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# Kinetic Study of the Crystallization of Stretched Polyisobutylene Using Synchrotron Radiation

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Summary: The change in the scattering pattern of polyisobutylene fibres following rapid stretching was measured using synchrotron radiation. The half-time for the crystallisation process is approximately 50 seconds. Upon release the crystalline portions disappear immediately.

It is well-known that many polymers crystallise upon stretching, but apart from one study on polyethylene (ODA and STEIN 1972) little or nothing is known about the dynamics of this process. The intense X-ray beams from storage rings offer new possibilities for the study of this type of phenomena.

To evaluate the feasibility of such kinetic studies on elastomers we used polyisobutylene (PIB) which is well-known to crystallise upon stretching. (FULLER et al. 1940, TANAKA et al. 1974).

The sample used was commercial unpurified PIB (Oppanol-B-200®) from BASF (Ludwigshafen, W. Germany) with a molecular weight ($M\bar{v}$) of 4.5 $10^6$. This material was extruded at 190 °C to form long fibres of 4 mm diameter. The molecular weight determined by viscosimetry in a cyclohexane solution at 30 °C after extrusion was $M\bar{v}$ = 3.2 $10^6$. A few measurements were also carried out with a filled polymer containing 5 % $CaCO_3$.

For the measurements the fibres were clamped at both ends. One end was kept fixed whereas the other was attached to the shaft of a pneumatically driven piston. Elongations varied between 300 and 800 percent and were determined from the distance between two marks on the fibre. All measurements were carried out at room temperature.

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The double focusing X-ray camera used for this work has been described in detail elsewhere (HENDRIX et al. 1979). It was equipped with a Gabriel delay line read out detector (GABRIEL 1977) with a total active length of 80 mm flushed with Argon-$CO_2$ (66 % Ar) connected to an IN90 (Intertechnique) programmable multichannel analyser. The measurements were triggered by a microswitch actuated by the shaft of the piston at the end of its travel. Data were then collected in 32 slots of 5, 10 or 30 seconds. The duration of the stretch which was not measured accurately was in any case shorter than half a second.

The distance between the sample and the detector was 20 cm and the wavelength used 0.15 nm. During the experiments the storage ring DORIS was operated in the multibunch mode at 3.2 GeV with currents varying between 30 and 70 mA.

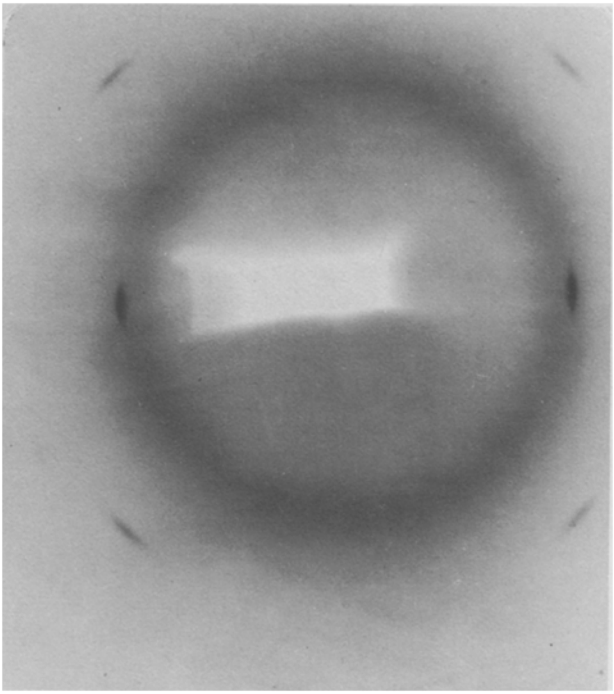

Figure 1:

Diffraction pattern of a stretched polyisobutylene fibre. The region of weak intensity in the centre corresponds to the beam stop. Exposure time: 3 minutes with OSRAY T4 film (Agfa-Gevaert). DORIS was running at 3.2 GeV, 30 mA.

Figure 1 shows a typical diffraction pattern of stretched PIB recorded photographically in front of the detector. By adapting the orientation of the detector one can follow the changes in the amorphous halo as well as the appearance of the two strong reflexions. These reflexions can be indexed as 020 (equatorial reflexion) and 113 according to the cell dimensions given by TANAKA et al. (1974). The evolution of the diffraction pattern and the time courses of the two reflexions are illustrated in figures 2 and 3.

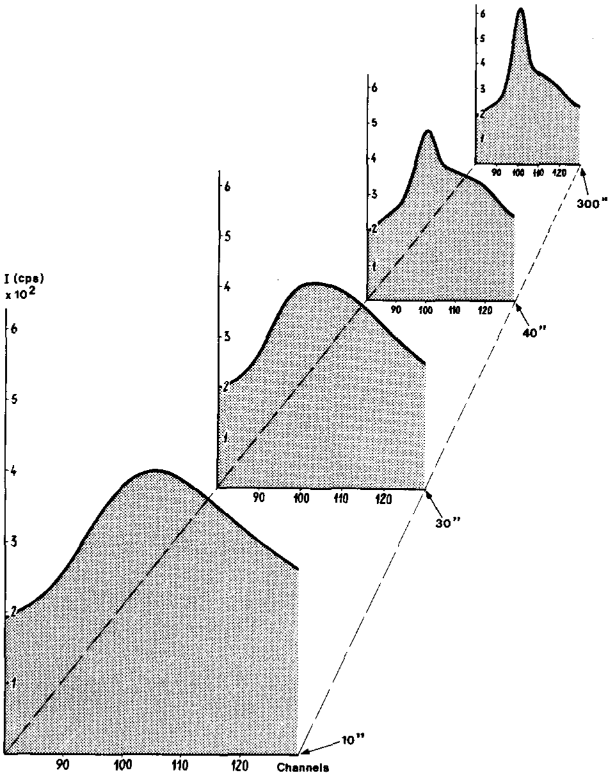

Figure 2:

Changes in the diffraction pattern after stretching as a function of time (in seconds) for the equatorial reflexion. The centre of the pattern is on the right hand side.

