

How polyethene came about

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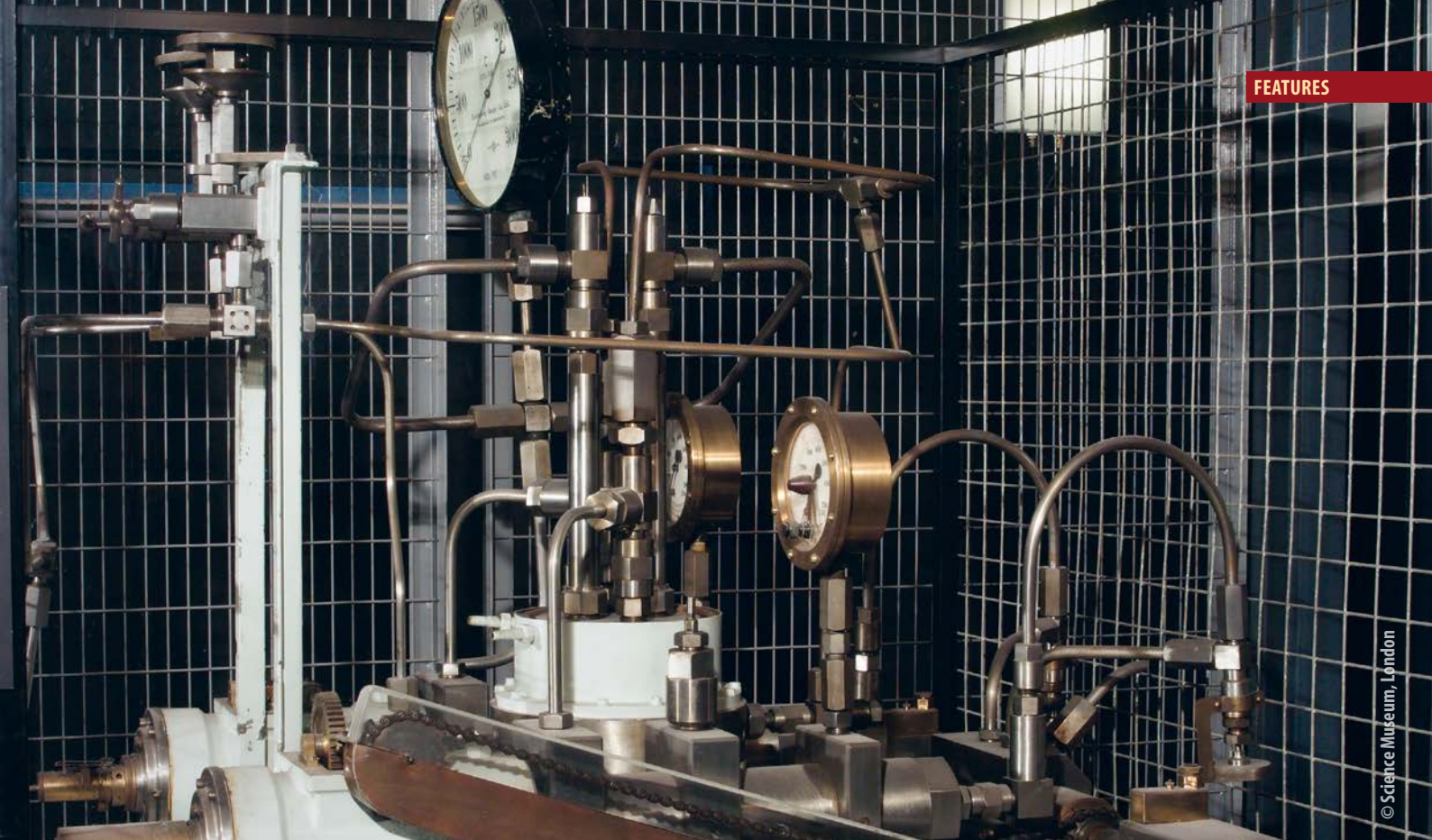
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HOW POLYETHENE CAME ABOUT

■ **Thijs Michels** – Applied Physics department, TU Eindhoven, m.a.j.michels@tue.nl – DOI: <https://doi.org/10.1051/epn/2018403>

Polyethene (PE) is the world's most common polymer, with applications from low-cost to extreme-performance products. Its origin, as low-density LDPE, can be traced back to a long tradition in fundamental thermodynamics and to a liberal international university-industry collaboration. A first application became of world-wide significance 75 years ago.

