# Planar deformation of a thermotropic copolyester below the crystal–nematic transition

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A solid-state forging experiment, developed in this laboratory, has been applied to a thermotropic copolyester of 4-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid. Uniplanar deformation (with a deformation ratio of 300%) and orientation have been achieved over the temperature range 60–170°C. Also noted is the possibility of unexpected creep well below the crystal–nematic transition (at 250°C). The mechanics of forging (essentially yield stresses) appeared to be strongly affected by the previous thermomechanical history. Among other results, sufficiently long annealing gives rise to a double yield phenomenon, which could be related either to the deformation of two distinct phases and/or to a two-step deformation mechanism. Differential scanning calorimetry and thermal shrinkage experiments above 250°C show the occurrence of strong relaxation processes in the forged copolyester, which could be related to the relaxation of internal stresses frozen in upon forging at low temperatures.

(Keywords: planar deformation; thermotropic copolyester; crystal–nematic transition)

## INTRODUCTION

A forging experiment has previously been used successfully in this laboratory to study the mechanisms of uniplanar deformation in the solid state of random-coil polymers[1,2]. Briefly, this process consists of a uniaxial compression between two axially aligned circular cylinders, at the desired draw temperature. The polymer so compressed is deformed in a plane perpendicular to the compression direction[1].

We have now applied this process to the case of a thermotropic copolyester of 4-hydroxybenzoic acid (HBA) and 2-hydroxy-4-naphthoic acid (HNA) of the following composition:
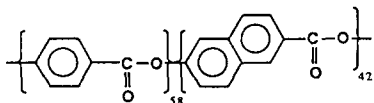


We find that the copolyester is readily deformable well below the crystal–nematic transition, and to as low as 60°C (about 200°C below the transition[3]). Such a plastic behaviour of a thermotropic polymer under uniaxial pressure had already been reported by Bechtold *et al.*[4]. We report here the first results of our study of the solid-state deformation behaviour of a thermotropic copolyester. The forging technique is expected to be a method of planar equibiaxial orientation of liquid-crystalline polymers. Therefore, our results are likely to have consequences concerning: (i) the properties achievable in planar orientation, for example mechanical and permeation control; and (ii) an unexpected creep process, which is likely well below the crystal–nematic transition.

Thermal shrinkage experiments have been carried out and may be a good way to characterize the orientation and deformation achieved by forging.

## EXPERIMENTAL

The pellets of HBA–HNA 58–42, as received from Hoechst Celanese, were compression moulded into plates of about 3 mm thickness. These plates were moulded at 300°C for 45 min before cooling. Three batches of plates were prepared, and were submitted to two different cooling procedures. The first batch was quenched at 0°C under atmospheric pressure (in ice–water), whereas the two others were cooled under pressure in a water-cooled (at 20°C) press. The cooling under pressure was aimed at avoiding the formation of porosity due to the shrinkage of the material upon cooling and crystallization. However, the fracture profiles of our plates still exhibited some porosity. Moreover, a slight darkening of the original tan-coloured copolyester occurred upon moulding. We prepared three sets of samples from the moulded plates by applying to them a further thermal treatment. The three sets will be referred to as I, II and III and are defined in *Table 1*.

The annealing treatment was performed in a vacuum oven. It was aimed at increasing the crystallinity of our samples so as to evaluate its influence on the mechanical behaviour of the HBA–HNA 58–42. Other studies have shown that this copolyester could reach up to 60% of crystallinity by annealing[5].

The WAXS patterns were obtained using a Statton camera with a sample-to-film distance of 75 mm and a pinhole diameter of 0.2 mm.

The d.s.c. scans were performed on a Perkin–Elmer DSC4 calorimeter, using an automatic baseline correction

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**Table 1** The three different series of samples

| Sample type | Type of cooling | Thermal treatment |
|---|---|---|
| I | Quench at 0°C at atmospheric pressure | None |
| II | Quench at 20°C under pressure | Annealing under vacuum at 200°C for 24 h |
| III | Quench at 20°C under pressure | Annealing under vacuum at 200°C for 48 h |
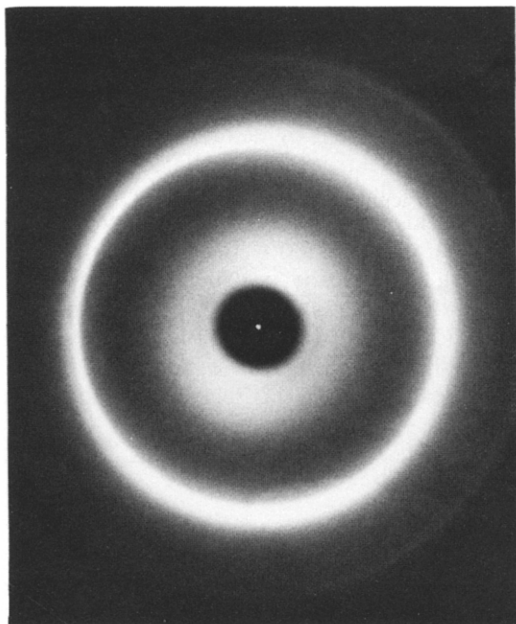


