On Working with Michael Polanyi

Peter H. Plesch

[**Editor's Note**: Immediately following are excerpts from P. H. Plesch's "Michael Polanyi and the Discovery of Co-Catalysis: Discussion of an Autobiographical Letter from Michael Polanyi, FRS to Peter H. Plesch of 17 December 1963." Although this is a technical article, it should be of interest also to those who know Polanyi's philosophy of science or are interested in Polanyi's role in the history of chemistry. This excerpted version of Professor Plesch's article includes a few annotations to help those without a background in chemistry. Plesch's full copyrighted article was published online on 5 February 2004 by Wiley InterScience (www.interscience.wiley.com) in *Journal of Polymer Science, Part A* (2004) 42, 7: 1537-1546. These excerpts are reprinted with permission of John Wiley and Sons, Inc. Thanks are due not only to John Wiley and Sons, Inc. but also to Will Stillwell, Peter Plesch, and Plesch's colleague Pauline Weston. Will Stillwell edited and annotated the original *Journal of Polymer Science*, *Part A* article, working with Professor Plesch, who also corresponded with *TAD* editor Phil Mullins about his original article. Subsequently, Professor Plesch wrote a short piece titled "Michael Polanyi and the Paranormal" that complements his original article's discussion of his work with Polanyi. This is included after the excerpts from Professor Plesch's *Journal of Polymer Science, Part A* article.]

ABSTRACT Key Words; Peter H. Plesch and Michael Polanyi, scientific discovery.

This two-part article includes the following: (1) excerpts from Peter H. Plesch's essay originally published in *Journal of Polymer Science*, *Part A* (2004) 42, 7: 1537-1546 which reflects on Plesch's research with Polanyi; (2) Plesch's short account titled "Michael Polanyi and the Paranormal" which complements his original article's discussion of his work with Polanyi. Together these two pieces provide interesting insights into Polanyi's work as a research scientist as well as reflections on the nature of scientific discovery.

I

Excerpts from P. H. Plesch's "Michael Polanyi and the Discovery of Co-Catalysis: Discussion of an Autobiographical Letter from Michael Polanyi, FRS to Peter H. Plesch of 17 December 1963"

ABSTRACT: The origin of this memoir was a letter from Michael Polanyi (M. P.) to the present writer (P. H. P.) about their researches in the mid-1940s into the mechanism of what are now called cationic polymerizations*, at the University of Manchester (England). When the Manchester-trained researchers had made little progress with what was a very recalcitrant problem, M. P. thinking that scientists from a different background might be more successful, got P. H. P. from Cambridge to work with an Oxford-trained chemist. In his letter, M. P. analyzes his tactics and the mistakes made in directing this research.The "Manchester" theory they successfully developed was rapidly accepted because it could also explain observations on other related reactions. The involvement of ions established a link with nonaqueous electrochemistry.

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* polymerization: a chemical reaction which provides very large molecules by a process of repetitive addition.

Peter Hariolf Plesch

Peter Hariolf Plesch was born on February 14, 1918, in Frankfurt am Main (Germany). He attended the Collège Français (Berlin) and Harrow School (England). He received his B.A. from Trinity College (Cambridge) in 1939, his Ph.D. from Manchester University in 1946, and his Sc.D. from Cambridge University in 1970. During the war (1940-1945), he worked on ceramics, alginates, and isobutene polymerization. He was an assistant lecturer at Manchester University (1946-1950) and a founding member of the first British postwar university, the University College of North Staffordshire (later the University of Keele), as a lecturer in 195l. He retired in 1985 as professor of physical chemistry and is still active there as a professor emeritus.

Introduction

The highly original polymath Michael Polanyi (M. P.) was such an influential physical chemist and philosopher and a personality so complex that any self-revelatory writing concerning his own motives and feelings must be of interest to those who try to understand him, and especially (of course) to any would-be biographers. That is my reason for making public a letter that I discovered recently while sifting my scientific archives.[1] It is reproduced here in facsimile. . .

