Communications to the Editor

Fluorination of Polyethylene Single Crystals

A recent study[1] concerning the surface treatment of polymers has revealed that the exposure of polytheylene to a fluorine ambient is sufficient to convert -CH_2- to a perfluorinated species of high mechanical strength.

Rudge[2] has reported that a film of polyethylene was converted completely to a perfluorinated species when left in contact with fluorine gas at 1 atm pressure. Miller and Dittman[3] and Bigelow[4] have pointed out that fluorination reactions involving elemental fluorine and *n*-hydrocarbons have all the characteristics associated with free-radical reactions. The approximate heat of

$$F_2 \longrightarrow 2F\cdot \qquad (1)$$

$$RH + F\cdot \longrightarrow R\cdot + HF \qquad (2)$$

$$R\cdot + F_2 \longrightarrow RF + F\cdot \qquad (3)$$

reaction of reactions 2 and 3 is −34.0 and −68.0 kcal/mol, respectively. The ease of fluorination of polyethylene is consistent with the above mechanism. Tedder[5] has reviewed briefly and informatively the theoretical aspects of fluorination as applied to organic compounds. Fredricks and Tedder[6] have suggested that a substituent fluorine deactivates the hydrogen atoms adjacent to it so that progressive fluorination becomes increasingly difficult. Fluorination of compounds ranging from methane to lubricating oils has been investigated.[6] These reactions, like other free-radical reactions, invariably have been accompanied by both fragmentation and polymerization. When polyethylene is treated with fluorine, it appears that more cross-linking occurs than fragmentation.

In this communication we wish to report the fluorination of polyethylene single crystal mats as well as an individual monolayer crystal of polyethylene. Provided the hydrogen atoms in polyethylene single crystals can be replaced by fluorine, it may be possible to obtain unique structures of a chain folded perfluorinated polymer.

Samples of single crystal polyethylene, Marlex 6050 (prepared from a 0.1% xylene at 85°), were placed on nickel supports in a fluorine reactor[7] and exposed for 1 hr to various fluorine–argon mixtures at atmospheric pressure. The flow rate was maintained at approximately 1 l./min. Those crystals exposed to pure fluorine and 50% fluorine reacted catastrophically leaving charred residues. The sample exposed to 10% fluorine was intact. Apparently, residual xylene from the preparation of the single crystal mats ignited when exposed to concentrated fluorine gas. Therefore, subsequent polyethylene mats were evacuated for a period of 24 hr prior to exposure to the fluorine gas. These treated crystals were placed in the reactor and exposed to pure fluorine as before. After 1 hr the flow was stopped and the reactor sealed under a slight positive pressure of fluorine. After 3 days the valve was opened and the reactor flushed with argon prior to removing the sample.

The fluorine treated polyethylene single crystal mats were extracted with refluxing xylene for a period of 16 hr. Essentially all the fluorine-treated crystals survived this treatment. Only those portions not reacted upon by the fluorine dissolved. Samples of polyethylene single crystals not exposed to fluorine were completely soluble under these conditions of reflux.

A variety of analytical data were collected to characterize the extracted mat of crystals. The density was determined by noting the buoyancy of the residues in a variety of fluorocarbon oils and other dense liquids. The apparent density was in excess of 2.2 g/cm³. This is indicative of extensive fluorination and is in agreement with the results of Rudge.[2] Microanalysis of the residue revealed a composition of approximately C_2F_4; little hydrogen was detected (~0.05%). Calorimetric studies of the residue revealed no endotherm in the vicinity of the melting temperature of polyethylene but there was some indication of an endotherm at above 300°. This is in agreement with the proposed fluorocarbon structure.

In Figure 1 are shown the infrared spectra of the polyethylene single crystal mat before fluorination (Figure 1a) and after (Figure 1b) fluorination and extraction in xylene. The strong prominent bands at 2800, 1460, and 720 cm^{-1} in Figure 1a are due to the CH_3 and CH_2 groups in the polyethylene structure. In Figure 1b it can be seen that only a trace of the CH_3/CH_2 band at 2800 cm^{-1} remains after fluorination and extraction in xylene, while a new strong broad band is observed in the 1200-cm^{-1} region due to CF and CF_2 groups. This spectrum is characteristic of fluorinated

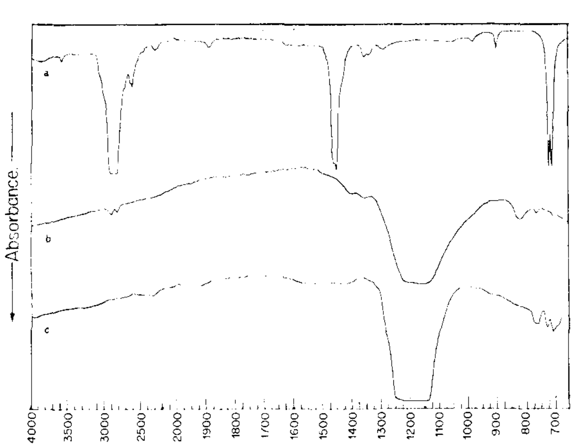

Figure 1. a. Infrared spectrum of Marlex 6050 polyethylene single crystals; b. infrared spectrum of Marlex 6050 polyethylene single crystal residue after fluorination and extraction with refluxing xylene; c. infrared spectrum of polytetrafluoroethylene.

