

FROM POLYMER TO MACROMOLECULE: ORIGINS AND HISTORICAL EVOLUTION OF POLYMER TERMINOLOGY

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Introduction

For anyone involved with the chemical sciences, the complexities of terminology and nomenclature are an accepted part of the subject, be it students, practicing chemists, or historians of the field. In fact, the mastery of chemical nomenclature and associated terminology has often been compared to the study of a foreign language, complete with separate “dialects,” each of which addresses different classes of chemical species and contains its own set of specialized rules and terms (1-4). Of course, nothing is constant and just as regional languages and dialects have changed over time, the meaning of chemical terms and systems of nomenclature have also evolved (5). Sometimes these progressions are gradual and of little real impact, but other times changes can be drastic and surprising, with the same terms adopting completely different meanings and uses over time (6).

As 2020 marks the 100-year anniversary (7-9) of the introduction of the macromolecular concept by Hermann Staudinger (1881-1965) (10), it seems appropriate to review the history behind the origin and evolution of various terms and their usage in polymer science. As much of the discussion here will focus on the terms *polymer* and *macromolecule*, it would be worthwhile to first give the modern definitions as a point of reference. According to IUPAC (11):

Conventionally, the word polymer used as a noun is ambiguous; it is commonly employed to refer to both

polymer substances and polymer molecules. Henceforth, macromolecule is used for individual molecules and polymer is used to denote a substance composed of macromolecules. Polymer may also be employed unambiguously as an adjective, according to accepted usage, e.g. polymer blend, polymer molecule.

As such, a polymer would refer to a powder or film comprised of macromolecules, where a macromolecule (or polymer molecule) is defined as (11):

A molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass.

In practice, however, both the terms polymer and macromolecule have continued to be used as interchangeable nouns, as illustrated by the following statement from a recent viewpoint article on the 100th anniversary of macromolecular science (12):

Macromolecules that exhibit both electron transport and ionic mass transport (i.e., mixed conducting polymers)...

The following discussion will attempt to present the origin of these terms, with a particular focus on the evolution of the meaning and use of the term polymer. In the process, the origins and use of other commonly used terms in polymer science (macromolecule, oligomer, copolymer, etc.) will also be discussed, along with the beginnings of formal polymer nomenclature.

Berzelius, from Isomer to Polymer

The first of our terms, *polymer* (from the Greek *polys* “many” and *meros* “part”), finds its origin with Swedish chemist Jacob Berzelius (1779-1848, Figure 1), who introduced the related terms *isomeric* and *polymeric* in 1831 (13) and 1832 (14), respectively. In the 1833 German translation of his original 1832 Swedish paper, Berzelius specified the difference between these two concepts as follows (14b):

But in order not to confuse phenomena of the same kind, it is necessary to determine precisely the concept of the word *Isomerism*. I mentioned that I understand this to include bodies which are composed of the same absolute and relative number of atoms of the same elements, and have the same atomic weight, as, for example, the two tin oxides, or the two phosphoric acids, which is not to be confused with the case where the relative number of atoms is equal, but the absolute number is unequal. For example, the relative number of carbon and hydrogen atoms in olefiant gas is absolutely the same as in oil of wine (the number of hydrogen atoms being twice as great as that of the carbon atoms). Yet, alone in one atom [i.e., molecule] of the gas there is only 1 atom of carbon and 2 atoms of hydrogen, CH_2 , while on the other hand, oil of wine contains 4 atoms of carbon and 8 atoms of hydrogen, C_4H_8 . In order to be able to describe this type of equality in composition, but inequality in properties, I would like to propose for these bodies the term *polymeric* (from πολυς , multiple).



Figure 1. Jöns Jacob Berzelius (1779-1848) (Stipple engraving by A. Tardieu after F. Krüger, 1828. Courtesy of Wellcome Library, London, under Creative Commons Attribution only license CC BY 4.0).

To put this in context, “olefiant gas” (ölbildendes Gas) is ethylene, for which Berzelius gives what would be considered its modern empirical formula (CH_2), rather than its molecular formula (C_2H_4). The second substance, “oil of wine” (Weinöl), refers to the oil by-product obtained during the production of ethylene (olefiant gas) from sulfuric acid-alcohol mixtures. The English chemist and apothecary Henry Hennell (1797-1842) had analyzed this oil in 1826 (15), ultimately determining it to be a mixture of diethyl sulfate and various olefins (Figure 2).

The complex composition of oil of wine has caused some to state that the example given by Berzelius was a poor choice, contained obvious errors, and did not correctly demonstrate the relationship under discussion (16, 17). However, the current author has previously given more detail and clarification on this point (18), explaining that Hennell also showed that diethyl sulfate could be removed by heating the crude oil of wine in water (15). Furthermore, it has been noted by later chemists of the 19th century that this purified olefin fraction was known as “light oil of wine,” while the original oil was called “heavy oil of wine,” and that these two oils were not always differentiated in the literature (19).