To make the full import of that letter intelligible, it is necessary to outline the personalities and the situations of those who figure in the events described, and also the state of polymer science in Britain in the early 1940s. An additional reason for doing this is that M. P.'s war work, to some of which I contributed, is not mentioned in any Obituary Notice that I have seen, and that M. P.'s thoughts about chemical mechanisms beyond transition-state theory are also very little known. This is also necessarily an account of the circumstances of my discovery of the phenomenon of cocatalysis* in cationic polymerizations during my Ph.D. research at Manchester University under M . P.'s joint direction[2], which he rated an important event in his scientific career and which has not been described previously. I have checked my recollections of the events of almost 60 years ago against the records in my *Laboratory Notebooks* of 1944-1947.[3, 4]

Personalities

My father, the physician and physiologist Janos Plesch, was well acquainted with his fellow Hungarian and fellow medic M. P. in Berlin.[5, 6] In 1933 M. P. moved from the Kaiser Wilhelm Institute for Physical Chemistry to the University of Manchester (United Kingdom), following an invitation to take the chair of Physical Chemistry there. My family fled from the Nazis to London in July 1933, and there it was that my father and M. P. took up contact again. . . M. P. asked my father whether his chemist son might be interested in a new vacancy for an assistant in his research group; that is how I came to join M. P. as a research assistant at Manchester University on November 7, 1944. . .

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*catalyst : a substance which affects the rate of a chemical reaction without being consumed in the reaction; "cationic" is the adjective; cocatalyst is a substance without which the catalyst cannot function.

The position of M. P. in the Britain of the late 1930s was similar to that of very many intellectuals, scholars, and scientists of Continental origin, many of whom had experienced the dire effects of the fascist dictators at first hand. With a few notable exceptions, the British Establishment, especially the Civil Servants, regarded foreigners, no matter who or whence, with strong suspicion. A detailed treatment of this theme is another story, but as far as M. P. was concerned, this generated a disillusionment that was not widely known outside the circle of his friends because M. P. never became bitter. He resigned himself to the fact that neither his formidable intellect nor his great experience in physicochemical research would be used in attempts to solve some of the really serious major scientific-technical problems that arose during the war; that was a contributory reason for the waning of his scientific interests and his increasing preoccupation with socio-economic problems, which culminated in his leaving chemistry and turning, via economics and sociology, to philosophy.

The Problem

However, because of M. P.'s experience with various forms of catalysis and reaction kinetics, he and his laboratory were assigned a problem that had been baffling chemists at Imperial Chemical Industries (ICI). It was the polymerization of isobutene (IB)* to poly-isobutene. This reaction is closely related to the formation of Butyl rubber, a copolymer* of IB and isoprene*, and which was one of the few synthetic rubbers known at that time, and that was a very recent invention.[7] The probable reasons for ICI choosing M. P.'s laboratory, although he had no previous experience of polymer chemistry, was that he and Manchester University were well known to the chemists concerned; it was conveniently near, and in any case one of the few facts known about the polymerizations of this type was that they are completely different from the free-radical polymerizations being studied by Harry (later Sir Harry) Melville and a very few others. For example, in contrast to the radical polymerizations, the catalysts involved were of the type used in the Friedel-Crafts reactions, which are metal halides such as the chlorides of aluminum, tin, titanium and boron trifluoride. The polymerization could yield products ranging from viscous oils to very tough rubbers, depending on the length of the polymer chains [molecular weight (MW)], and it could be very fast, almost explosive. The polymerizations were usually done in a solvent such as hexane or ethyl chloride at temperatures below ambient, but although the reaction had been known for several years, there were few publications, largely because of its great rate and because the MW of the polymer and its yield were extremely irreproducible.[8] However, a few features seemed to be consistent and general. The lower the temperature at which the reaction was done, the faster it would go and the higher the MW and the yield of the product, and very often the polymerization would stop when there was still some unreacted monomer* and catalyst present together in solution in the reactor. These features are so unusual that they presented a serious challenge to chemists.

Directly in charge of the research students doing this work were A. G. Evans, a lecturer in physical chemistry, who had done his first degree and his Ph.D. at Manchester University, and Fred Fairbrother, an inorganic chemist, also Manchester-trained and a specialist in the chemistry of the Friedel-Crafts metal halides. Under his guidance one of the research students had done a (rather rough and ready, quick and dirty)

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*isobutene: an easily polymerizable four-carbon hydrocarbon.
*copolymer: polymer formed from more than one monomer.
*isoprene: an easily polymerizable five-carbon hydrocarbon.
*monomer: substance which forms polymers.

comparative study of a range of metal halides with IB, from which it emerged that titanium tetrachloride was probably the most suitable one to use for a more detailed study (see M. P.'s letter).

In an attempt to circumvent an intractable problem, M. P. had also called upon his experience with other catalyzed reactions and expected to gain useful information by a study of an analogous reaction, the much slower formation of a mixture of oligomers* (dimmers to tetramers) from diisobutene (DIB), a mixture of the two isomeric dimers of IB, with the same catalysts, and several of the Ph.D. students were working on that reaction.

