Polymer Crystallization With Folded Chains

The Hoffman-Lauritzen theory of the formation of polymer crystals with folded chains, set forth four decades ago [1,2,3], owes its origin to the discovery in 1957 [4,5,6] that characteristically thin single crystals of polyethylene can be grown from dilute solutions. These crystals are thin platelets or lamellae, typically about 10 nm thick. As first proposed by Keller of the University of Bristol (UK) in his seminal paper [5], the long polymer chains are more or less regularly folded between the upper and lower lamella surfaces with the chain stems between successive folds oriented preferentially normal to the plane of the lamellae. Following very shortly after this discovery was the realization that lamellar crystals of polymers other than polyethylene also exhibited chain folding. More than that, chain folding was an essential feature of the crystallization of polymers from the molten state. In the latter case, polymers were found to undergo spherulitic crystallization, but the spherulites were composed of radiating structural units that were found to be lamellar and bore a kinship to solution grown crystals. In short, following the events of 1957, it was evident that a theory was needed to explain the then startling occurrence of chain folding and its general effects on polymer crystallization.

In 1961 and 1962 [1,2] Hoffman and Lauritzen presented their theory for the formation of chain-folded crystals based on surface nucleation concepts. Hoffman had visited Keller in Bristol earlier (in 1959) and had discussed the subject with him. Returning from the UK by air (traveling *via* the Azores because of a storm in the North Atlantic), Hoffman began to develop certain aspects of the theory. (The authors later joked that this was likely the only theory germinated between the Azores and New York that year). In their two papers, Hoffman and Lauritzen established the foundation of the kinetic theory of polymer crystallization from solution [1] and from the melt [2], paying particular attention to the energetics of the formation of chain-folded nuclei. Definite predictions were given under certain assumptions concerning the experimentally observed variation in lamellar thickness with crystallization temperature, the metastability and the melting point of lamellae, and the temperature dependence of the kinetics of crystallization rate. As the theory was extended, it began to receive attention and experimental support at NBS and elsewhere. In 1971, Hoffman and Lauritzen were awarded the High Polymer Physics Prize of the American Physical Society. The citation read in part "for their Kinetic Theory of Polymer Crystallization."

The theory was presented in a book chapter [3] in which Hoffman and Lauritzen benefitted substantially from the participation of G. T. Davis. The chapter was written at the behest of N. B. Hannay, who was then vice president of research at Bell Telephone Laboratories, where a number of scientists were working in the field of polymer physics and polymer crystallization in particular. In this chapter, the treatment of chain-folded crystallization was further extended and organized, and the extended work was applied to various polymers covering such topics as spherulite growth rate, the crystallization temperature dependence of the lamellar thickness, as well as the thermodynamic properties of chain-folded crystals. The chapter is especially notable in that it has been used extensively for teaching purposes.

From time to time since the original papers, other NBS personnel have been involved in the 'chain-folding' venture. Noteworthy contributions, mostly but not entirely experimental, were made by J. J. Weeks, G. S. Ross, L. Frolen, F. Gornick, and F. Khoury, and significant theoretical developments were made by E. A. Di Marzio, C. M. Guttman, E. Passaglia, and I. C. Sanchez. Further, from the broad perspective of the NBS/NIST history, it may be noted that research on polymer crystallization at NBS preceded by many years the discovery of chain folding. The long tradition of research on crystallizable polymers is exemplified by the pioneering works of L. A. Wood and N. Bekkedahl in the later 1930s and 1940s [7] and L. Mandelkern in the 1950s [8].

John Hoffman received his B.S. degree in chemistry in 1942 from Franklin Marshall College and his Ph.D. in physical chemistry in 1949 from Princeton University. He participated in the Manhattan Project (1944-1946, while in U. S. Army) and subsequently (1949-1954) was in the R&D branch of General Electric. In 1954, Hoffman joined NBS as a Research Chemist, becoming Chief of the Dielectrics Section in 1957 and Chief of the Polymers Division in 1964. From there, he advanced to Director of the Institute for Materials Research (1967-1978) and then Director of the National Measurement Laboratory (1978-82). Hoffman retired from NBS in 1982, but continued his career as Professor at the University of Maryland (1982-1985), Director and CEO of the Michigan Molecular Institute (1985-1990), and as Research Professor in the Department of Materials

Fig. 1. John Hoffman, 1961.

