$$\frac{d[\text{ester}]}{dt} = \frac{-dC}{dt} = kKa^{1/2}C^{2.5}$$

if [COOH] = [OH] = C at a time t.

Then if the fractional conversion of acid groups to ester groups at time t is p then:

$$\frac{1}{(1-p)^{1.5}} = 1.5kKa^{1/2}Co^{1.5}t + 1 \qquad (5)$$

According to equation (5) a plot of $1/(1-p)^{1.5}$ against t should be a straight line. *Figure 1* shows such a plot for the experiments carried out by Flory. This plot shows that there is, in the initial stages of the reaction, i.e. up to 80% conversion, a linear dependence of $1/(1-p)^{1.5}$ upon time and that the correct substitution to be made in equation (1) was that shown in equation (4). Moreover, the intercept shown in *Figure 1* is close to the value predicted by equation (5), i.e. unity.

However, a close inspection of *Figure 2,* a plot covering much longer reaction times, shows that there is now a deviation from the predicted behaviour at higher conversions and the system behaves as predicted by Flory at these times. It should however be recognised that carboxylic acids are weak electrolytes and whereas at high concentrations the degree of dissociation (α) is low, α will increase with dilution. Without recourse to detailed calculations, it is obvious that in the case of high conversions (> 80%), [COOH] will be extremely low and the degree of dissocation will increase so that the substitution [COOH] $\propto$ [H$^{\oplus}$] becomes valid.

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Deformation in hard elastic polypropylene fibre

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Hard elastic fibre, which shows a large degree of elastic recovery, has been studied morphologically by electron microscopy and it has been proved that the lamellae are stacked perpendicular to the fibre axis. The mechanism of elasticity proposed by several investigators$^{1-3}$ was based on a splaying-apart of these lamellae, involving a reversible bending deformation during macroscopic deformation of the material. However, it was not clear how this deformation causes lengthening of the lamellae in the crystal lattice. The deformations in the lamellae have been studied by X-ray diffraction in this Note.

Isotactic polypropylene (Tokuyama Soda No F-105T) was spun into fibres at 200°C under an N_2 atmosphere at a reel speed of 15 m/min. The birefringence was 0.014. The fibres were annealed at 138°C for 30 min. The annealed sample showed a high value of elastic recovery, i.e. 96% on 100% elongation, which was characteristic of the hard elastic fibre.

The X-ray diffraction pattern was obtained using a Rigaku–Denki diffractometer with a scintillation counter and a pulse height analyser using CuKα radiation. The percentage orientation (π) was calculated from the equation:

$$\pi = \frac{180° - \Delta\Theta}{180°} \qquad (1)$$

where ΔΘ is the half-width of azimuthal breadth of the reflection.

If the crystal lattice is deformed for various times under a constant deformation ratio, we can study the dependence of the deformation ratio on the deformation of the lamellae. Initially the time dependence of π and spacing, d of two reflections, (110) and (040), were under a constant draw ratio of 2.0, measured as shown in *Figures 1* and *2.* Since these are independent of the time, we can investigate