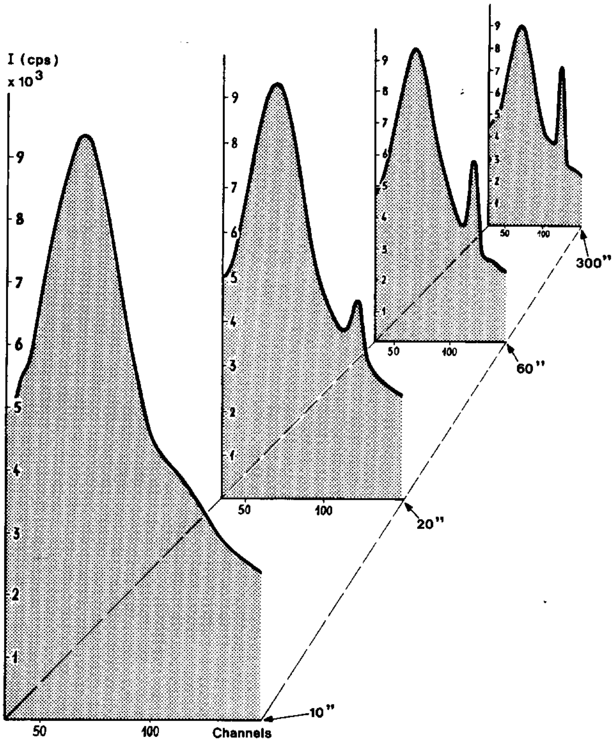

Figure 3:

Changes in the diffraction pattern after stretching as a function of time (in seconds) for the 113 reflexion. The centre of the pattern is on the left hand side.

The plots of intensity of the crystalline reflexions vs time (figure 4) can be interpreted by adapting Avrami's equation (AVRAMI 1939):

$$I(t) = I_{\infty} \left(1 - \exp\left(-kt^{n}\right)\right)$$

where I(t) is the difference between instantaneous intensity and the intensity before the onset of the crystallisation process. The latter value was determined from static measurements on an unstretched fibre taking into account the reduction of the cross section of the fibre upon stretching. $I_{\infty}$ is the value of I(t) when the effect has reached its maximum.

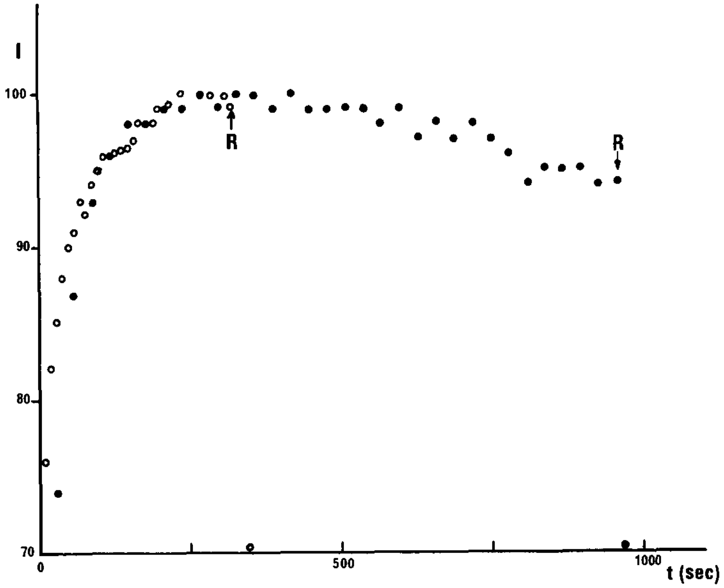

Figure 4:

Time course of the intensities below the peak for the 020 reflexion (●) (time resolution: 30 seconds) and for the 113 reflexion (O) (time resolution 10 seconds). As soon as the fibre is released (R) the intensity drops back to its initial value. (Note the points near the abscissa).

Using the data obtained during the first 100 seconds one obtains k = 0.014 (± 0.005) $s^{-1}$ and n = 1 for both reflexions. This value of n is characteristic of the athermal formation of rods or fibrils.

When the fibre is released it returns, within a few percent, to its original length and the crystalline portions disappear immediately. Even measured with a time resolution of 5 seconds it appears that all signs of crystallinity have already disappeared in the first frame.

When the fibres were stretched a second time if any crystallisation was detectable it was less pronounced than in the first experiment. This can probably be ascribed to preorientation of the polymer chains as well as to the fact that the elongation is smaller than in the first experiment.

At low elongation one only observes a slight decrease of intensity in the region where the reflexions would appear. This can be interpreted as an orientation effect resulting in a decrease of the intensity of the amorphous halo which is not compensated by the appearance of crystalline reflexions.

The measurements on the filled material show as expected an increase in the rate of the crystallisation process. The extent of crystallisation seems however less pronounced than in the unfilled fibres.

Although the present experiments are only very crude, they illustrate the promises of synchrotron radiation for dynamical studies on polymers.

Presently the availability of beam time on storage rings precludes more than exploratory experiments in this field. The situation is however likely to change with the construction of new dedicated sources.

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