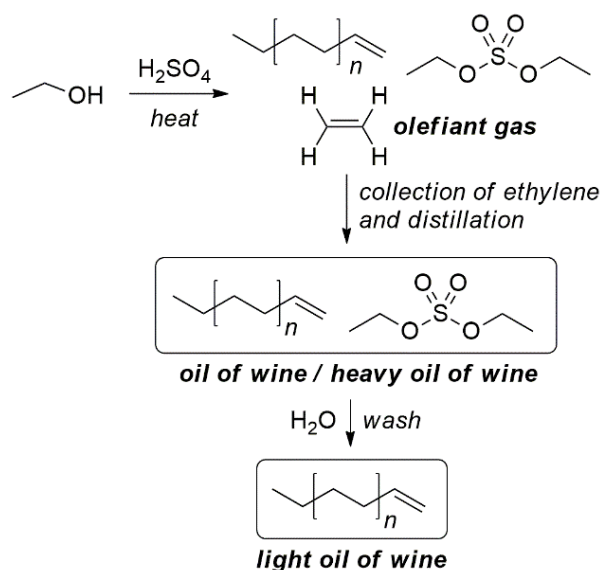


Figure 2. Production of oil of wine.

Although the isolated light oil of wine is still comprised of a mixture of different olefins, Hennell’s characterization revealed properties consistent with a mixture with a compositional average of octene (C_8H_{16}) (15). If one assumes that the formula given by Berzelius for oil of wine (C_4H_8) was also halved in the same way as that of ethylene, this would then give a corrected formula of C_8H_{16} , which is in good agreement with that of octene.

As such, it appears that Berzelius is referencing light oil of wine here, and the relationship between ethylene (C_2H_4) and this oil (i.e., $4 \times C_2H_4$) is fully consistent with his given definition.

Due to the inherent confusion associated with this example, many authors avoid it altogether when presenting the concept of polymerism as introduced by Berzelius, instead comparing ethylene and isobutylene (16, 20), which had been previously isolated from oil gas by Michael Faraday (1791-1867) in 1825 (21). In his previous paper on isomerism (13), Berzelius had stated that this pair of compounds differed from the isomeric examples discussed, as they exhibited the same relative number of elements, but with different absolute numbers. He did not specifically state, however, that this was a representative example of a polymeric relationship. Nevertheless, both of these sets of examples correctly demonstrate polymeric relationships as originally defined by Berzelius (Figure 3).

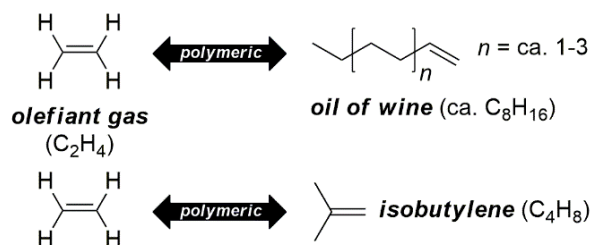


Figure 3. Examples of early polymeric relationships.

The relationship between ethylene and isobutylene illustrates an important distinction of Berzelius' polymer concept, however, as he never specifically stated that a polymer is a molecule formed from the chemical combination of the smaller unit. Thus, while it could be argued that oil of wine can be produced via the chemical reaction of ethylene, this is not the case for isobutylene.

Evolution of the Polymer Definition

Following its initial introduction by Berzelius, the polymer concept was then revisited and modified over time. A notable example of this can be seen in the contributions of the French chemist Marcelin Berthelot (1827-1907, Figure 4). In his *Leçons sur l'isomérisie* presented before the Société Chimique de Paris in 1863, he gives polymerism as one of five types of chemical isomerism, presenting his view of polymers as follows (22):

I designate, under the name of polymer bodies, bodies formed of the same elements, in the same proportion, but under a different state of condensation, and capable of being produced from one another.