Science and Engineering at Johns Hopkins University (1990-present). Throughout his career, he has received numerous awards, including the Soldiers Medal (military decoration, 1946), the U. S. Department of Commerce Gold Medal (1965), the Samuel Wesley Stratton Award of NBS (1967), and election to the National Academy of Engineering (1980).

John Lauritzen, Jr. received an A.B. in mathematics in 1949 (University of Miami, Ohio) and a Ph.D. in physics in 1955 (California Institute of Technology). He came to NBS as a physicist in the Electricity Division in 1956, before joining the Polymers Division in 1964. In 1968, he was appointed Senior Scientist, NBS Institute for Materials Research, a post he held until his death (October 11, 1976). His research included the theory of polymer crystallization, dielectric relaxation in molecular compounds, statistical mechanics, and multi-component rate theory. His distinguished career was acknowledged in receiving the Samuel Wesley Stratton Award with E. Di Marzio and E. Passaglia in 1971.

G. T. (Tom) Davis received his B. Chem. Eng. in 1956 from Cornell University and his Ph.D. in physical chemistry in 1963 from Princeton University. In his early work, he was a research chemist in the Chemical Research Division, Esso Research and Engineering Co. (1956-1960) and an Assistant Professor of Chemistry at the University of Virginia (1963-1964). In 1964-1966, he was awarded an NRC-NSF Post Doctoral Fellowship at NBS and, two years later, he was appointed a research chemist in the Polymers Division of NBS.

He advanced to the position of Group Leader in the Polymers Division in 1984 and served in that position until 1998, before retiring in 1999. For his meritorious work in polymer science and engineering, he was awarded the U. S. Department of Commerce Bronze Medal in 1980.

Fig. 2. John Lauritzen, 1961.

Prepared by Freddy Khoury in consultation with John Hoffman and Tom Davis.

Bibliography

[1] John I. Lauritzen, Jr. and John D. Hoffman, Theory of Formation of Polymer Crystals with Folded Chains in Dilute Solution, *J. Res. Natl. Bur. Stand.* **64A**, 73-102 (1960).

[2] John D. Hoffman and John I. Lauritzen, Jr., Crystallization of Bulk Polymers With Chain Folding: Theory of Growth of Lamellar Spherulites, *J. Res. Natl. Bur. Stand.* **65A**, 297-336 (1961).

[3] John D. Hoffman, G. Thomas Davis, and John I. Lauritzen, Jr., The Rate of Crystallization of Linear Polymers With Chain Folding, Chapter 7 in *Treatise on Solid State Chemistry: Vol. 3: Crystalline and Noncrystalline Solids,* N. B. Hannay (ed.), Plenum Press, New York (1976) pp. 497-614.

[4] P. H. Till, Jr., The Growth of Single Crystals of Linear Polyethylene, *J. Polym. Sci.* **24**, 301-306 (1957).

[5] A. Keller, A Note on Single Crystals in Polymers: Evidence for a Folded Chain Configuration, *Philos. Mag., Ser. 8,* **2**, 1171-1175 (1957).

[6] E. W. Fischer, Stufen- und spiralförmiges Kristallwachstum bei Hochpolymeren, *Z. Naturforsch.* **12a**, 753-754 (1957).

[7] Lawrence A. Wood and Norman Bekkedahl, Crystallization of Unvulcanized Rubber at Different Temperatures, *J. Res. Natl. Bur. Stand.* **36**, 489-510 (1946).

[8] L. Mandelkern, Crystallization Kinetics in Polymeric Systems, in *Growth and Perfection of Crystals* (Proceedings of an International Conference on Crystal Growth held in Cooperstown, New York, August 1958), R. H. Doremus, B. W. Roberts, and D. Turnbull (eds.), John Wiley and Sons, New York (1958) pp. 467-595.