By roughly the first quarter of 1944, M. P. decided that the lack of progress on controlling or understanding Friedel-Crafts-catalyzed oligomerizations and polymerizations indicated the need for a different approach. As he explained it to me a few years after I had joined his research group, he judged that what was needed were scientists with a totally different background and training because all those engaged upon that project had been Manchester-trained and entirely academic. So he assigned me, from Cambridge and with four years of war-time industrial research experience, to work under the direct supervision of a young lecturer who had obtained his first and second degrees at Oxford, one H. A. Skinner (H. A. S.), known as Hank. He had recently left war-related work on fluorine chemistry at ICI and was persuaded by M. P. to join in what was then M. P.'s major enterprise and center of interest, chemical energetics. Essentially, this is based on thermochemistry, and that was the field in which H. A. S. subsequently made his very considerable reputation. . . . .

To understand the significance of M. P.'s action, it is necessary to realize that in the 1940s there were distinctly different paradigms in many areas of chemistry that reflected the views of the influential "grand old men", some of them the authors of the textbooks regarded as "authoritative"; there was a diversity of theories and points of view, such as the controversy between the followers of, the collision theory and the transition state theory of chemical reactions and the equally irreconcilable views of Irving Langmuir and M. P. on adsorption. It took someone of the philosophical insight of M. P. to realize that this diversity of theories as well as other differences of scientific training in different centers would influence the approach to problem solving of the scientists coming from various traditions. It became clear before long that M. P.'s insight led to the desired progress.

The events following my entry into the field that became known as cationic polymerization can be summarized rapidly. I started my experimental work on the polymerization of IB with the technique developed by my predecessors ... It is unnecessary to describe here the then prevailing technique and how I introduced various palliative modifications by more than 50 experiments over nearly a year, but I could not devise any satisfactory improvement ... It was urgent to devise some method by which the monomer (IB or DIB) could be introduced into the solvent, the mixture cooled to the required temperature, and a solution of the catalyst then added to it, all in a closed system. It thus became clear that a really adequate solution of the technical problem required a fundamentally new device, and so I invented one: a pseudo-Dewar vessel.

When I described my invention to M. P. to get his approval for our glass blower to make me such a device, he was most skeptical that a sufficiently good vacuum could be obtained to provide the required adiabatic* conditions. Because of his very extensive experience with high-vacuum apparatus in his own

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*oligomers: polymerized molecules

laboratory and as a consultant to industry, his doubts had great weight. Nonetheless, he agreed to have the vessel made, and within a very few days I had it rigged up and working, and it worked well.

As happens so often, a new technique revealed new phenomena. The first few experiments showed that with hexane as the solvent, IB as the monomer, and titanium tetrachloride as the catalyst, the polymerizations starting at about -80 degrees Celsius generally did not go to completion, but when the reactor was opened, the remaining monomer polymerized. The polymerizations could also be restarted by blowing moist air, but not well-dried air, through the reaction mixture. Two things then happened. We remembered that one of A. G. Evans' (A. G. E.'s) students, working with DIB, had found a very similar behavior, which was known as the "Allen effect" among us research students after him to whom it had happened; it was far from clear why A. G. E. had not followed it up nor M. P. urged him to do so (see M. P.'s letter), and it became an obvious next job to find out which constituent of the atmosphere was responsible for restarting a reaction that had stopped. It took me almost a month to establish firmly that it was water, that is, atmospheric moisture.

A discovery of the type described requires several consequential developments. First, I took the view that a new phenomenon requires a new name. As the term "promoter" was being used extensively, especially in the United States, by industrial chemists to denote a substance that accelerates a catalyzed reaction that would go (more slowly) without it, I devised the term cocatalyst by analogy with coenzyme to denote a substance that is necessary to make the reaction go at all[9]. To fit the new finding into the corpus of existing chemistry, we needed to devise an explanatory theory. This was not too difficult…and it became the essence of what I subsequently called the Manchester theory because I considered it the result of a collaborative effort there, but its origins go back to the hydrocarbon chemistry of the 1930s. It gave the discovery of cocatalysis the status of a significant discovery because it linked the cationic polymerizations to the chemistry of positively charged species and provided a physicochemical dimension by linking it to the (then very young) field of non-aqueous electrochemistry.

