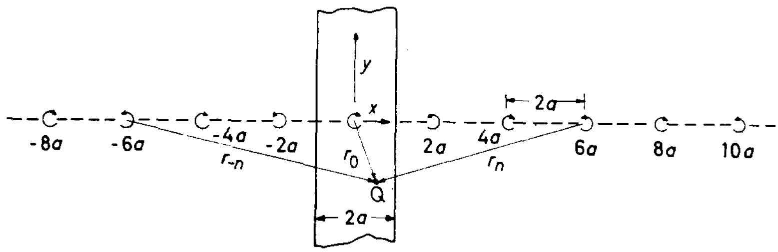

Figure 3—Image disclocation model used to calculate twisting along the axial fibre. Positive and negative image dislocations parallel to the real dislocation are denoted by + and —. Axes of the problem are illustrated, y being the ribbon axes, z the thickness direction, and x being a widthwise coordinate

While this method enables us to cancel the shear fields on the new surfaces, new normal stresses have been set up. In principle these normal stresses can be removed by an additional set of proper images. But they need not concern us here, since we are interested only in the twisting of the ribbons.

The quantities required for the calculation of the degree of twist are $\partial u_x/\partial z$ and $\partial u_z/\partial x$. For the system depicted in *Figure 3*, these quantities evaluated along the y axis ($x=0$, $z=0$) are

$$\frac{-\pi d}{b}\frac{\partial u_x}{\partial z}=\frac{y}{d}\sum_{p=0}^{\infty}(-1)^p\left\{\frac{1+\left[\frac{(2p+1)}{\{(2p+1)^2+(y/d)^2\}^{1/2}}\right]}{[(2p+1)+\{(2p+1)^2+(y/d)^2\}^{1/2}]^2}\right\}$$

$$+\frac{2y}{d}\sum_{n=1}^{\infty}(-1)^n\sum_{p=0}^{\infty}(-1)^p\frac{\left\{1+\frac{2p+1}{[(2p+1)^2+(2n\,a/d)^2+(y/d)^2]^{1/2}}\right\}}{\{(2p+1)+[(2p+1)^2+(2na/d)^2+(y/d)^2]^{1/2}\}^2}\qquad(2)$$

and

$$\frac{-2\pi}{b/d}\frac{\partial u_z}{\partial x}=\frac{1}{(y/d)}+2\sum_{n=1}^{\infty}(-1)^n\frac{(y/d)}{[(2na/d)^2+(y/d)^2]}\qquad(3)$$

where $2d$ is the thickness of the ribbon and $2a$ is its width. These expressions arise from differentiation of the E–S expressions for the displacement fields within an infinitely broad disc:

$$u_x=\{-y/(x^2+y^2)^{1/2}\}u_\theta\qquad(4)$$

$$= \frac{b}{2\pi} \frac{y}{(x^2+y^2)^{1/2}} \sum_{p=0}^{\infty} \left\{ \frac{(x^2+y^2)^{1/2}}{(2p+1)\,d - z + \{[(2p+1)\,d-z]^2 + (x^2+y^2)\}^{1/2}} + \frac{(x^2+y^2)^{1/2}}{(2p+1)\,d + z + \{[(2p+1)\,d+z]^2 + (x^2+y^2)\}^{1/2}} \right\}$$

and

$$u_z = (b/2\pi) \quad \arctan (y/x) \tag{5}$$

Numerical solutions to equation (1) have been computed, and these results have been extended to the case of a ribbon with evenly spaced transverse screw dislocations of the same sign. In this case, the displacement fields for *nearest neighbour* dislocations were superposed. As long as the dislocations are relatively far apart, such superposition should be a good approximation. In this manner the twist can be determined as a function of dislocation spacing. The results of these calculations are shown in *Figure 4* where values $b/d = 1$ (a growth dislocation) and

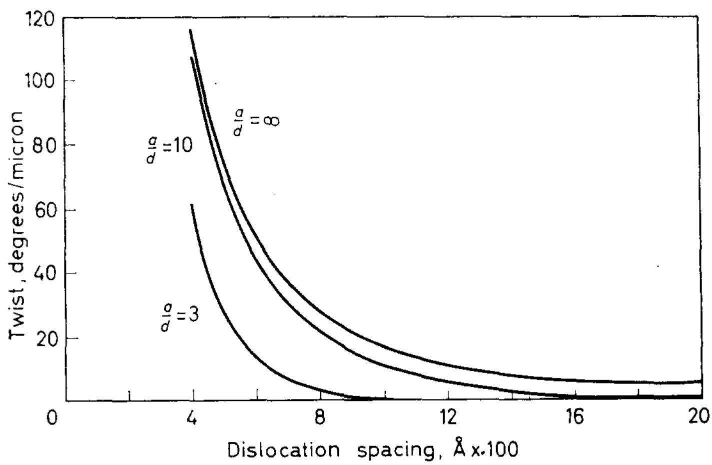

Figure 4—Twist of a 100 Å thick ribbon as a function of the dislocation spacing

$a/d = 3$, 10, and ∞ were used. The figure shows that for any nearest dislocation separation the degree of twist increases with increasing crystallite thickness (larger a/d). The values of twist reported by Lindenmeyer and Holland for linear polyethylene crystallized at temperatures between 115°C and 127°C all lie in the range 6·6 to 66 degrees/μ. Such values are accommodated by dislocation spacings of several hundred to thousands of Ångström units[7].

DISCUSSION

We now demonstrate that a sequence of dislocations will be constrained by chain folds to propagate a Burgers vector sign and that the temperature dependence of the present model agrees with that observed in experiment.