**Figure 1** WAXS pattern of a type III sample prior to forging

system. All scans were recorded at a heating rate of 20°C min⁻¹ between 50 and 300°C.

*Figure 1* shows an X-ray pattern of the material after the type III thermal treatment and prior to forging, i.e. before any deformation. The incident X-ray beam is parallel to the compression-moulded plate plane. The resulting pattern does not exhibit any azimuthal dependence of intensity, which shows that the compression moulding yields a macroscopically isotropic material: the starting material is free of orientation. Therefore, any anisotropy observed after forging should be considered as achieved by forging.

The uniaxial compression device used is described in ref. 1. It is installed in an Instron 1333 hydraulic machine equipped with a 55 000 lb ($\sim$25 000 kg) load cell and a servohydraulic control of the ram speed, which allows one to control accurately the compression speed $W$. We have used $W = 0.026$ inch min⁻¹ (0.011 mm s⁻¹). The compression experiments were performed over the temperature range 90–170°C. The Instron allows us to record the compression load vs. ram stroke curve. The load is directly proportional to the compression stress, since the compression area remains constant in the forging process[1]. The forging experiment indeed consists of squeezing the polymer out of the compression zone. In other words, the volume of copolymer actually compressed is not a constant: it decreases while the material is squeezed out, the compression area remaining unchanged (see ref. 1 for a complete description). These

curves thus give access to a yield stress $\sigma_y$. *Figure 2* shows a typical load vs. stroke curve. The 3 mm thick plates were typically pressed into films between 0.2 and 0.5 mm thick, depending on the forging temperature.

## RESULTS AND DISCUSSION

### Yield-stress results

The compression-moulded plates exhibited a spectacular plastic flow at temperatures as low as 60°C. Both types I and II samples showed a single, marked yield stress, whereas type III samples exhibited systematically two consecutive yields, as shown in *Figure 3*. The yield stresses measured in the experimental temperature range appeared to fit satisfactorily an Arrhenius law, as the plot of $\ln(\sigma_y)$ vs. $1/T$ shows (*Figure 4*). The corresponding activation energy was found to be approximately constant for the three sets of samples at a value of $22 \pm 1$ kJ mol⁻¹. There is a simple proportionality
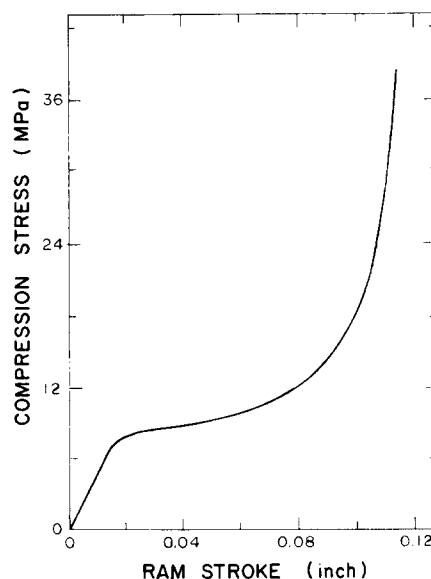


**Figure 2** Typical stress vs. displacement curve recorded during forging test (type II sample; $T_{forging} = 140°C$; $W = 0.026$ inch min⁻¹)
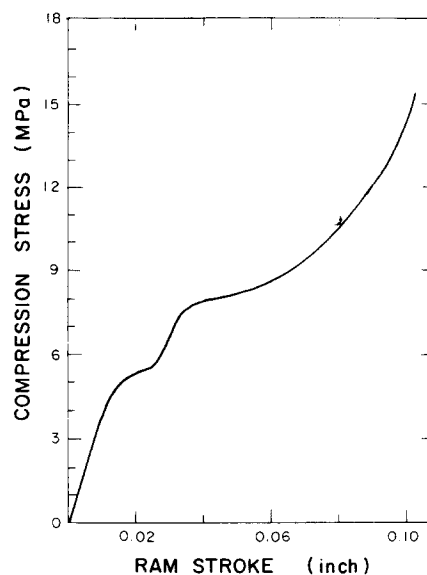