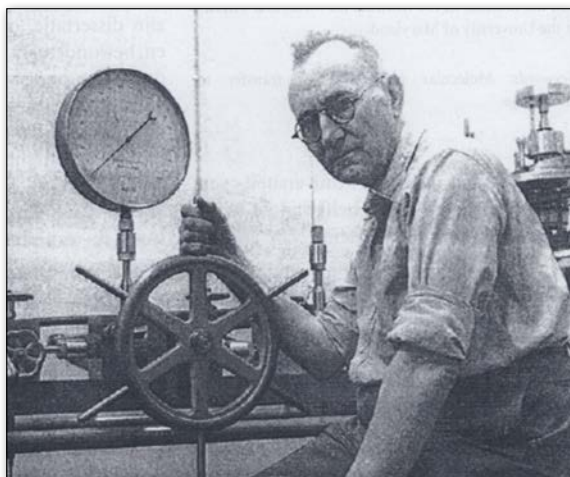
When Van der Waals received his Nobel Prize in 1910, two years after his retirement, the field of fluid thermodynamics that he had initiated was flourishing already for more than thirty years. His successor in Amsterdam Philipp Kohnstamm and other prominent researchers had expanded it into a strong Dutch scientific tradition [1]. The existence of molecules and their universal interaction was a daring assumption by Van der Waals in 1873 against much opposition at that time, but with scientific progress in the early 20th century his views became universally accepted. In spite of this progress, a more detailed picture of the molecular properties and of the origin of the intermolecular interaction remained elusive. As a consequence the field became stagnant around 1915-1920. Kohnstamm's interests shifted to pedagogy

and philosophy. Students preferred the new quantum theory, particularly in Amsterdam, where Nobelist Pieter Zeeman broke new ground in atomic spectra.

High-pressure physics

One of the few students who continued in the Van der Waals tradition was A.M.J.F. Michels (Fig. 1), my father, who had entered the university in 1909. He recognised that quantum theory promised insight also in molecules, which could open new avenues for the understanding of compressed gases and liquids. Conversely, by compressing gases to levels where molecules get in close contact, thermodynamic and electromagnetic studies could become informative about molecular details that should obey quantum theory. He figured that this would require pressures up to a few thousand atmospheres. In 1929, as a successor to

► FIG. 1: Antonius (Teun) Michels, with his oil press for generating high pressures [Source: Michels family archive]



Kohnstamm, he presented all this as the agenda for a future specialised high-precision high-pressure laboratory. But back in 1920 there were significant technical hurdles to take first before such academic questions could be addressed. The accuracy in methods of measuring temperature and especially pressure were far below what was needed, and he spent a decade and longer on developing improvements. His most conspicuous achievement was the design in 1924 of what is now known as the 'Michels pressure balance'; with its frictionless rotating piston it instantly improved the accuracy in pressure measurement up to 3000 atm. by more than a factor 100, to 1:100,000. For calibration a 27.5 m mercury column was erected in Amsterdam's tallest church spire, the 'Westertoren'. This and other technical high-pressure work was a long and necessary preparation for his real agenda, but at the university it earned him an unwanted reputation of being more technically than scientifically motivated. He used it to his advantage when by chance he came in contact with industry.

ICI

Michels had very limited university funding. But still a bachelor, with a strong motivation and much energy, he had side-jobs as a high-school teacher and worked in the laboratory at evening and night hours, spending personal earnings on equipment and assistance. In this situation he was visited in 1925 by Reginald Gibson (Fig. 2), a young chemist from London who was temporarily hired by Kamerlingh Onnes in Leiden and would join the British Imperial Chemical Industries a year later; Gibson was facing a technical problem on which he thought Michels could help. Gibson was immediately interested in the pioneering work in Amsterdam and offered to assist part-time. After joining ICI, Gibson invited Michels for a Christmas stay in England, where he also introduced him to ICI management - with far-reaching consequences on both sides. When a delegation of ICI visited the Amsterdam laboratory in 1928, they recognised the enormous potential of the new high-pressure techniques for their own goals, their thoughts being mainly on phase behaviour

► FIG. 2: Reginald Gibson in his Amsterdam period [Source: Michels family archive]

and material characterisation; no ideas occurred on links to chemistry. In their visit report they did conclude that "if there were an army of research workers co-operating with Amsterdam [...], results of industrial application would undoubtedly be obtained too quickly to be assimilated". The outcome was that ICI agreed to support Michels with substantial means, on the condition that he would stop his side-job teaching and that ICI staff would be trained in Amsterdam in the high-pressure techniques. As a result Kohnstamm stepped aside and Michels became reader in thermodynamics. Gibson was the first ICI employee to work in Amsterdam, where he also obtained his PhD. His arrival was soon followed in 1929 by that of Michael Perrin (Fig. 3), who had already degrees from Oxford and Toronto and who stayed in Amsterdam till 1933 [2].