The extent to which M. P. was involved in what was for him a new field at the end of his chemical career seems to have been largely forgotten, and it is not even mentioned in his Royal Society Obituary[6]. However, M. P. showed his interest very clearly by convening on September 15, 1945 what was the first discussion meeting on Friedel-Crafts polymerizations[10], and by the way in which he wrote about it in his letters to me; see, for example, the beginning of the second paragraph of the letter under discussion here.

Toward the end of the 1950s, the surge of interest leading to an increasing volume of publications on cationic polymerizations indicated a need for gathering together authoritative and critical reviews of the different parts of the subject. I undertook the production of such a work with the help of l8 contributors, and in 1963 presented a copy of the resulting 700-page volume to M. P.[11] It was this gift that moved him to write the letter of thanks of December 17, 1963 that is the central subject of this article.

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*adiabatic: occurring without an exchange of heat with the surroundings.

The Letter

22 UPLAND PARK ROAD
Oxford
17th December 1963

My dear Peter,

I have looked through your book in a hurry and want to congratulate you on this achievement. The work is lucidly organized and carried out with meticulous care.

The collective enquiry from which much of this material has taken its origin is one of my most precious experiences. May I tell you something about the mistakes which have delayed the discovery of the co-catalyst. The main stumbling block was a fault of mine which has made me miss a number of discoveries. It was excessive ambition. I knew that the theory of energy transmission made it difficult to understand rapid exchanges of vibrational energy between molecules. I hoped to discover evidence of this in the curious behaviour of isobutene polymerization. When A.G. Evans first reported that a di-isobutene sample failed to react when BF_3 was bubbled through it, I jumped to the conclusion that we had hit on an obstruction of the transmission of vibrational energy necessary for the reaction. I tried not to think of water and hence never succeeded in reproducing the inert di-isobutene. (Actually, A.G. poured water into the inert sample and caused it to react, but this told us nothing, since it was normal for isobutene to react anyway.) I should have then and there asked for drying experiments to be made with metallic sodium, but this idea was discouraged in me by excessive ambition.

Another thing which I seem to remember – but you must correct me, if I am wrong – is that you had just started mixing your $TiCl_4$ with di-isobutene (?) and called me in alarm at its failure to react. Then, as it is on such occasions (my memory is blurred), it suddenly seemed to have become obvious to all that you had just succeeded in your purpose of clearing up the mechanism (page 2) of the reaction by conducting it under carefully controlled conditions. The result was, of course, to some extent strategic, since it was the systematic variation of the reagent which made us finally hit on one which needed so large a concentration of water that even rather primitive drying conditions revealed the necessity of this component.

(You know that Richard Ong, who committed suicide about two years ago, had ruined himself professionally by always aiming at a greater discovery than that which the problem in hand could offer and thus missing its solution. He did a beautiful piece of work when limiting himself, for once, to something as simple as the monomolecular dissociation of N_2O_5.

Students should be told about this pitfall.)

I wonder whether your memory bears out my recollection.

Yours ever,

Michael (hand-signed)

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Detailed Comments on M.P.'s Letter of December 17, 1963

After the foregoing necessary scene-setting, I can now make some detailed comments on that letter, which is the principal theme of this article.

The significance of the first sentence of the second paragraph has been mentioned, and the same message is expressed by M. P. in several other letters to me. He says clearly that his venture into polymerization chemistry and kinetics* had been for him a valued experience, and I am sure that this is more than a polite turn of phrase from an exceptionally kind man. The rest of this paragraph has many implications and manifold connections. Its central theme is the theory of energy chains as the propagators of a polymerization. From my recollections, it emerges that the energy chain theory of chain reactions that was occupying M. P. seemed to us research students too vague and therefore difficult to visualize, and it seemed unsuitable for testable calculations.[12] The form in which it found its way into the Manchester publications on Friedel-Crafts polymerizations involved the excess vibrational energy resulting from the initiation step being renewed at each propagation step by the enthalpy* of polymerization. It was unclear to the critics how such an accumulation of vibrational energy could be renewed and preserved to produce a chain reaction. Even without calculations, chemical common sense seemed to indicate to most of us that any excess of energy would be dissipated at the next collision; I at least was content to leave that matter un-understood for the time being. However, I am confident that M. P. would have discussed it thoroughly with his close friend and frequent collaborator M. G. Evans (M.G.E.)[13].

