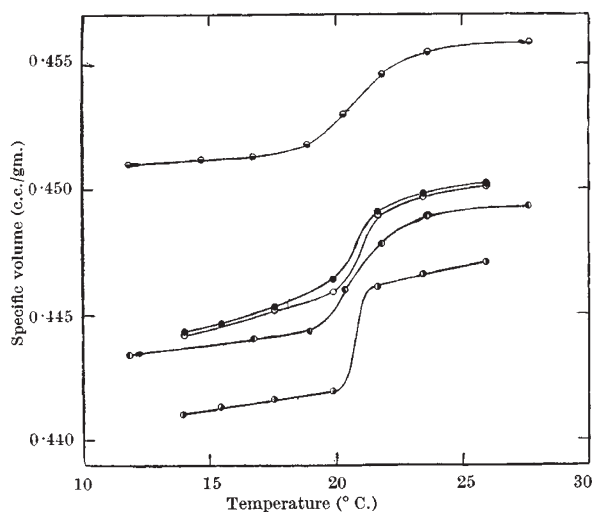


A Room-Temperature Transition in Polytetrafluoroethylene

IN the course of determinations of the variation of the specific volume of polytetrafluoroethylene with temperatures between -30° and $+360^{\circ}$ C., a phenomenon was observed at about 20° C. which is, to the best of our knowledge, unique in the polymer field. Below 15° and above 25° C., the cubical coefficients of expansion are roughly the same and of the order of 3×10^{-4} c.c./c.c./ $^{\circ}$ C., but at about 20° C. there is a 1 per cent increase in volume; data for five different samples of polytetrafluoroethylene are presented in the accompanying curves. The results for any single sample are reproducible, and the same curve is obtained on approaching the transition region from low and high temperatures.



Specific volume vs. temperature for polytetrafluoroethylene

The variation in specific volume from sample to sample is presumably due to their different degrees of crystallization, these being dependent upon the past thermal history of the specimens. The time required to attain equilibrium at temperatures in the transition region is of the order of two hours. The process is therefore quite slow.

This phenomenon is definitely not a 'second-order transition', as this would be characterized by a change in a first derivative only, in this case that of the specific volume, that is, the coefficient of thermal expansion. Moreover, it is thought that 'second-order transitions' are associated with changes in the amorphous regions of polymers¹, whereas the X-ray evidence given below suggests that this phenomenon is associated with a change in the crystal structure of polytetrafluoroethylene.

The initial measurements were made using a glass dilatometer, mercury being the enclosing liquid. The results presented were obtained by determining the densities of the samples by flotation in methyl iodide-chloroform mixtures, the densities of the mixtures being measured with a pycnometer.

X-ray diffraction photographs of the specimens taken above and below 20° C. show that a reversible change in the diffraction pattern takes place; reflexions from crystal planes parallel to the chain axis remain sharp and unchanged in relative intensity, though slightly changed in position, while those from

planes inclined to the chain axis either become weaker and diffuse or disappear altogether. There is evidently a change of crystal structure; it is, however, not a change from one precise arrangement to another, but a change from three-dimensional (fully crystalline) order below 20° C. to a lower degree of order above 20° C. The chain repeat distance (2.62 Å) remains unchanged; but there is an increase of about 0.5 per cent in the side spacings at the transition point. This means an increase of specific volume of the crystals of about 1 per cent. It therefore appears that the 1 per cent increase in volume found by density measurements is due to this change of crystal structure, and not to any change in the amorphous regions or to a change in the proportions of crystalline and amorphous regions.

The observed changes in the diffraction pattern can be accounted for by a gain in freedom of position of the molecules by movement along their chain axes, the small increase of side-spacings being a by-product of this longitudinal freedom. Although a detailed picture can only be given when the crystal structure below 20° C. is fully determined (a problem on which we are now working), it may be said that the unit cell is either monoclinic or triclinic, and that the spreading of certain reflexions above 20° C. represents a variation of unit cell angles of several degrees. Whether this is a static variation from one crystal to another or a dynamic variation cannot be determined from X-ray results, though the former seems more likely. This variation of unit-cell angles means that, with respect to a given molecule, a neighbouring molecule may occupy a range of positions along its chain axis varying by something like 0.5 Å. This is one-fifth the chain repeat-distance. It is remarkable that such a transition occurs so far below the melting point (330° C.).

The X-ray diffraction pattern above 20° C. is similar in type to those of shock-cooled polyamides², but in the polyamides the disorder is not associated with a definite temperature of transition, and can be removed by annealing.

The results of a detailed investigation of the behaviour of polytetrafluoroethylene over the wider temperature range will be published elsewhere.

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H. A. RIGBY
C. W. BUNN

Imperial Chemical Industries, Ltd.,
Plastics Division,
Research Department,
Welwyn Garden City, Herts.
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¹ Boyer and Spencer, "Advances in Colloid Science", 2, 1 (Interscience, New York, 1946).

² Bunn and Garner, *Proc. Roy. Soc., A*, 189, 39 (1947).

Raman and Infra-Red Spectra of β -Quartz

THE Raman spectrum of β -quartz has been investigated by Narayanswami¹. He finds that the frequency 466 of α -quartz appears at 452.5, whereas the frequencies 207, 356 and 1,082 of α -quartz are absent from the spectrum. He also finds frequencies at 97, 250, 395, 686, 792, 1,060 and 1,154 cm^{-1} , which correspond to the doubly degenerate frequencies 128, 265, 395-403, 695, 795-807, 1,063 and 1,159 of