Ask the Historian

The Origin of the Polymer Concept

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Question

What is the origin of the polymer concept?

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Answer

As noted in an earlier column, the term "polymer" (from the Greek *polys* meaning "many" and *meros* meaning "part") was first introduced in 1833 by the Swedish chemist, Jöns Jakob Berzelius (1, 2). Though only a year had passed since he had introduced the term "isomer" (from the Greek *isos* meaning "equal" and *meros* meaning "part") in order to describe substances having identical compositions but differing properties (3), he now felt it was necessary to further distinguish between two possible types of isomerism. The first of these dealt with the isomerism of two substances having identical absolute compositional formulas in which the difference in properties was attributable to *metamerism* or a difference in the arrangement of the component atomic groupings (e.g., ethyl formate versus methyl acetate). The second dealt with the isomerism of two substances having identical relative compositional formulas but different absolute compositional formulas in which the difference in properties was attributable to *polymerism* or a difference in the total number of atoms present (e.g., ethene versus butene).

With the rise of organic chemistry in the 1840s and 1850s, Berzelius' original distinctions became muddled. Thus, writing in 1888, the British chemist, Henry Armstrong, observed that (4);

Even a superficial reader of the chemical literature will soon become aware that the terms isomeric and the kindred expressions allotropic, metameric, and polymeric are by no means used in consistent senses, and he will have considerable trouble in clearly realizing their exact and relative import.

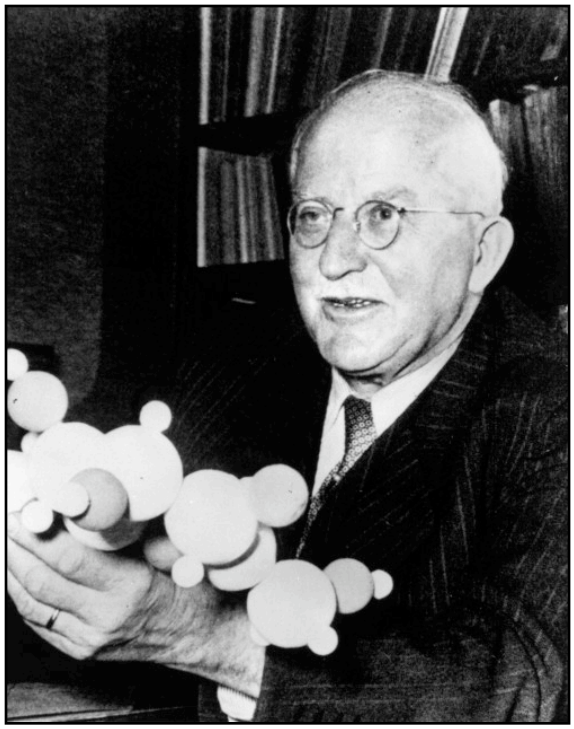

Figure 1. Hermann Staudinger (1881-1965).

In the end, polymerism was given coequal status with isomerism as a separate and distinct phenomenon and metamerism became but one of several varieties of structural isomerism. However, despite this change in status, polymerism, in keeping with Berzelius's original intent, continued to describe a purely compositional relationship between two substances which carried no requirements concerning the nature of the molecules (e.g. organic versus inorganic), their relative sizes, their structures, or their ability to interconvert (5).

Indeed, it was because the original meaning of the term polymer did not carry any connotation concerning size that the German chemist, Hermann Staudinger (figure 1), felt it necessary to coin the word "macromolecule" in 1922 to describe large covalently bonded organic chain molecules containing more than 10^3 atoms (6). Strictly speaking, the terms macromolecule and polymer stand for logically distinct concepts.

There are many polymers which are not macromolecules (e.g. the S_3O_9 ring as a trimer of SO_3) and many macromolecules which do not compositionally qualify as polymers of the materials from which they are made (e.g. so-called copolymers and condensation polymers). It goes without saying, of course, that the niceties of these logical distinctions have long been ignored by present-day chemists, most of whom now use the term polymer as a trivialized synonym for a covalently bonded organic macromolecular chain molecule (7). Attempts to partially remedy this situation through the coining of additional terms, such as "oligomer", have not proven helpful (8), in part because the term polymer is still used in its original sense in the literature dealing with glasses, ceramics and inorganic polymers, many of which are noncovalently bonded and may contain not only infinitely polymerized chains but also infinitely polymerized layer and framework structures as well (9).

Literature Cited

1. W. B. Jensen, "The Origin of the Term Allotrope," *J. Chem. Educ.*, **2006**, *83*, 838-839.

2. J. Berzelius, "Isomerie, Unterscheidung von damit analogen Verhältnissen," *Jahres-Bericht*, **1833**, *12,* 63-67. Definition on p. 64. We have cited the dates for the widely circulated German edition of Berzelius' *Jahrs-Bericht*. Since these are dated one year later than the Swedish originals, it can be argued that Berzelius first coined these terms in 1832 and 1831 respectively.

3. J. Berzelius, "Körper von gleicher Zusammensetzung und verschiedenen Eigenschaften," *Jahres-Bericht*, **1832**, *11*, 44-48. Definition on p. 47.

4. H. E. Armstrong, "Isomerism," in H. Forster Morley, M. M. Pattison Muir, Eds., *Watts' Dictionary of Chemistry*, Vol. 3, Longmans, Green & Co: London, 1888, pp. 79-88.

5. M. M. Pattison Muir, "Polymerism," in H. Forster Morley, M. M. Pattison Muir, Eds., *Watts' Dictionary of Chemistry*, Vol. 4, Longmans, Green & Co.: London, 1894, p. 297.

6. H. Staudinger, J. Fritschi "Über die Hydrierung des Kautschuks und über seine Konstitution," *Helv. Chim. Acta*, **1922**, *5*, 785-806. Term on p. 788. Staudinger originally used the term *hochmolekulare Verbindungen* (high molecular compounds).

7. The author recalls attending a seminar on the history of polymer chemistry by a noted polymer chemist who was so indoctrinated with this current trivialized usage that he expressed great puzzlement over that fact that 19th-century books listed such species as acetylene (C_2H_2) and benzene (C_6H_6) as examples of polymerism. He ended by making the delightfully ahistorical observation that Berzelius apparently did not understand what a polymer was, never suspecting that it was the modern polymer chemist who had corrupted Berzelius' original definition rather than vice versa.

8. L. V. Larsen, "Origin of the Term 'Oligomer,'" *Chem. Eng. News*, **1984**, *62 (Jan. 23)*, 58.

9. The first comprehensive treatment of nonmolecular inorganic solids from the standpoint of the polymer concept appeared in K. Meyer, *Natural and Synthetic High Polymers*, Interscience: New York, NY, 1942, Chapter BI. Since the 1960s an increasing number of specialist monographs have appeared, including F. Stone, W. Graham, Eds., *Inorganic Polymers,* Academic Press: New York, NY, 1962; D. N. Hunter, *Inorganic Polymers*, Wiley: New York, NY, 1963; and N. H. Ray, *Inorganic Polymers*, Academic Press: New York, NY, 1978.

Do you have a question about the historical origins of a symbol, name, concept or experimental procedure used in your teaching? Address them to Dr. William B. Jensen, Oesper Collections in the History of Chemistry, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172 or e-mail them to jensenwb@ucmail.uc.edu