From physics to chemistry

Publications, notably by Bridgman and Conant at Harvard, reported that polymerisation reactions may be affected by very high pressures; but measurements remained crude and results unclear. First theoretical thoughts about possible novel effects of pressures on reactivity appeared on paper in 1930, after Michels participated in a Royal Society Discussion Meeting on high-pressure chemistry. The account of this meeting [3] starts with contributions by British specialists, discussing chemical processes up to a few hundred atm.; here the main pressure effects are the classical ones of shifting reaction equilibria or changing solvency. Apparently not without self-confidence in this illustrious gathering, Michels starts his contribution by stating that "in Amsterdam [...] we refer to pressures up to 2500 atm. as low, pressures between 2500 and 10,000 atm. are regarded as medium, and pressures above 10,000 atm. are regarded as high". Then he points out how in compressing gases potential energy is stored which may ultimately be sufficient to distort molecules and trigger chemical reactions that normally will not occur (see Box). In personal notes from the same time Michels (who also had a degree in chemistry) showed a particular interest in



organic reactions. He is then invited in 1931 to present his ideas to the research committee of the ICI Dyestuff Group, under the title “Suggestions as to the influence of high pressure upon chemical reactions”. No written version of the presentation seems to have survived, but in 1932 Perrin (still in Amsterdam) and John Swallow (at ICI) discuss its theoretical arguments in a proposal to the ICI Alkali Division for a research programme on chemistry between 1000 and 20,000 atm., aiming to connect these arguments with Bridgman’s type of experiments. The 1931 presentation by Michels aroused direct interest and at the request of ICI one external member of the committee, professor Robert Robinson, listed a number of candidate reactions; Gibson and Eric Fawcett were asked to make a start with it.

Polyethene

One of the attempts was to react ethene and benzaldehyde into a lubricant. On Friday March 24, 1933 Fawcett and Gibson filled the reactor and left it at 170 C and 1900 atm. (Fig. 4). When they returned on Monday a leak had developed and the pressure had gone. Opening the reactor they discovered a “waxy solid in reaction tube”, as it was recorded in Gibson’s notebook. After some study it was realised that ethene had polymerised. But when the reaction was repeated with ethene alone it frequently ended in an explosive decomposition, producing just hydrogen, methane and amorphous carbon. A ban was ordered on working with ethene, the early results were left as an academic curiosity and the focus shifted to other reactions. In December 1935 Perrin, after discussion with ICI’s engineer Dermot Manning, revisited the problem in a ‘clandestine’ experiment, as Manning told later. They benefitted from experience now gained with other reactions and from improved equipment, but for safety operated after normal working hours. Not surprised, Perrin saw the pressure slowly drop and supposed that ethene was reacting away; continuously readjusting the pressure by feeding in fresh ethene, he got the polymerisation under control and a test tube filled with white powder was obtained. Afterwards it was discovered that the pressure drop had been partly due to a leak again. On December 20 the first official controlled ethene polymerisation was recorded by Perrin, John Paton and Edmond Williams. But in later attempts explosions returned. It took months of analysis to recognise that oxygen impurities in the ethene are essential to initiate the reaction at the chosen pressures (see Box); in the first try the impurity in the continued feed just happened to be high enough for sustained reaction but low enough to avoid explosion. The new polymer was now taken seriously and it soon turned out that it could be very easily processed and shaped, was chemically resistant and water-repellent, did not embrittle at very low temperatures or melt in boiling water, and had exceptional properties as an electric insulator. In 1938 a pilot plant, with an unconventional continuous gas compressor that had to be designed in



◀ FIG. 3: Michael Perrin (left), with Michels’ theoretician Arend Rutgers (a student of Ehrenfest and later professor of Physical Chemistry in Ghent) in the wooden annex to the old laboratory. Perrin also played a leading role in British and Allied nuclear research during and after WW II; he was knighted in 1967 [Source: Michels family archive]

Amsterdam [4] (see introductory illustration), produced the first tonnes of polyethene. Application as insulation of subsea communication cables was envisaged.