I had largely forgotten about this theory until 1999, when I prepared for publication in the *Notes and Records of the Royal Society* the proceedings of the symposium on Friedel-Crafts polymerizations, which M. P. had convened at Manchester in September 1945. I there came across the lecture by M.G. E. on energy chains and wondered why that had been included. Then, when in 2002 I discovered the letter under discussion here and thereupon reread our earliest publications on the Friedel-Crafts polymerizations in which energy chains are mentioned, the pieces of the puzzle began to fall into place, and I understood why M. P. had asked M. G. E. to give that talk about energy chains at the 1945 Symposium. Further, I began to see what had been the excessive ambition that forms the central theme of M. P.'s letter; actually, M. P. himself says so fairly clearly. He had hoped to find in the IB polymerization an unequivocal instance of an energy chain, and that would have been a major innovation in reaction theory. The implication is that he considered that finding an explanation of the bizarre behavior of the IB polymerizations in terms of known reaction mechanisms would not be such a big deal. He could not know just how difficult that quest would be and just how many theoretical and technical innovations would be needed to build up the carbenium ion theory*, which was rapidly accepted as most likely to explain the Friedel-Crafts polymerizations.

The passage beginning "I hoped to discover..." shows more than just the consequences of obsession with one pet theory. There is also here a demonstration "*in optima forma*" of how even a very experienced researcher can come to grief, that is, miss an obvious clue to the solution of a problem, by deliberately ignoring

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*kinetics: theory of the rates at which chemical reactions occur.

*enthalpy: heat content of a substance, a thermodynamic property defined by internal energy, pressure, and volume.

*carbenium ion theory: a theory based on positive carbon ions as reactive intermediates.

an alternative theory, that is, bypassing a possibility of falsifying his pet theory. As it is, M. P.'s phrase "I tried not to think about water..." opens up another nexus of facts, opportunities, and mysteries to be explored.

In the proceedings of the September 1945 Symposium, a report is included by one L. B. Morgan of ICI, Billingham, dated August 1944, but which was not actually presented at the meeting in which it is recognized that with BF_3 as the catalyst, water plays an important part in the polymerization. Morgan's research group seems to have made use of the results in a Manchester thesis by E. T. Butler, which indicated that water is important. It would have been normal practice for the results of Morgan's apparently quite extensive experimental work to have been made available to M. P. because the Manchester project was sponsored by ICI, but although I remember Morgan and other researchers from ICI taking part in our departmental discussions, I do not recall being offered sight of the ICI results. I cannot say whether this was due to industrial secrecy or because M. P. did not consider them really useful or important. In addition, there was at that time already plentiful evidence in the literature, which was noted subsequently in our early papers, of the role played by water in several reactions involving catalysis by metal halides[14]. I was familiar with that work, but I do not recall to what extent M. P. was aware of it. With regard to some events in his laboratory, his memory (as recounted at the end of p 1 of the letter) is not accurate. I never experimented with DIB, [di-isobutene]being particularly careful not to encroach on the territory of A. G. E. who was rather touchy about such matters, and who never got over the fact that the discovery of cocatalysis had slipped through his fingers.

On checking the record in my *Laboratory Notebooks*, I found that, contrary to my recollection, progress after my invention of the pseudo-Dewar vessel was not fast, mainly because of technical difficulties. It took a month and 12 experiments after my invention went into service before I wrote on November 12. 1945 under "Preliminary Conclusions", "Some constituent of the atmosphere is required before the reaction will proceed". It took almost another month before we were reasonably sure that it was the moisture in the air that was the active substance, as we called it at first.

On December 5, 1945 by Experiment 78, I tested a theory that it might be merely the addition of a hot liquid (i.e., one at room temperature) to the cold reaction mix (from -60 to -100 degrees C) that started the polymerization; it did not. Evidently this theory stemmed from M. P.'s ideas about energy chains. These vanished after 1945, preserved perhaps in the Museum of Extinct Chemical Species.

There is, however, another phantasm that needs to be recorded in this context, as it sheds light on M. P.'s chemical thinking at that time. I remember very clearly that before the discovery of cocatalysis, M . P. discussed frequently the possibility that the Friedel-Crafts polymerizations might belong to the category of random phenomena, such as the fracturing of solids, the exact course of which is not predictable, that is, those of which one can only say that they will happen under certain experimental circumstances, but for which one cannot predict when or exactly how they will occur. This intuitive analogy must have originated from M. P.'s experiences with the study and testing of crystalline materials[15]. It is clear, however, that the recognition of a phenomenon as of indeterminate origin may tell us little or nothing useful about its nature and mechanism, and so that idea did not take us any further. However, in an attempt to find a rational basis for an apparently random phenomenon, the erratic course of the IB polymerizations, M. P. suggested that I make enquiries at the Cosmic Ray Research unit in the Manchester Physics Department under P. M. S. Blackett. M. P. speculated that we may find exceptionally strong cosmic ray showers coinciding with unusually fast polymerizations-or the reverse. I do not recall what I found there, but it cannot have been very startling, as that line of enquiry was abandoned quite soon. What is important about this episode is that because cosmic rays were a subject of active research and therefore of discussion in the Staff House coffee room, M. P. was very much aware of them and could think of them as a possible origin of an apparently random phenomenon[16, 17].

