Comments on the kineticsof uncatalysed polyesterification reactions

Allan J. Amass
Department of Chemistry, University of Aston in Birmingham, Gosta Green, Birmingham B4 7ET
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In 1939 Flory[1] described the kinetics of polyesterification in a paper that has become accepted as a standard text for this topic. The paper describes the uncatalysed polycondensation of 1,6-hexan-dioic acid and ethanediol over a wide range of temperatures. It was suggested by Flory that the reaction should be third order overall since in the general equation:

$$\frac{d[\text{ester}]}{dt} = k[\text{COOH}]\ [\text{OH}]\ [\text{H}^{\oplus}] \qquad (1)$$

one could substitute [COOH] for $[\text{H}^{\oplus}]$ because the catalysing proton was, in this case, supplied by the dissociation of the carboxylic acid. This substitution would then lead to the well-known equation:

$$\frac{1}{(1-p)^2} = 2k'Co^2t + 1 \qquad (2)$$

The plot of $1/(1-p)^2$ against time was not linear in any of the experiments except at high conversions and this deviation from linearity was attributed to the change in dielectric constant, and hence the dissociation constant of the acid, asthe reaction proceeded.

However, Flory's original substitution of [COOH] for the $[\text{H}^{\oplus}]$ must be challenged because the terminal carboxyl group of a polymer chain can be expected to be part of a weak acid of which the dissociation

$$\text{R COOH} \rightleftharpoons \text{R COO}^{\ominus} + \text{H}^{\oplus}$$

is governed by the dissociation constant (*Ka*) given by

$$\text{Ka} = \frac{[\text{R COO}^{\ominus}]\ [\text{H}^{\oplus}]}{[\text{R COOH}]} \qquad (3)$$

In the system under study, no common ion $(\text{R}\cdot\text{COO}^{\ominus})$ was added extraneously, so that during the reaction $[\text{R}\cdot\text{COO}^{\ominus}]$ and $[\text{H}^{\oplus}]$ were identical. Hence equation (3) can be rewritten as:

$$Ka = \frac{[\text{H}^{\oplus}]^2}{[\text{R COOH}]}$$

and it becomes obvious that the substitution made in equation (1) for the $[\text{H}^{\oplus}]$ should have been:

$$[\text{H}^{\oplus}] = (Ka[\text{R COOH}])^{1/2} \qquad (4)$$

Making such a substitution and setting the initial concentrations of diacid and diol equal then:

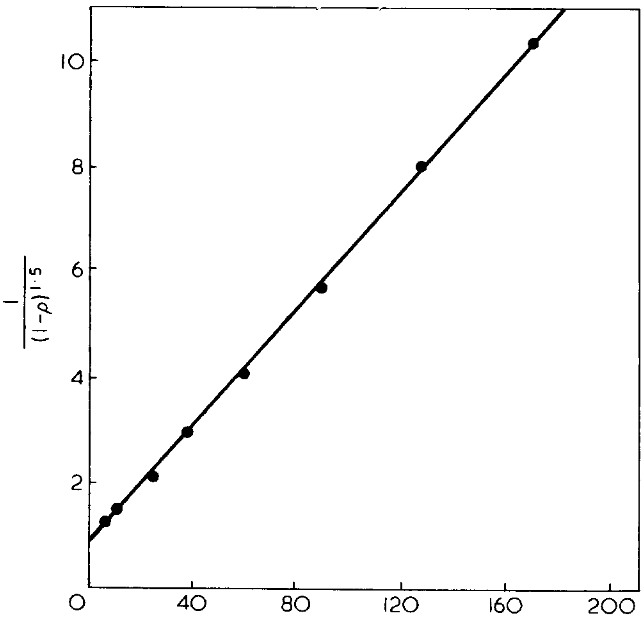

Figure 1 Dependence of $1/(1-p)^{1.5}$ on time during initial stages of polyesterification

