

The observed values for several perfluoroalkylmethylenes are $D \sim 0.72$ and $E \sim 0.021 \text{ cm.}^{-1}$ indicating an angle of $150\text{--}160^\circ$ at the divalent carbon atom.¹¹ Comparison should be made with the corresponding linear structure which would have $D \sim 0.75 \text{ cm.}^{-1}$,¹² in fair agreement with Z^3 dependence.

An interaction between the unpaired electrons, similar in magnitude to those observed in the alkyl nitrenes, was determined for methylsulfonylnitrene which has $D = 1.581 \text{ cm.}^{-1}$, $E = 0.0036 \text{ cm.}^{-1}$. In contrast, the values for phenylnitrene ($D = 0.99 \text{ cm.}^{-1}$, $E < 0.002 \text{ cm.}^{-1}$) indicate significant delocalization of one unpaired electron into the aromatic system.

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Preparation of Biaxially Oriented Polycapramide by the Solid State Polycondensation of a Single Crystal of ϵ -Aminocaproic Acid¹

Sir:

The possibility of preparing oriented polymer chains by polymerization in single monomer crystals was first demonstrated by the conversion of trioxane to polyoxymethylene.² Later it was shown that the polymer chains are oriented not only in the direction of the fiber axis but also in the plane perpendicular to it.³ The relationship of the orientation of the polymer crystallites to the crystallographic directions of the parent monomer has been fully clarified.⁴

More recently, it has been shown that the heating of a single crystal of phthalanilic acid at temperatures 50° below its melting point leads to highly oriented crystallites of N-phenylphthalimide.⁵ This example of topotaxy is remarkable in view of the fact that the water split off in the reaction has to diffuse out of the crystal. We have now shown that an analogous phenomenon is possible in a polycondensation. Single crystals of ϵ -aminocaproic acid (m.p. $204\text{--}205^\circ$) heated *in vacuo* for 16 hr. at 173° yielded highly oriented polycapramide as indicated by the X-ray diffraction photograph (rotation around b -axis of monomer) on Fig. 1. Weissenberg photographs proved that biaxial orientation was involved. The monomer crystal belongs to space group $P2_1/c$, $a = 8.56 \text{ \AA.}$, $b = 5.90 \text{ \AA.}$, $c = 15.13 \text{ \AA.}$, and $\beta = 103.13^\circ$,⁶ while the polymer has space group

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Figure 1.

$P2_1$, $a = 9.56 \text{ \AA.}$, $b = 17.2 \text{ \AA.}$, $c = 8.01 \text{ \AA.}$, and $\beta = 67.5^\circ$, with the polymer chains parallel to b .⁷ Weissenberg photographs of partially converted monomer crystals showed that the following crystallographic planes of monomer and polymer are parallel to each other: $11\bar{2}_{\text{mon}} \parallel 200_{\text{pol}}$; $112_{\text{mon}} \parallel 202_{\text{pol}}$; $004_{\text{mon}} \parallel 002_{\text{pol}}$.

These data indicate that the polymer chains grow parallel to the intersection of the 004 plane with the 110 or $1\bar{1}0$ plane of the monomer. The polymerization involves a contraction of 17% in the direction of the chain axis and an 18% reduction of volume; it is remarkable that this may be accomplished with retention of chain orientation.

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The Photochemical Reduction of Rare Earth Ions in Fused Halides¹

Sir:

The reduction by X-rays² and γ -rays^{3,4} of rare earth ions incorporated in crystalline halide hosts to lower oxidation states is well known. Recent studies at these laboratories⁵ have shown that only the locally uncompensated rare earth ions are capable of being photoreduced, and, in addition, the divalent rare earths so produced are readily reoxidized by thermal and optical processes. The instability of the divalent state is due to interstitial halogen atoms which remain in the crystal after irradiation and which eventually recapture their electrons.

Irradiations of molten halides containing rare earths, which would eliminate most of the inherent difficulties associated with the solid-state irradiations, were therefore carried out. In preliminary studies, molten solutions of dried and brominated BaBr_2 with 0.2 mole %

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