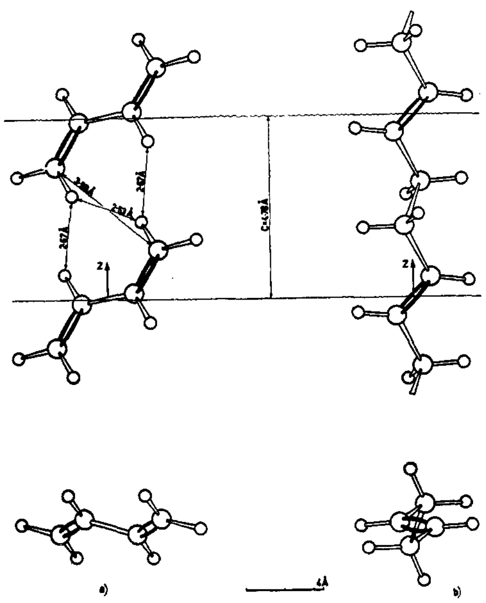

Figure 6. (a) Relative orientation of successive butadiene molecules within the channels of I, in a view at right angles to the *c* axis (above) and along the axis (below). (b) The corresponding views of the included polymer.

Figure 6a shows the arrangement of the butadiene molecules within the rows, arrived at on the basis both of the Fourier image reported in Figure 2a and of packing criteria. It is interesting to point out that the distance between terminal C atoms of neighboring molecules (~3.50 Å) is very close to the van der Waals value, which certainly favors the 1,4 addition that takes place under γ or X radiation. Figure 6b shows the chain model of poly(*trans*-1,4-butadiene), as derived from X-ray investigations on the crystalline polymer, with only a slight change in the torsional angles (2–4°) to bring the repeat distance from 4.85 to 4.78 Å, as it is in the inclusion compound.

Final Remarks

Very few cases of single crystal to single crystal transformation during a solid-state reaction have been reported hitherto, and we wish to recall in this context the radiation polymerization of trioxane,[13] tritiane,[14] triselenane,[15] and vinyl stearate.[16] However, the polymerization of butadiene included in PHTP is peculiar insofar as a chemical transformation involving the guest molecules is able to determine a packing rearrangement of the host molecules which extends throughout the crystal with three-dimensional order. We believe that the circumstance that the *initial monomer:PHTP molar ratio is identical* with the (monomer units):PHTP ratio after the polymerization is very favorable to the regularity of the crystalline rearrangement, insofar as it does not require any long-range shift of included molecules within the channels during the polymerization process, thus presumably minimizing the strain within the crystals.

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Nuclear Magnetic Relaxation in Polytetrafluoroethylene Fibers

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ABSTRACT: Nmr relaxation studies have been carried out on fibers of polytetrafluoroethylene (PTFE). Spin–spin relaxation time, T_2, orientation dependences provide confirmation of the onset of chain rotation at the 20° crystalline transition and support the view that longitudinal chain translation sets in at the ~35° transition. The amorphous regions evidence no apparent orientation.

Molecular relaxation processes in polytetrafluoroethylene (PTFE) have been studied extensively by ^{19}F nmr, both in the bulk[1,2] and in the oriented fiber form.[3–6] The use of oriented fiber samples has facilitated the interpretation of the relaxation processes because of the additional information contained in the anisotropy of the nmr absorption signal as a function of the direction of the applied magnetic field.

PTFE is a partially crystalline polymer with crystalline and amorphous phases. Consequently, the recorded nuclear signal is a superposition of two decay curves. Although Hyndman and Origlio[4] have reported second-moment data for the ^{19}F resonance in PTFE fibers, their calculations refer only to the composite signal. Here we report spin–spin relaxation data which have been analyzed in terms of two distinct relaxation times with the result that more precise comparisons between theoretical predictions and experimental data can be made.

Spin–lattice (T_1) and rotating-frame ($T_{1\rho}$) data have also been recorded. However, T_1 measurements provide no further information in addition to that reported for the bulk polymer.[1] The rotating-frame data are too complicated to extract any useful information at this point.

The spectrometer was operated at a frequency of 30 Mcps

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(1) The work on PTFE up to 1967 is reviewed in the paper by D. W. McCall, D. C. Douglass, and D. R. Falcone, *J. Phys. Chem.*, **71**, 998 (1967).

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Figure 1. Bloch decay for PTFE fiber at 5°. The fiber axis is at 54° with the magnetic field direction. The 90° pulse ended at the extreme left side of the graticule. A 6-μsec recovery time is indicated by the absence of nuclear signal. The method of separation of the long and short T_2 signals is indicated. The time scale is 10 μsec/division.

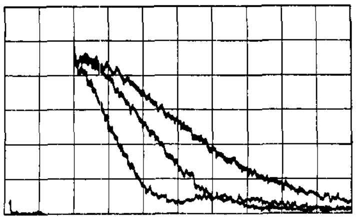

Figure 2. Bloch decay for a PTFE fiber at 25°. From left to right, $\gamma = 0, 90, 54°$. The time scale is 10 μsec/division.