**Figure 3** Double yield curve of type III samples ($T_{forging} = 170°C$; $W = 0.026$ inch min⁻¹)
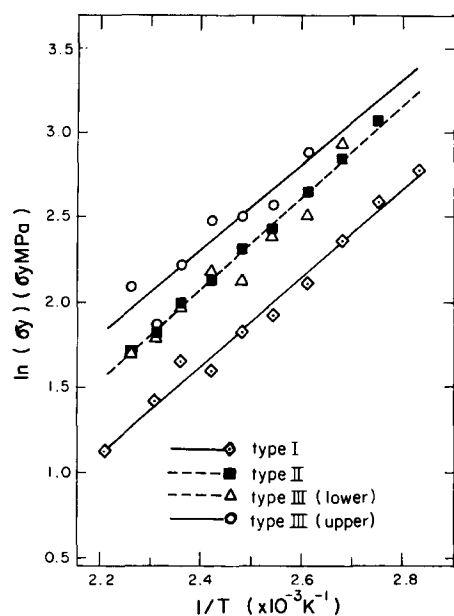
**Figure 4** Arrhenius plot of yield stresses for all three types of samples

relationship between the $\sigma_y(1/T)$ curves obtained for the different thermal treatments. This argument fits all except the case of the upper yield stress of type III samples, where the data scatter. The lower yield-stress values of the type III samples and that of the type II samples appear to fit the same line on the Arrhenius plot. This suggests that the two yield phenomena are identical, and that the further annealing has little effect on the level of this lower yield stress.

The evolution of the yield stresses $\sigma_y$ with experimental temperature is a clue for understanding the solid-state deformation mechanisms of this copolyester. That the activation energy is a constant independent of thermal treatment suggests that the nature of the yield mechanisms does not change among the samples. Another interesting feature is the occurrence of two consecutive yield stresses after long annealing. This could indicate either the deformation of a two-phase material and/or the occurrence of a two-step deformation mechanism.

*Thermal analysis*

*Figure 5* shows the d.s.c. scans at 20°C min$^{-1}$ of the type III samples after forging. The d.s.c. samples were 6 mm diameter discs cut from the forged films. This particular geometry was adopted to optimize the stacking of the polymer in the d.s.c. pans and thus to avoid eventual flow effects on the scans. This appeared to improve substantially the resolution of the curves, especially in the crystal–nematic transition zone. The scans shown in *Figure 5* have been smoothed and corrected for baseline slopes. All scans exhibit a marked endothermic peak between 240.3 and 252.7°C. *Figure 6* compares a heating scan of a type III sample prior to forging. The transition here is much sharper and occurs at higher temperatures. This peak can be attributed to the crystal–nematic transition of the copolyester. An immediate conclusion is that the forging has lowered the overall crystallinity (as shown by rough enthalpy calculations) and broadened the crystallite size distribution.

A broad inflection around 100°C is probably a $T_g$ relaxation, as reported for this copolyester by dynamic

mechanical and thermal data[3,6,7]. A broad exothermic tail, preceding the crystal–nematic transition, can be seen on the undeformed samples as well as on the films forged at higher temperatures. This weak relaxation tends to vanish as the forging temperature was decreased, whereas another, marked exothermic process takes place in the $T_g$ zone. This evolution of the heating thermograms suggests that at least two consecutive exothermic processes take place in the material upon heating: a very slow relaxation, which occurs at high temperatures, and a much more sharp one, which takes place in the $T_g$ zone. The latter probably corresponds to a relaxation, at $T_g$, of stresses induced by forging. It should be noted that this exothermic phenomenon could also be related to other macromolecular reorganization processes, occurring upon heating in d.s.c., such as crystallization or perfection of the crystals distorted by deformation. Moreover, the onset of this relaxation is shifted towards high temperatures as the forging temperature is increased.