Because of M. P.'s fascination with irregular natural phenomena[18], it seems appropriate to mention that, as far as I know, M. P. did not draw explicitly a well-defined distinction between repeatability and reproducibility. However. in 1999, still imbued with his ideas, I gave a definition of the distinction that-as happens so often now seems obvious. Repeatability is a term that applies to phenomena, such as the occurrence of corrosion, whereas the concept of reproducibility applies to numbers, the numerical magnitude of physical quantities, such as the rate constant of a chemical reaction[19]. M . P. evidently recognized the difference between the two concepts. As an experienced experimentalist, he admitted not being much bothered by irreproducibility because he knew that probably its origin would be found soon. However—like most serious scientists—any well-established but unaccountable unrepeatability troubled him because it marks out an area where there is a lack of understanding, and that brings us back to the status of cationic polymerizations in the 1940s. As he wrote later in the letter we are considering here, he thought that my discovery of cocatalysis had "solved the problem". What he could not know was that there turned out to be several different mechanisms of initiation of these polymerizations, nor that I would be essentially involved in their elucidation by several laborious investigations over the next half-century[20].

One further point that emerges from this letter (last line on p 1) is that M. P. considered me to be the discoverer of cocatalysis, despite the numerous observations of the same, or of clearly related, phenomena by others; I always thought of myself as a codiscoverer, and this seems to be an implication of the multiple authorship of the first publication on the subject[21].

In this connection it seems useful to recognize two kinds of discovery: mere discoveries and significant discoveries. Implicitly, M. P. is ignoring the several mere discoveries (without consequences) of the effect of water on Friedel-Crafts polymerizations and similar reactions, and evidently recognizing that it was my work that led to the significant discovery of the phenomenon. That was because we could now place the Friedel-Crafts polymerizations into the general category of acid-catalyzed reactions involving a proton transfer and the formation of carbenium ions, as has been indicated previously. In my view, a significant discovery is one that can be placed, not necessarily by the actual discoverer, into an appropriate context because it has happened at the right time; in fact, timeliness manifested by public recognition is an important facet of a significant discovery, such as was that of co-catalysis.

References and Notes

l. The scientific correspondence lecture notes and other scientific papers of the author will be deposited in the archives of the Deutsche Museum, 80306 Munich, Germany.
2. Plesch, P . H. Researches into the Catalysed Low-Temperature Polymerisation of Isobutene. Ph.D. Thesis, University of Manchester. England. 1946.
3. Plesch, P. H. Laborarory Notebooks; 1944-1945; Vol. 1 (deposited in the P. H. Plesch Archive in the Deutsche Museum, Munich, Germany).
4. Plesch, P. H. Laboratory Notebooks; 1946-1947; Vol. 2 (deposited in the P. H. Plesch Archive in the Deutsche Museum, Munich, Germany).
5. M. P.'s first academic qualification was as a Doctor of Medicine in Budapest.

6. For details of M. P.'s career, see Wigner, E. P.; Hodgkin, R. A. Michael Polanyi (1891-1976). Biographical Memoirs of Fellows of the Royal Society of London: l997;Vol. 23, pp 413-448.

7. Butyl rubber was developed by the Esso Petroleum Co. as a result of a cooperative enterprise with I. G. Farben Industrie, which was only terminated by the U.S.'s entry into WW2.

8. The *locus classicus* was a joint article from Esso and I. G.Farben: Thomas, R. M.; Sparks, W. J.; Frolich, P. K.; Otto, M.; Mueller-CunradiM, . J Am Chem Soc 1940,62,276.

9. From about the mid-1970s, the nomenclature was reversed at the instigation of J. P. Kennedy whose research group has been one of the major contributors to the exploration of cationic polymerizations. They called the metal halide the cocatalyst and the third component, such as water, the catalyst because it is, or provides the species that, by cationating the monomer, initiates the polymerization. Latterly, the term "catalyst" has largely been replaced by "initiator" and cocatalyst (now the metal halide) by "coinitiator".