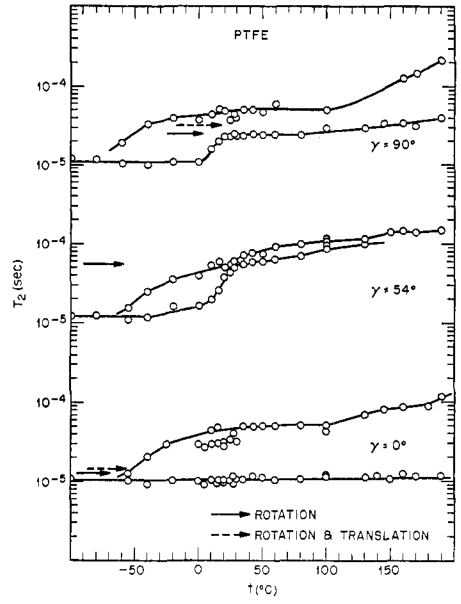

Figure 3. Temperature dependence of T_2 for fiber orientations $\gamma = 0$, 54, and 90°. The arrows indicate calculated T_2's based on the model of rotating chains and rotating and translating chains; see text. Resolution of amorphous and crystalline T_2's that are not very different is possible owing to the fact that the respective T_1's are quite different.

and has been described elsewhere.[7] The sample temperature was controlled by means of a gas-flow thermostat to an accuracy of about 1°.

The Teflon fiber used in the experiments was obtained commercially from the Du Pont Co. and X-ray patterns indicated a high degree of orientation. The degree of crystallinity was estimated by nmr to be about 75%. The preparation of the samples suitable for nmr studies has been described in a previous paper.[6]

T_2 is measured as the decay time associated with a free-induction decay following a 90° pulse, and is taken to be $t_{1/2}/\ln 2$, where $t_{1/2}$ is the time taken for the nuclear signal to fall to half its initial observed value, regardless of the shape of the decay curve. It is important to bear in mind that the nuclear signal is not observed for a period t_r, the recovery time of the apparatus (~6 μsec) after the 90° pulse. The observed free-induction decay is a superposition of a short T_2 signal which is identified with the crystalline regions and a long T_2 signal which is identified with the amorphous regions.[1] The method of decomposition is illustrated in Figure 1.

Typical fiber T_2 decay curves are illustrated in Figure 2, where the fiber axis is parallel, at 54°, and perpendicular to the applied magnetic field direction. Figure 3 shows T_2 as a function of temperature for the three orientations. The temperature behavior of the long T_2 is approximately the same for the three orientations. For the $\gamma = 0°$ orientation, the short T_2 remains almost invariant with the exception of a small increase between 15 and 30°. The short T_2 for the $\gamma = 54°$ orientation increases by about a factor of 5 from 0 to 35°, after which a more gradual increase is observed. A similar temperature behavior of the short T_2 is observed for the $\gamma = 90°$ orientation, but the increase between 0 and 35° is about a factor of 2 in this case.

The data are consistent with a model in which the amorphous regions are randomly oriented from an nmr viewpoint. Calculations of T_2 have been made for the case where the PTFE chains are rotating about their long axis, and the results are shown in Figure 3.[6] The transition in the crystalline regions at room temperature is one of rotational disorder. It is not possible to distinguish between hindered rotation and free rotation in this context. These results confirm the interpretations of Slichter[3] and Hyndman and Origlio.[4]

The β process in PTFE has been interpreted in terms of longitudinal motions of chains.[1] T_2 has been calculated for the case where the intermolecular contribution to the dipole field is averaged to zero by this process. This result is also included in Figure 3.[6] The TFE chain is helical, and it is known that the pitch of the helix changes from 13 CF's to 15 CF_2's per 180° twist of the helix just above room temperature.[8] The nmr effects which have been attributed to a translational motion of the chains may in fact result from a rapid interchange between the two helical forms. In order to test this possibility, the intramolecular contribution to T_2 was computed for both helical conformations, and it was found that T_2 for the 15-CF_2 arrangement was about 2% lower than for the 13-CF_2 arrangement. It is therefore not possible to confirm or deny the existence of this interchange mechanism by nmr.

The increase in the long T_2 in the region of −60° indicates the onset of extensive motion in the amorphous regions. This T_2 behavior is consistent with the amorphous $T_{1\rho}$ minimum which has been observed at this temperature for the unoriented sample[1] and which has been assigned to the γ or glass II process. No anisotropy is observed in the long T_2 component. It is interesting to note that the crystalline fraction T_2 at high temperatures and $\gamma \cong 54°$, *i.e.*, near the "magic" angle, crosses over and becomes longer than the amorphous fraction T_2.

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