We were also able to forge the copolyester at temperatures as low as 60°C. An interesting feature of the resulting d.s.c. scans is worthy of comment. The marked exothermic relaxation occurring in the $T_g$ zone was present, but started far below $T_g$, around 66°C. Rough enthalpy calculations have shown that the amount of energy released during this relaxation is at least twice
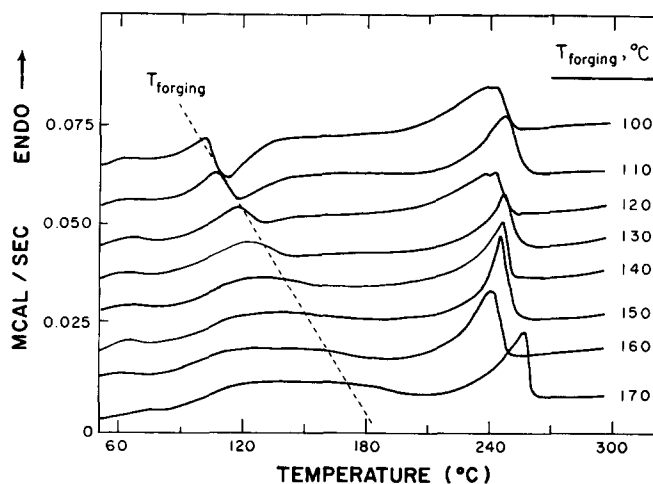


**Figure 5** D.s.c. traces of type III samples after forging at scanning rate of 20°C min$^{-1}$; parameter is forging temperature
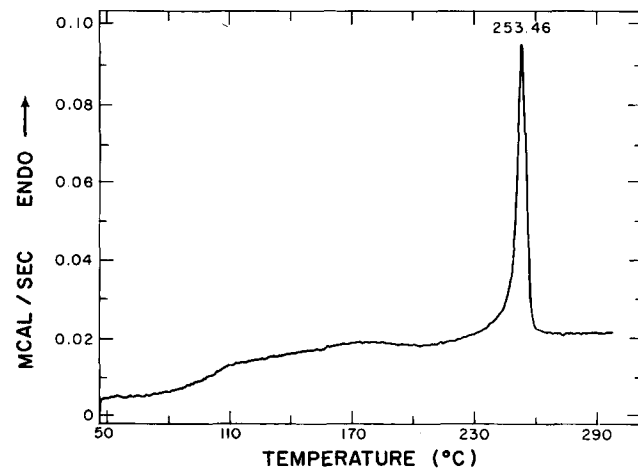


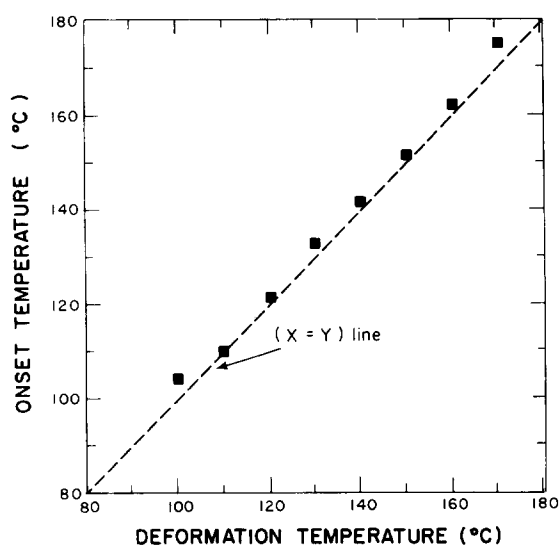**Figure 6** D.s.c. trace of type III sample prior to forging at scanning rate of 20°C min$^{-1}$

**Figure 7** Onset temperature of predominant relaxation process

as important as the following crystal–nematic transition enthalpy. This proves that the hypothesis of crystallization (or crystal perfection) upon heating is not sufficient to explain this exothermic phenomenon. The occurrence of this low-temperature relaxation can be related to other works on this copolymer, which have shown the existence of a strong $\beta$ relaxation[6,7] in this copolyester around 50°C. This might explain the occurrence of a sharp exothermic process far below $T_g$.

We find then two exothermic processes occurring upon heating in our forged films, one being predominant for a given deformation temperature. We plot in *Figure 7* the onset temperature of the predominant process as a

function of the forging temperature. It may be noted that the deformation temperature leaves a sharp marker in the morphology.

### Thermal shrinkage

Thermal shrinkage experiments have been carried out in a silicone oil bath at $252 \pm 1°C$. This is slightly above the crystal–nematic transition temperature. Squares of $1 \times 1\,cm^2$ were cut from the forged films and immersed in the oil bath for a few minutes until shrinkage was apparently complete. These squares shrunk markedly and biaxially, with an area reduction around 60%. No obvious correlation between the forging conditions and the amount of thermal shrinkage has yet been established. This point will be studied with further details in a subsequent paper.

### ACKNOWLEDGEMENTS

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