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## This Week's Citation Classic \* DECEMBER 11, 1989

Plesch P H, ed. Cationic polymerisation and related complexes. Cambridge, England: Heffer & Sons, 1953. 166 p.; and Plesch P H, ed. The chemistry of cationic polymerization. Oxford, England: Pergamon Press, 1963. 728 p. [Department of Chemistry, University of Keele, Staffordshire, England]

The two books on cationic polymerization deal with the role of the carbonium ion in causing the combination of repeated units of hydrocarbons and permit an interpretation of the Friedel-Crafts catalysis of olefin polymerization. [The SCI® indicates that these two books on cationic polymerization have been cited in over 435 publications.]

## Adventures in Cationic Polymerization

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The popularity of my two books is principally due to the fact that up to 1982 they were the only ones devoted entirely to the subject, but I like to think that an important contributory factor was the very personal style of the many "editor's comments" and cross-references by means of which I tied together the component parts of both works. I have always considered science to be a very personal activity.

The origins of these books are easy to explain. After my BA at Cambridge in 1940 and war work in the ceramic and alginate industries, I finished my PhD work at the University of Manchester on the polymerization of isobutene in 1946. When I was subsequently appointed as an assistant lecturer, I had complete freedom to select a research subject and decided to continue with cationic polymerization because this subject offered considerable intellectual and practical challenges and because it seemed to be generally unpopular. I always enjoyed doing what others thought too difficult, and my third book, High Vacuum Techniques for Chemical Syntheses and Measurements, is the outcome of over 40 years of doing just that.

Cationic polymerization, however, did have a certain following in British universities and in industry outside Britain, as shown by the success of the First Symposium on Cationic Polymerization convened by D.C. Pepper in Dublin in 1949. Therefore, when I joined the newly established University College of North Staffordshire (now the University of Keele) as a founder-member in 1951 and was at first without a research laboratory, I convened the Second Symposium in March 1952. There were over 80 participants from five countries, and my first book (1953, above) contains the papers and discussions of that meeting.

With the MS as my stock-in-trade, I did my first very extensive lecturing and consulting tour of the US in the summer of that year. By the later 1950s, the developments in the fields of Ziegler-Natta and stereoregular polymers had catalysed increased interest in cationic polymerizations, and I saw that it would not be long before the subject would outgrow my capacity to comprehend it. Up till then I had digested critically virtually every paper on the subject. As there was an evident need for a book, I found a publisher easily, assembled 17 contributors and thus produced the second book. As one of them said: "A quick way of making 17 enemies all at once." Happily it turned out otherwise, although my decided views on the functions of an editor, and on the use of the English language, produced some very sharp exchanges.

Ostensibly, most of my life's work (ca. 140 chemical papers + ca. 10 others) has been in cationic polymerization, but despite my contributions, such as the discovery of cocatalysis by water,<sup>1</sup> the elucidation of the mechanism of initiation by aluminium halides,<sup>2</sup> and the discovery of pseudocationic polymerization,<sup>3</sup> I feel that I have helped to develop an existing, but immature, subject rather than created a new one. However, this work did generate two lines of research in both of which there were only episodic and unsystematic studies before we took them up. One is the characterization of carbenium and oxonium ions by polarography; this resulted from my attempt to circumvent the inadequacy of spectroscopy as a general means of detecting very small concentrations of organic cations. Unfortunately, I was unable to complete this work by doing a polarographic analysis on a polymerizing solution, but many other useful insights resulted from this research.<sup>4</sup> The other novelty is the study of binary ionogenic equilibria (two molecules in equilibrium with two ions), the elucidation of which proved to be essential for understanding some fundamental features of cationic polymerizations.<sup>5</sup> Both originated from our studies on organic cations and then developed a life of their own. The latter, especially, I consider to be probably my most useful contribution to general physical chemistry.

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<sup>1.</sup> Plesch P H. Friedel-Crafts polymerizations. Research 2:267-75, 1949. (Cited 15 times.)

<sup>2.</sup> Grattan D W & Plesch P H. The initiation of polymerizations by aluminium halides. Makromol. Chem. 181:751-75, 1980. (Cited 15 times.)

<sup>3.</sup> Gandini A & Piesch P H. Pseudocationic and true cationic polymerization of styrene by various catalysts. J. Polym. Sci. B-Polym. Phys. 3:127-9, 1965. (Cited 40 times.)

<sup>4.</sup> Plesch P H. Relation between reduction potentials and solvation energies for some aryl methylium ions. J. Chem. Soc. Perkin Trans. II 1989:1139-42.

<sup>5.</sup> Grattan D W & Plesch P H. Binary ionogenic equilibria. J. Electroanal. Chem. Interfac. 103:81-94, 1979. (Cited 10 times.)