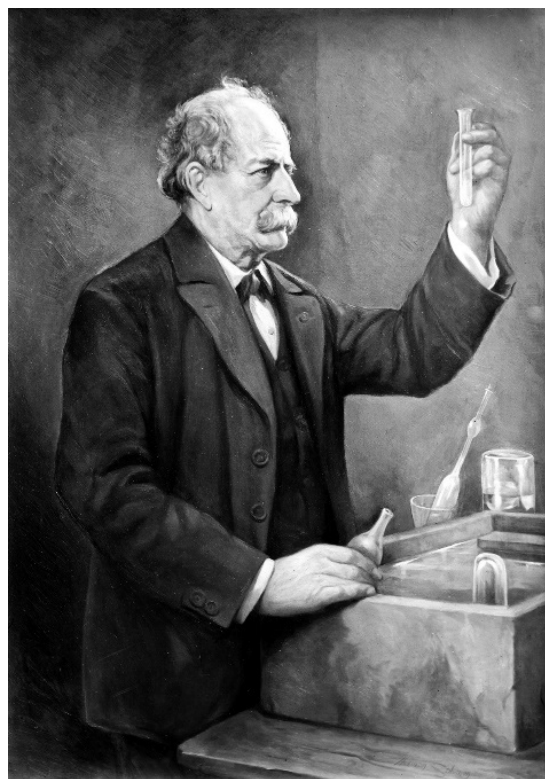


Figure 4. Pierre Eugène Marcelin Berthelot (1827 -1907) (Courtesy of Wellcome Library, London, under Creative Commons Attribution only license CC BY 4.0).

Berthelot then gave several examples to illustrate this relationship. It should be noted that while his definition above could be read to imply reversibility, this was never explicitly stated by Berthelot. Furthermore, both his discussion of polymer bodies and the presented examples dealt solely in the formation of larger bodies from reactant species. Such examples included turpentine (now known to be primarily composed of α - and β -pinene) and di-turpentine (23), as well as amylenes (2-methyl-2-butene) and its products diamylene, triamylenes, and tetramylenes (Figure 5). He then concluded with the following observation (22):

Polymerism is nothing more than a particular case of chemical combination: it is the combination of a molecule of a body with another molecule of the same body.

Thus, as put forth by Berthelot, polymers not only shared the same empirical formula, but now included a direct relationship in which the larger molecule was produced from the smaller, an aspect not present when originally introduced by Berzelius. Berthelot then introduced yet another example in 1866, while detailing the action of heat upon acetylene (24). When heating acetylene over

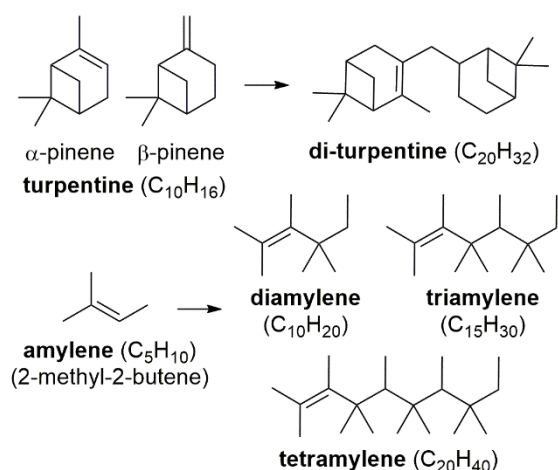


Figure 5. Modern representation of Berthelot's examples of polymer bodies.

mercury in a bell at extreme temperatures, he observed the formation of benzene, styrene, and a resinous solid (Figure 6). The last of these is generally considered to be the acetylene polymer later given the name cuprene (25). Of course, it is important to note that Berthelot's definition of polymer did not include any minimum size requirement, so all three of these products were polymers of acetylene in his view (18, 26).

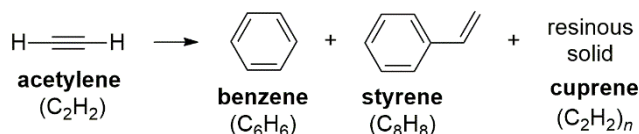


Figure 6. Berthelot's polymers of acetylene.

This definition underwent a bit further modification through the beginnings of the 20th century, as illustrated by the description of the Dutch chemist Arnold Frederick Holleman (1859-1953) (18, 26, 27). In the 3rd edition of his *A Text-Book of Organic Chemistry*, published in 1910, he stated (28):

The union of two or more molecules of a substance to form a body from which the original compound can be regenerated is called polymerization.

Again, this definition made no real specification about size or molecular weight.

This changed somewhat in 1920, when the German chemist Hermann Staudinger gave his own views on polymerization (10). To begin with, he felt Holleman's requirement concerning the ability to regenerate the original species was not essential and did not accurately describe all polymerization products. Instead, Staudinger offered a more general definition as follows (10):

Polymerization processes in the broader sense are all processes in which two or more molecules combine to form a product with the same composition, but a higher molecular weight.

Staudinger then went on to show that these polymerization processes could be subdivided into two groups: one in which the bonding of the initial molecule is retained in the polymer product and another in which polymerization results in atomic shifts such that the bonding of the product differs from the initial species. As examples of the first group, he included the production of metastyrene (modern polystyrene) from styrene, rubber from isoprene, and paraformaldehyde from formaldehyde. For the second group, his examples consisted primarily of various bimolecular condensation reactions such as aldol condensation or benzoin formation.