Airborne radar and the U-boat war

World War II changed it all. Radar had already been developed, but its installation in planes called for shorter wavelengths (using the recently invented cavity magnetron) and faced the very cold and humid conditions high in the air. With the weak reflection signal, cable insulation proved to be the critical problem; but the moisture-repellent polymer, with its excellent mechanical and exceptional high-frequency dielectric properties, could solve it. Robert Watson-Watt, the pioneer of British radar (and a descendant of James Watt), later declared that polyethene transformed the construction of airborne radar “*from the almost insoluble to the comfortably manageable*” [4]; it had some success already at the end of the Blitz on London. But early 1943 the Nazi-German U-boat campaign threatened to starve Britain from the essential supplies needed for its survival and for the future liberation of Europe. Churchill has confessed in his memoirs that the



◀ FIG. 4: Apparatus used by Fawcett and Gibson in the discovery of polyethene in 1933. Next to the ethene feed are a primary gas compressor, the reactor vessel (filled with oil, a mercury interphase, and liquid benzaldehyde) and the oil press for reaching up to 3000 atm. [© Science Museum, London]

only thing that ever really frightened him during the war was the U-boat peril [5]. In the spring of that year, 75 years ago, the centrimetric radar with polyethene insulation came in operation. Within a month the tide turned completely and U-boat losses suddenly rose to huge numbers. Admiral Dönitz realised that his campaign had failed and that “*the U-boats could be located at a great distance by the enemy’s radar, apparently on short wave, without previous warning on their own receivers. [...] The enemy air force with its modern methods of searching had produced this change in U-boat warfare*” [6]. The critical role of polyethene and how it originated were recalled directly after the war by an ICI manager in a letter to Michels: “*There has been public acknowledgement of the value of our products in the war effort and I am glad to think that some share of it is due to you*” [7].

Epilogue

The liberal industry-university collaboration proved beneficial also in other ways to the parties involved. Although ICI recently has ceased to exist as an independent company, its high-pressure process is still operated today by many manufacturers of LDPE. Michels obtained a professorial chair in 1939 and the industrial support was instrumental to open a splendid new ‘Van der Waals laboratory’ already

in 1935; after the war it became world-leading in the molecular study of gases and liquids by high pressure. When in the 1950’s Michels could not be persuaded to emigrate to the USA, he was asked to build a copy of his laboratory at the University of Maryland: the ‘Institute of Molecular Physics’ [8]. ICI equipment in which polyethene was synthesised and the continuous gas compressor from the Van der Waals laboratory are now at the Science Museum in London. Looking back in 1980, Reginald Gibson concluded with the philosophy of the industry’s founder Ludwig Mond: referring to the common notion that ‘necessity is the mother of invention’, Mond rather trusted that “*the steady methodical investigation of natural phenomena is the father of industrial progress*” [2]. A philosophy that was fittingly written on the commemoration plaque in the ICI Winton laboratory where polyethene was discovered. ■

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About the author



M.A.J. (Thijs) Michels is emeritus professor of Theoretical and Polymer Physics at the Eindhoven University of Technology and a former Scientific Director of the Dutch Polymer Institute (DPI), an international public-private partnership in polymer research. He has also worked 20 years in research of oil processes and products at the Shell laboratory, Amsterdam.

BOX: THE INTERMOLECULAR AND INTRAMOLECULAR ENERGIES OF ISOTHERMALLY COMPRESSED GASES

Equation of state and internal energy. The thermodynamic relation $(\partial U/\partial V)_T = -p + T(\partial p/\partial T)_V$, tells that internal energy ΔU due to molecular interaction increases with isothermal compression as soon as $(\partial \log p/\partial \log T)_V < 1$. By integration along accurately measured isotherms $p(V, T)$ it was found in Amsterdam that at a few thousand atm. ΔU might reach values comparable to chemical activation energies. *The Schottky relation and intramolecular energy.* Equations of state are often derived as power series in V by applying the well-known virial theorem to the interacting molecules, with virial coefficients that are complicated integrals over the interaction potential. The virial theorem can also be applied to the charged electrons and nuclei that constitute the same molecules and that interact via the simple Coulomb potential. This leads to the compact Schottky relation $U = 3pV - K$, with K the kinetic energy. At isothermal compression any change in K should be of intramolecular origin, *i.e.*, due to molecular deformation. For ethene $\Delta K_{\text{intramol}}$ has been calculated from isotherms [9], giving about 7 kcal/mol at 170 C and 1900 atm. *The role of nuclei and the reaction initiation by oxygen.* A quantum-chemical treatment of the distortion of the ethene molecule was still out of order many years later, but in 1950 Cottrell could address simpler molecules [10]. He showed that much of the rise in K was compensated by a virial contribution of shifting nuclear positions, and that the rise in electronic energies was at least one order smaller than otherwise expected. This explains why traces of oxygen were also necessary as reaction initiator.

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