cm.$^{-1}$, which was reduced by lithium in ethylenediamine[12,13] and acetylated to give α-amyrin acetate, m.p. 223.5–225°, undepressed upon admixture with an authentic sample.[14] The X-ray powder diffraction patterns, infrared spectra and optical rotatory dispersion curves of synthetic I acetate and α-amyrin acetate were found to be identical.

The establishment of stereoformula I for α-amyrin renders the proposed[2,15] biosynthetic path from the lupanyl cation all the more attractive.

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[12] R. A. Benkeser, G. Schroll and D. M. Sauve, THIS JOURNAL, **77**, 3378 (1955).

[13] L. Reggel, R. A. Friedel and I. Wender, *J. Org. Chem.*, **22**, 891 (1957).

[14] The equatorial (α) orientation of the 20-methyl group produced by this reduction follows from data on reduction of model compounds of known configuration (3-methylene cholestane → 3β-methylcholestane stereospecifically). See also D. H. R. Barton, A. Campos-Neves and R. C. Cookson, *J. Chem. Soc.*, 3500 (1956), and *cf.* reduction of cyclohexanones by metals.

[15] A. Eschenmoser, L. Ruzicka, O. Jeger and D. Arigoni, *Helv. Chim. Acta*, **38**, 1890 (1955); A. Melera, D. Arigoni, A. Eschenmoser, O. Jeger and L. Ruzicka, *ibid.*, **39**, 441 (1956). The latter publication describes an elegant proof of configuration at C_{18} in α-amyrin.

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REVERSIBLE CONTRACTILE PROCESSES IN FIBROUS MACROMOLECULES

Sir:

It is known that the crystallization of an oriented polymer fiber is accompanied by an increase in length, while contraction will occur on melting such a system.[1–3] In previous reports[2,3] the orientation has always been imposed by the application of a tensile stress, and the dimensional changes that occur during the melting–crystallization cycle can be considered reversible only if an equilibrium stress is maintained. We wish to report that by appropriately cross-linking a fibrous polymer a material is obtained which has the property of not only contracting on melting and spontaneously elongating on crystallization but does so in a cyclic manner *without* the application of any external force.

A highly oriented sample of fibrous poly-(ethylene)[4] was cross-linked by the action of γ-ray irradiation from a Co^{60} source. The wide angle X-ray pattern of the fiber prior to cross-linking indicates almost perfect alignment of the polymer chains along the fiber axis, and the pattern is not significantly altered by the introduction of cross-links. The high state of orientation is further evidenced by the fact that about a forty-fold irreversible shrinkage[5,6] occurs on melting the non-cross-linked material. After being cross-linked, the fibers were melted and then allowed to recrystallize at room temperature. Three distinct states of the cross-linked fiber can then be distinguished: the initial state, the liquid state, and the final state achieved by recrystallization from the liquid state. Each of these states is further characterized by the fact that no external force is applied. The change which occurs in going from the initial state to the liquid state represents an irreversible process[5,6] since the original cross-linked fibers can no longer be regenerated merely by cooling. In accord with theoretical considerations[7] and previous experimental results[6,8] the lengths of the recrystallized fibers increase as the cross-linking density is increased. For the range of cross-linking encompassed by these experiments a twenty-five fold increase in length is observed in this state.

An X-ray diffraction analysis of the recrystallized materials at room temperature indicates that the crystallites are randomly arranged in the specimen into which no cross-links have been introduced. However, as the cross-linking density is increased, the concomitant increase in length that occurs manifests itself in the fact that an axial orientation of the crystallites begins to develop. Thus a specimen which has received a radiation dose of 650 megareps. possesses a rather marked axial orientation. Hence by sufficiently cross-linking a highly oriented fiber a large proportion of the order of the system is maintained even after melting and subsequent recrystallization.[6,7] It should be emphasized that the orientation is present without the imposition of any external force and is a sole consequence of a sufficient number of cross-linkages being appropriately introduced.

It is then found that the fibers which display crystallite orientation contract on melting and when slightly under-cooled spontaneously elongate back to their equilibrium length. This process can be repeated indefinitely without any external force being applied, and, depending on the cross-linking density, dimensional changes of from 5 to 30% have been observed. This contractile process is reversible and sharp, and is a consequence of the basic principle that an oriented macromolecular system will contract on melting and reelongate on cooling. As Flory already has pointed out,[1] fibers such as have been described here can serve as the working substance of an engine which converts thermal energy into mechanical energy.

A more thorough discussion and analysis of these and related observations will appear in a forthcoming paper.[9]

[1] P. J. Flory, *Science*, **124**, 53 (1956).

[2] W. H. Smith and C. P. Saylor, *J. Research Natl. Bur. Standards*, **21**, 257 (1938).

[3] A. V. Tobolsky and G. M. Brown, *J. Polymer Sci.*, **17**, 547 (1955).

[4] We wish to thank the Research Department of the American Viscose Corporation for supplying this material.

[5] J. M. Oth and P. J. Flory, THIS JOURNAL, **80**, in press (1958).

[6] D. E. Roberts and L. Mandelkern, *ibid.*, **80**, in press (1958).

[7] P. J. Flory, *ibid.* **78**, 5222 (1956).

[8] D. E. Roberts, L. Mandelkern and P. J. Flory, *ibid.*, **79**, 1515 (1957).

[9] L. Mandelkern, D. E. Roberts and A. F. Diorio, in preparation.

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