Consider the orientation of chains within a ribbon. Keller and Sawada have shown that these chains in bulk polyethylene are misoriented about the b axis (the ribbon axis) by 15° for quenched material and 35° in carefully crystallized material[11]. Similar magnitudes of the angle between chain axis and platelet normal are observed in solution grown polyethylene single crystals. This is attributed to the staggering of tight chain folds in a regular manner so as to eliminate strains due to the bulkiness of adjacent folds[15,16]. The rotation of the chain axis from the ribbon normal in bulk polyethylene may be similarly construed to indicate the presence of some significant proportion of tight chain folds at the crystallite surfaces.

If transverse screw dislocations are created at the growing tip of the ribbon, their sign will be such that their shear field will move chain folds in adjacent fold planes apart rather than together. The differentiation made is depicted in *Figure 5*, a schematic view of a crystalline ribbon

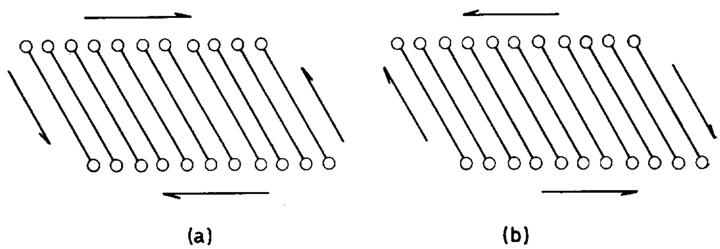

Figure 5—Shearing effects of screw dislocations of opposite sign. (a) indicates a shear tending to push bulky chain folds together, while (b) indicates a shear pushing them apart

viewed parallel to the fold planes. *Figures 5* (a) and *5* (b) indicate the shearing effects of screw dislocations of opposite sign. Of these two the screw dislocation represented by *Figure 5* (b) will be favoured, because the bulky folds are sheared apart by its action. As the ribbon continues to grow, the new material will be sheared in the direction shown in *Figure 5* (a). The next dislocation formed will again choose its sign so as to create a favourable shear field in the material behind it. Thus the sign of the dislocation is propagated along the ribbon. Indeed, the sign of the twist will be dictated by the primary nucleus of the spherulite if the creation of new ribbons occurs always by a screw dislocation mechanism.

Finally, we show that the temperature dependence of the helical twisting is compatible with the proposed mechanism. The strain energy E per unit length of a dislocation is given in general by an expression of the form

$$E = Cb^2 \tag{6}$$

where C is a constant and b is the magnitude of the Burgers vector. The probability of finding a dislocation at some position (x, y, z) along the ribbon is proportional to exp $(-Cb^2l/RT)$, where l is the length of the dislocation line. The mean spacing of dislocations along the ribbon will be inversely proportional to this probability of occurrence and will.

hence, be proportional to $\exp(Cb^2l/T)$. For growth dislocations, the Burgers vector and the dislocation line length are both identical to the thickness of the crystal. Hence, the spacing S of the dislocation is given by

$$S \propto \exp(Cl^3/T) \tag{7}$$

Since we are ultimately concerned with comparing predicted and measured values of φ, we need a functional dependence of S and φ. To this end it is noted that the curves of *Figure 4* are very closely fitted by a function of the form

$$\varphi = C_1/S \tag{8}$$

where C_1 is a constant. Thus inserting equation (7) into equation (8), we have

$$\varphi \propto C_2 \exp(-Cl^3/T) \tag{9}$$

The molecular kinetic theory of polymer crystallization predicts an expression of the type

$$l \propto 1/\Delta T \tag{10}$$

for the thickness of the polymer crystal, where ΔT is the undercooling[8]. Substituting equation (10) into (9) and taking the logarithm, we have

$$\ln \varphi = \ln C_2 - (\text{const.})\, 1/T(\Delta T)^3 \tag{11}$$

The data of Lindenmeyer and Holland for the twisting of crystals of a fractionated polymer crystallized at several temperatures (Figure 2 of ref. 7) are plotted in *Figure 6* according to equation (11). The data points are easily fitted by a straight line. Thus, the assumed thermal generation of growth dislocations is seen to predict correctly the trend for the dependence of radial twisting on growth temperature.

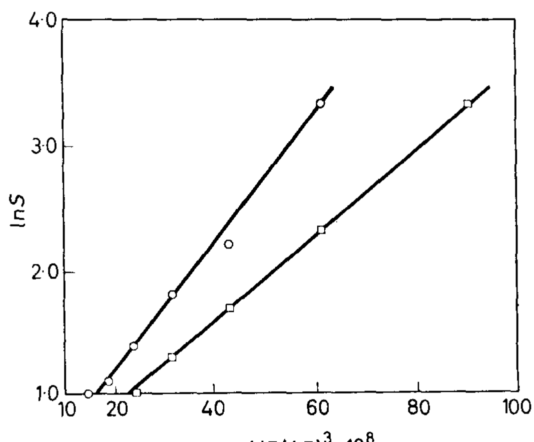

Figure 6—Experimental values[7] of φ versus $1/T(\Delta T)^3$

SUMMARY

A screw dislocation model to account for the twisting of ribbonlike crystals in polymer spherulites is proposed. Calculations of the degree of twisting and its dependence on dislocation spacing show that the observed degrees of twist for polyethylene correspond to reasonable dislocation spacings. The dependence of the degree of twist on crystallization temperature predicted by the new model and with the assumption of thermal generation of dislocations is shown to be in agreement with the observed temperature dependence. The generation of a string of screw dislocations of the same sign is shown to be a result of the preponderantly tight chain folding at the surfaces of the ribbon.

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