10. Polanyi. M.; Plesch, P. H. Symposium on Friedel-Crafts Polymerisations Notes Rec R Soc London; 1990; Vol. 53, pp 135-141. This was followed by a series of meetings on Ionic Polymerisations (1949 Dublin. 1952 Keele. 1973 Rouen, etc.), which continues.

11. The Chemistry of Cationic Polymerisation; Plesch, P. H., Ed.; Pergamon: London. 1963. The book carries the inscription: "This book is dedicated to the memory of my father, Janos O. Plesch, from whom I learnt to appreciate the Koennenschaftler who can do things; and to Michael Polanyi who showed me the importance of the Wissenschaftler who tries to understand."

12. At that time we were unaware, because M . P. seems not to have mentioned it to us, of the article in which it is shown how to calculate the "time of expectation" required for a bond to acquire a particular energy by collision: Polanyi, M.; Wigner, E. Z f Physik Chem (A), Haber-Band 1928, 439. This article came to my notice while writing this Highlight.

13. M. G. Evans was then professor of physical chemistry at the University of Leeds, and in 1948 he took the Chair at Manchester University that M. P. had vacated. For a brief but illuminating account of their relation, see ref. 6. He was a brother of A. G. Evans.

14. Plesch, P. H. Research 1949, 2. 267-275.

15. Polanyi, M. My Time with X-rays and Crystals. In Fifty Years of X-ray Diffraction; Ewald, P. P., Ed.; A. Oosthoek's Uitgevers-mij: Utrecht, 1962. This excellent read gives a valuable picture of life and times and contains an analysis by M. P. of the mistakes he made in those studies.

16. That cationic polymerizations can be initiated by ionizing radiations was discovered in the 1950s, and this phenomenon was studied by several research groups up to the 1990s. However, a comprehensive theoretical treatment of these polymerizations. which required some quite new ideas, was not given until 1993.[17]

17. Plesch, P. H. Philos Trans R Soc London 1993, 342, 469-504.

18. Polanyi, M. Science, Faith and Society. The Riddell Lectures; Oxford University Press: London, 1946 (extended version, University of Chicago Press: Chicago, 1964). In this work M. Polanyi discusses several instances of such apparently irregular phenomena.

19. Plesch, P. H. Found Chem 1999, l,7-16.

20. Plesch, P. H. Developments in the Theory of Cationoid Polymerisations; RAPRA: Shawbury,2001, ix + 772 pg. This contains the complete chemical Publications List of P. H. P.

21. Evans, A. G.; Holden, D.; Plesch, P.; Polanyi, M.; Skinner, H. A.; Weinberger, M. Nature (London) 1946, 157, 102.

II. Michael Polanyi and the Paranormal

My academic career started when in October 1944 at the age of 26 I accepted a Research Assistantship in the research group of Michael Polanyi, professor of. of Physical Chemistry at the University of Manchester (England). That happened because my father, Janos Plesch, a fellow Hungarian, and M.P. had known each other in Berlin and had made contact again in England after my family's emigration in 1933; and M.P. had asked him whether his chemist son might be interested in joining him, which he, I, did. Because of this common multi-lingual, multi-cultural background, there developed a close affinity between M.P. and me, and I regarded him in many respects as a second father. I had an enormous respect for his intellectual abilities, knowing that he had changed very successfully from medicine to physical chemistry, although I had not read many of his writings except those connected with Transition State Theory, which was a hot topic at the time amongst chemists. Polanyi's theory of unimolecular gas-phase reactions had by then been discredited, and his ideas about the function of energy chains in chemical reactions seemed to lack plausibility, but that did not affect the very high regard in which he was held also by the other research students working alongside me, the other academics, and the industrialists from I.C.I. and the Manchester Oil Refineries who attended our seminars. I doubt that anyone of us would have admitted readily that our Master might have had at least a few "toes of clay."