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(1) H. Schonhorn and R. H. Hansen, *J. Appl. Polym. Sci.* **12,** 1231 (1968).

(2) A. J. Rudge, British Patent 710,523 (June 1954).

(3) W. T. Miller and A. L. Dittman, *J. Amer. Chem. Soc.*, **78,** 2793 (1956).

(4) L. A. Bigelow, *Chem. Rev.*, **40,** 51 (1947).

(5) J. M. Tedder, *Advan. Fluorine Chem.*, **2,** 104 (1961).

(6) P. S. Fredericks and J. M. Tedder, *J. Chem. Soc.*, 144 (1960).

(7) J. H. Swisher, F. Schrey, P. K. Gallagher, and E. O. Fuchs, *J. Elecrochem. Soc.*, **117,** 537 (1970).

long chain hydrocarbons such as polytetrafluoroethylene (Figure 1c). The intensity (*i.e.*, the amount) of CH stretch absorption at 2800 cm^{-1} in Figure 1b is similar to that found in the spectrum of a 1% solution of mineral oil $(CH_2)_n$ in perfluorokerosene $(CF_2)_n$. This agrees with the microanalysis which indicates that there is approximately 1% residual hydrocarbon in the fluorinated specimen. Since relatively thick mats of polyethylene single crystals were fluorinated, the interior regions of the polymer single crystal mats may remain partially hydrogenated. This could account for the traces of CH_3 and CH_2 absorption that remain in Figure 1b. There is no indication of olefinic structures (C═C) in the 900–1000-cm^{-1} region. This is evidence that virtually all the hydrogen atoms have been replaced by fluorine.

Monolayer single crystals of polyethylene treated with fluorine in a fashion similar to the polyethylene single crystal mats were extracted in refluxing xylene for 24 hr and examined (Figure 2). Single crystals not exposed to fluorine were completely soluble in the refluxing solvent. Fluorinated single crystals were insoluble and, as can be seen from Figure 2, showed no obvious evidence of morphological rearrangement. Apparently, fluorine atoms can be incorporated into the carbon skeleton without disrupting the structure. Since no solvents are available for these materials, the extent of cross-linking, if any, cannot be assessed. Preliminary electron diffraction results suggest that in the *c*-axis projection chain packing similar to that of the orthorhombic polyethylene unit cell is maintained but with expanded *a* and *b* dimensions. This is in contrast to the hexagonal symmetry found in polytetrafluoroethylene. X-Ray and electron diffraction studies are being continued.

Other single crystal hydrocarbon polymers should be amenable to fluorination to prepare novel perfluorinated single crystals.

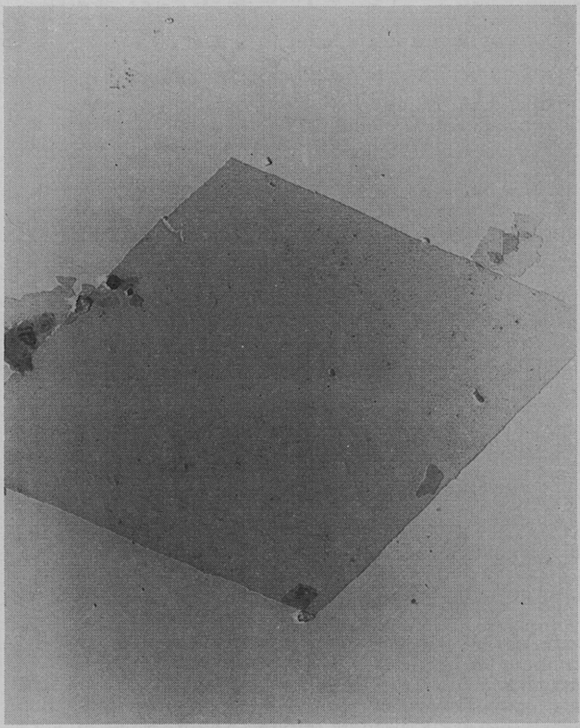

Figure 2. Fluorinated monolayer single crystal of Marlex 6050 polyethylene after extraction with refluxing xylene.

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A. E. Tonelli, Anne I. Brewster, and F. A. Bovey: The Conformational Characteristics of Dipeptides

Page 413. The last sentence in the Experimental Section should read as follows. A third diastereoisomer, D,L-alanylalanine, was also observed, although for reasons to be indicated in the Results, it was not specifically included in the conformational energy calculations. (The remaining isomer, D,D, is obviously enantiomorphous with the L,L isomer and does not require separate study.)