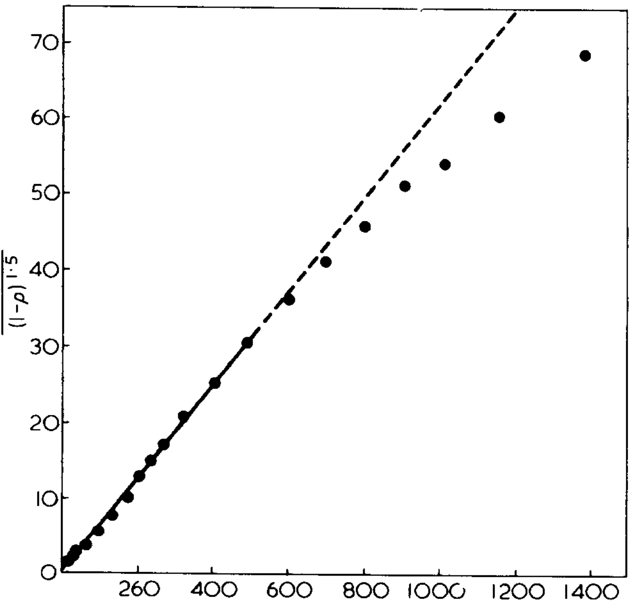

Figure 2 Dependence of $1/(1-p)^{1.5}$ on time for prolonged polyesterification reaction times

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

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.

REFERENCES

1 Flory, P. J. *J. Amer. Chem. Soc.* 1939, **61**, 3334

Deformation in hard elastic polypropylene fibre

Hiroshi Ishikawa, Hideaki Numa and Masanobu Nagura
Faculty of Textile Sciences and Technology, Shinshu University, Ueda, Japan
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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:

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

where $\Delta\Theta$ 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

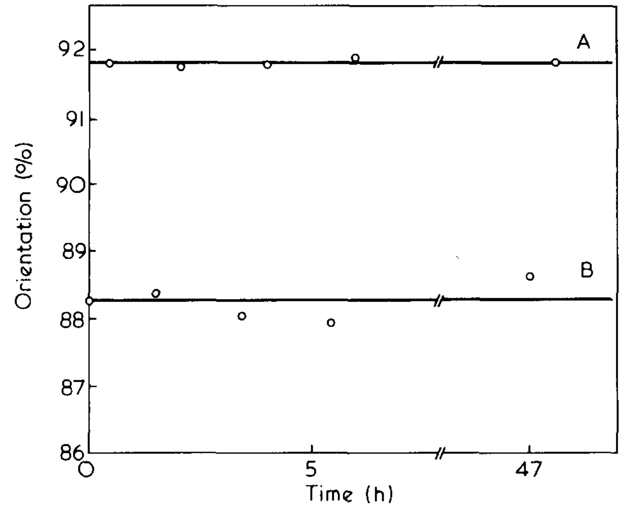

Figure 1 Time dependences of percent orientation for (110) and (040) reflections

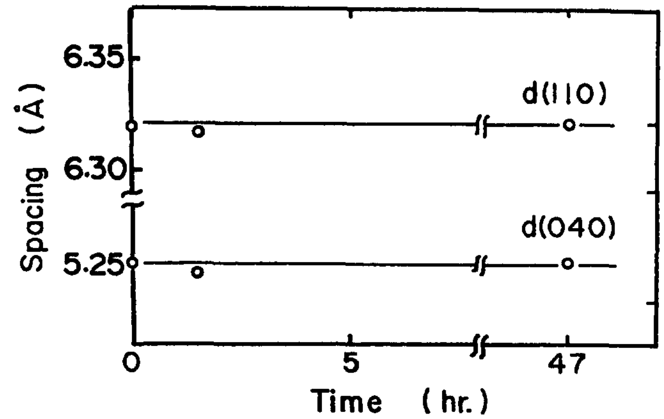

Figure 2 Time dependences of spacings for (110) and (040) reflections

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