This is the background of the encounter which is the substance of my story. It stems from my early interest in what is now encompassed in the term "paranormal." During the early 1940s I had met a fellow-chemist who was a member of the (London) Society for Psychical Research, the oldest society of its kind, which I then joined. I thus gained access to and became part of that area of intellectual activity, met some other research students interested in these matters, and went to a few seances. I also found a book,[1] by a mechanical engineer, in which the author gives descriptions of seances. The numerous measurements of sizes and distances and weights of the participants and objects during levitations and other manifestations are exactly what one would have expected from an engineer. It seemed a methodical, quantitative investigation such as I intended to do "once I got around" to actually doing research into the paranormal. Meanwhile (ca.1945) I was much too preoccupied with my Ph.D. researches into the mysteries of cationic polymerizations to stray into the realm of the paranormal. However, I was sufficiently intrigued by that book to want to discuss it with Michael Polanyi who, I felt confident, would have something useful and interesting to say on the subject. This the more so, since in his then recently published Riddell Lectures[2] he had concerned himself with several very different natural phenomena for which no explanations could be found. So I asked his secretary for an appointment, if possible open-ended. I outlined to M.P. some of the results and especially the measurements recorded in that book.

I do not remember much of what was said, except the phrase which effectively ended our talk: "I cannot really concern myself with such irreproducible phenomena." He may, with his usual kindness, have prefaced or followed this with some mitigating words, but that was what he meant, and for me that was that, as far as he was concerned; but it did not put me off my interest in the paranormal, nor did it diminish my determination that, eventually, I would give it serious attention. "Eventually" for me meant when I had established myself as a serious scientist in a conventional area, and "Eventually'' also turned out to be a span of almost fifty years.

Since I am a slow thinker, and my thinking has been occupied with many and various matters, it took me several decades to realise that M.P.'s parting, summarising remark bordered on the absurd; but I have also heard the same from other natural scientists, and it is a quite common reaction. I have called M.P.'s comment "almost absurd" because it seems so incompatible with his own direct experience of natural phenomena and with his writings, and I came to regard it as an excuse for not wanting to become involved with something so different, so difficult, and potentially so vast.

In his Riddell Lectures, M.P. cites examples of un-understood phenomena. One is a case of irreproducibility of a number, the rate-constant of a chemical reaction. Usually, such irreproducibilities of numbers leave scientists not seriously bothered because they are confident that sooner or later the reason for the discrepancy will be identified.

Another example involves the appearance of certain patterns on the surface of crystals of tin when they were stretched. These lines had been found in M.P.'s own and one other laboratory, but since then could not be made to appear anywhere else. This was an example of an unrepeatable phenomenon, something much more worrying to a natural scientist.[3] And, most pertinent of all, the very reason for my presence in his research group was that he wanted my help in trying to find the cause of the irreproducibility of a certain polymerisation, a problem which had been assigned to M.P. as part of the wartime Synthetic Rubber Program of the Allies. In this case there was both irreproducibility - of the rate of the reaction and of the molecular weight of its product, - and also an unrepeatability, in that the reaction, instead of proceeding until all the monomer had been consumed, sometimes unaccountably just stopped.[4]

So the notorious irreproducibility of paranormal phenomena seemed a strange reason. But the incident is an illustration of a situation which was occupying M.P. in the context of his views on how opinions are formed.

In his writings there are many passages in which he deals with various aspects of the reactions of observers to unexpected natural events, and how their attitudes are affected by cultural matters, such as their beliefs about the world. He emphasises how all this affects the observer - scientist's all-important decisions about what to accept or reject, and the effects of these decisions on discovery, that is the very expansion of the range of the Natural Sciences into new domains.[5] Furthermore, irreproducibility is always and necessarily involved in pioneering work. As M.P. knew well, successful experimentation, which means the achievement of reproducibility, requires knowledge and control of the factors that govern the phenomenon under investigation. But, by definition, to achieve that in a new field must always involve a slow, hard struggle.

References

[1] Crawford, W.J. *The Reality of Psychic Phenomena*, (J.M.Watkins, London, 1916).

[2] Polanyi, M. *Science, Faith, and Society* (O.U.P., London, 1946; University of Chicago Press, 1963 with Preface).

[3] Plesch, P.H. "On the Distinctness of Chemistry," *Foundations of Chemistry*, 1999,1,7. It seems that this is where the distinction between "repeatable" and "reproducible" was first defined explicitly.

[4] Plesch, P.H. "Michael Polanyi and the Discovery of Co-Catalysis: Discussion of an Autobiographical letter from Michael Polanyi, FRS to Peter H. Plesch of 17 December 1963," *Journal of Polymer Science, Part A* (2004) 42, 7: 1537-1546.

[5] The classical example is that several observers before Herschel had seen through their telescopes a disc that moved amongst the stars, but they had dismissed it because a new planet (Uranus) was beyond their "boggle-limit."