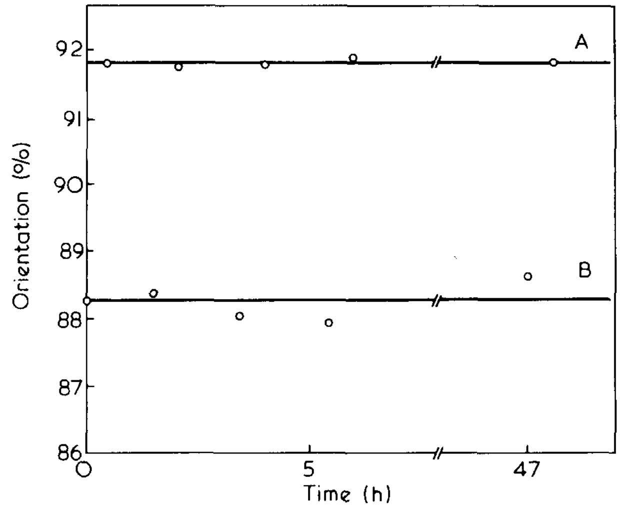

Figure 1 Time dependences of percent orientation for (110) and (040) reflections

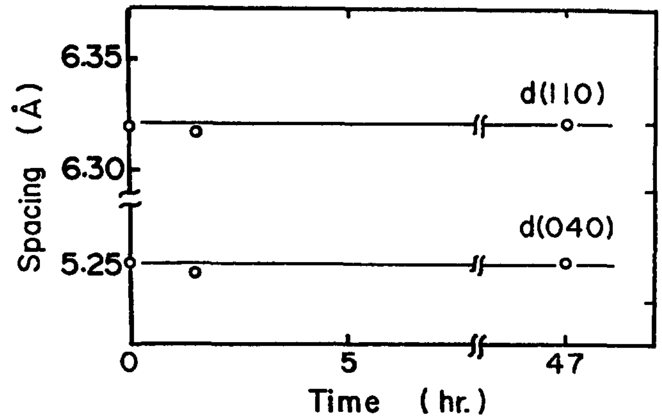

Figure 2 Time dependences of spacings for (110) and (040) reflections

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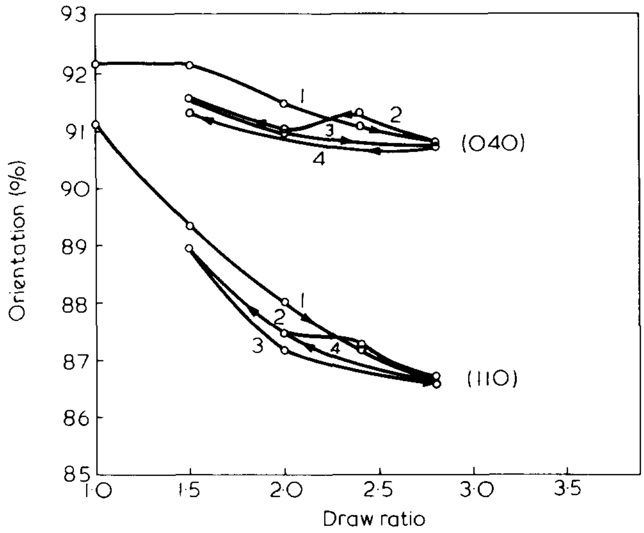

Figure 3 Draw ratio dependences of percentage orientation (110) and (040) reflections

the deformation of the lamellae as a function of the draw ratio as follows.

Figure 3 shows the draw ratio dependence of π for (110) and (040). Both of these quantities decrease with increasing draw ratio, but π of (110) decreases more rapidly than that of (040). Since the molecular chains in the lamellae, which are stacked perpendicular to fibre axis, are arranged almost parallel to fibre axis (c-axis)[1], the decrease in π for the two reflections indicates that the molecular chains in the lamellae incline to fibre axis. The larger the value of d, the smaller the van der Waals force, which is the only intermolecular force in the polypropylene; d(110) is larger than d(040) for this sample. Therefore, the van der Waals force in the (110) direction is weaker than that in the (040) direction and consequently π for the (110) reflection decreases more rapidly than that of (040) with increasing draw ratio.

On the other hand d (110) and d (040) were independent of the draw ratio in the second cycle of hysteresis curve (*Figure 4*). This means that every average value of d in the lamellae does not change in spite of the incline of the molecular chains.

From these results the mechanism of the draw was drawn schematically in *Figure 5*. It is reasonable to consider from this model that the elastic deformation may be based on the increase of the intermolecular distance against van der Waals force, and based on the changes of bond and rotation angles in the polypropylene molecules. Thus the elastic force will be calculated finally as a function of the intermolecular potential and the changes of the bond and rotation angles in the molecular chains.

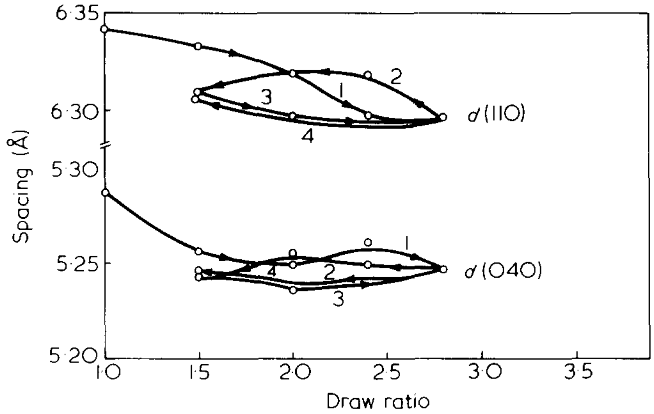

Figure 4 Draw ratio dependences of spacings for (110) and (040) reflections

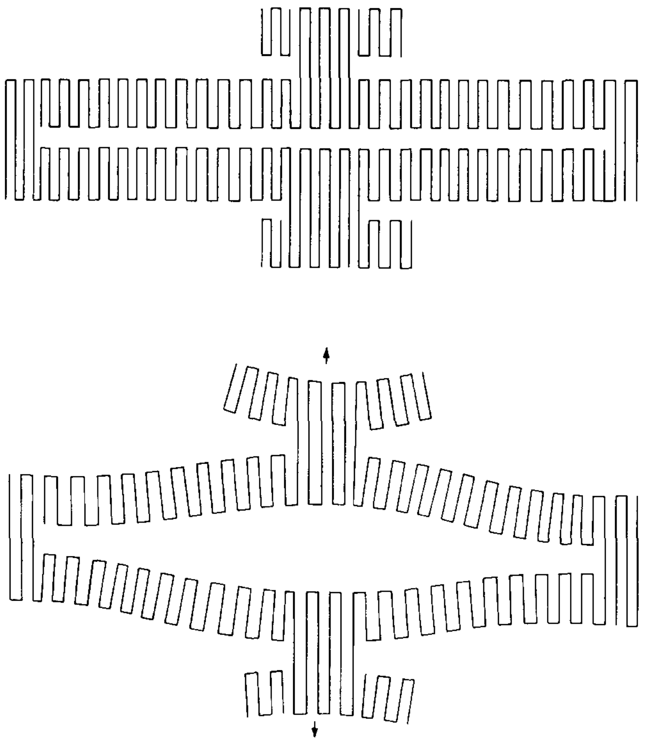

Figure 5 Schematic model of deformation of lamellae

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