occur than would normally be expected. He considers the critical size in the chain direction for the crystalline nucleus to be of the same order of magnitude as that of the length of the chain for low molecular weight samples and, therefore, concludes that these crystals have essentially extended chains. A similar argument could be applied to the radiation-initiated PVF$_2$ using acetone as a solvent. Since the lower entropy of melting in this material is presumably related to a higher entropy in the solid state, the increased melting point and lower entropy of melting may be indicative of larger but less perfect crystallites when compared to suspension polymerized PVF$_2$. Defects in these presumably extended-chain crystals could produce higher densities than less crystalline samples having greater crystal perfection.

By comparing the melting behavior of all the phases of the homopolymer of PVF$_2$ (Fig. 6), it can be seen that phase II has the lowest change in entropy upon melting. These samples can be directly compared since they were all crystallized from the same homopolymer. The high-pressure-crystallized form of PVF$_2$ was originally designated as "phase III" by Doll and Lando [23], although it has since been shown that this high-pressure-crystallized form is in actuality a high-melting mixture of phases I and II [31].

Studies on the effect of pressure on the melting behavior of PVF$_2$ and its copolymers help to give some insight into the complexity of systems which are able to undergo isomorphous substitution. While the van der Waals radius of the fluorine atom is very similar to that of hydrogen (1.35 vs. 1.1 Å), the isomorphous substitution of a fluorine atom has a definite effect on the melting behavior. Since the melting point for most copolymers is not appreciably different than that of the homopolymer, although the entropy of fusion is reduced, the enthalpy of fusion must also be reduced. Therefore, by understanding the effects of this isomorphic substitution, copolymers having most of the properties of PVF$_2$ but which would require less thermal energy to process can be formulated.

Certain applications of PVF$_2$ require the polymer to have a particular chain conformation, and by the proper polymerization or copolymerization conditions one can obtain either the TGTG′ conformation (phase II) or the planar zig-zag conformation (phase I) as the most thermodynamically favorable form.

CONCLUSIONS

High-pressure melting behavior obtained for samples of vinylidene fluoride copolymerized with vinyl fluoride, trifluoroethylene, or tetrafluoroethylene indicated that the copolymers have lower entropy and

enthalpy of melting values than poly(vinylidene fluoride) in the same phase. As the comonomer size was increased, the entropy and enthalpy of melting decreased.

For samples that have been high-pressure-crystallized the entropy and enthalpy of melting and the melting point all increase when compared with the corresponding values for the low-pressure-crystallized samples.

It has been previously shown [21] that fluoroolefin comonomers with vinylidene fluoride act as pseudo head-to-head linkages and, therefore, the copolymers of VF_2 tend to favor crystallization under atmospheric conditions in phase I. The data in this paper have indicated that high-pressure crystallization of the copolymers also favors crystallization in phase I.

REFERENCES

[1] B. Wunderlich and T. Arakawa, *J. Polymer Sci.*, **A2**, 3697 (1964).
[2] P. H. Geil, F. R. Anderson, B. Wunderlich, and T. Arakawa, *J. Polymer Sci.*, **A2**, 3707 (1964).
[3] P. J. Holdsworth and A. Keller, *J. Macromol. Sci.*, **B1**, 597 (1967).
[4] A. Turner-Jones, *J. Polymer Sci.*, **62**, S53 (1962).
[5] T. Davidson and B. Wunderlich, *J. Polymer Sci.*, **(A-2)7**, 377 (1969).
[6] P. H. Geil, *Polymer Single Crystals*, Wiley-Interscience, New York, 1963, p. 393.
[7] C. D. Armeniades and E. Baer, *J. Macromol. Sci.*, **B1**, 309 (1967).
[8] S. Y. Choi, J. P. Rakus, and J. L. O'Toole, *Polymer Eng. Sci.*, **6**, 3 (1966).
[9] J. L. Kardos, A. Christiansen, and E. Baer, *J. Polymer Sci.*, **(A-2)4**, 777 (1966).
[10] K. D. Pae, *J. Polymer Sci.*, **(A-2)6**, 657 (1968).
[11] D. R. Morrow, *J. Macromol. Sci.*, **B3**, 53 (1969).
[12] C. E. Weir, *J. Res. Natl. Bur. Std.*, **53**, 245 (1954).
[13] R. I. Beecroft and C. A. Swenson, *J. Appl. Phys.*, **30**, 1793 (1959).
[14] L. D. Liushits, Y. S. Genschaft, V. C. Markov, and Y. N. Ryabinin, *Vysokomolekul Soedin.*, **3**, 624 (1961).
[15] C. E. Weir, *J. Res. Natl. Bur. Std.*, **50**, 95 (1953).
[16] G. M. Martin and R. K. Eby, *J. Res. Natl. Bur. Std.*, **72A**, 467 (1968).