Staudinger proposed that the first group should be regarded as real polymerization processes and products, while the second class should be referred to as false polymerizations or condensed polymerization products (10). Thus, in his view, polymers must retain the basic structural nature of the initial molecule polymerized. Staudinger also continued to note that polymerizations often form high molecular weight products, but did not specifically make such high molecular weights a requirement of what defines a polymer.

While Staudinger did much to clarify polymers and polymerization processes, this did not bring an end to the evolving views on the topic. Even as late as 1929, the American chemist Wallace Carothers (1896-1937) pointed out that the polymer definition was unsatisfactory and felt a more useful description of polymers was as follows (29):

They are characterized by a recurring structural unit, so that if this is represented by $-R-$, the structure of these polymers may be represented in part by the general formula $-R-R-R-R-R-R-R-$, etc., or $(-R-)_n$ The structural units $-R-$ are bivalent radicals which, in general, are not capable of independent existence.

Staudinger and Macromolecules

By the early 1900's, significant interest had developed in *high molecular compounds* (30), operationally defined as products that cannot be vaporized in high vacuum. Furthermore, it was generally viewed that the molecular weight of these species was essentially too high to determine (31). At the same time, focus was also directed to *colloid phenomena*. As introduced by

Thomas Graham (1805-1869) in 1861, colloidal (glue-like) materials were characterized as non-crystalline substances with slow diffusion, whose solutions did not pass through semipermeable membranes (32-34). These collective properties were generally viewed to be due to large particle size. At the time, however, neither large particle size nor high molecular weight was considered evidence for large chemical molecules and many considered both colloids and high molecular compounds as physical aggregations of small molecules (25, 35-38). Thus, these terms generally referred to collections of small molecules.

At odds with this view, Hermann Staudinger (Figure 7) speculated that many of these species instead consisted of covalently-bonded, long-chain molecules (35, 39-41). At the time, however, the established term polymer did not effectively differentiate between the accepted aggregate view and his preferred model of long-chain molecules (26, 30, 42), which led to his introduction of the new term *makromolekül* (*macromolecule*, from the Greek *makros* "large," i.e., literally "*large molecule*") in 1922 (43):

Caoutchouc [natural rubber] is then a very high molecular weight hydrocarbon with many ethylene bonds, and the chemical behavior fully corresponds to this view. Some or all of the ethylene bonds can be saturated...without the colloidal properties changing, i.e., without the "macromolecule" disintegrating.



Figure 7. Hermann Staudinger (1881-1965).

This was followed two years later with a more formalized definition, stating (44):

For those colloid particles in which the molecule is identical to the primary particles, in which the indi-

vidual atoms of the colloid molecule are bound by normal valences, we propose the term macromolecule for differentiation. Colloidal particles constituted in this way, which occur primarily in organic chemistry and organic nature according to the ability of carbon to bind, form the actual colloidal substances. Here the colloid properties are due to the structure and size of the molecule...

Ultimately, Staudinger preferred to refer to his new model of high molecular weight compounds as *makromolekulare Chemie* (*macromolecular chemistry*), which is still widely used in Germany (30). The general concept of macromolecules, however, was not well received for some time (26, 36, 38, 40, 45). Still, by 1930, significant evidence had been accumulated in favor of the macromolecular hypothesis. The final part in establishing the concept was due to Wallace Carothers, who had successfully demonstrated the relationship between the structure and properties for a number of such polymers (26, 35, 46). It should be pointed out that the bulk of the characterization efforts up to this point had focused on natural and synthetic polymers comprised of a single repeat unit (cellulose, rubber, polystyrene, etc.), as more complex materials provided too many variables to accurately determine useful relationships between the polymer structure and its properties. It was only later that it was determined that more complex systems such as biological polymers (proteins, etc.) also fit this model. Nevertheless, it eventually became widely accepted that polymeric materials consist of macromolecules, for which Staudinger received the 1953 Nobel Prize in Chemistry.

Meyer, Mark, and High Polymers

During the early years of the macromolecular model, Staudinger became embroiled in arguments with Kurt Heinrich Meyer (1883-1952, Figure 8) and Herman Francis Mark (1895-1992). At the time, both men were working at I. G. Farben, with Mark joining Meyer there at the beginning of 1927 (47-50). Originally trained in organic chemistry, Mark had developed particular expertise in X-ray crystallography, while Meyer was an organic chemist strongly influenced by physical chemistry. With this combined focus, the two collaborated on the study of natural polymers.



Figure 8. Kurt Heinrich Meyer (1883-1952) (Reprinted with permission from Reference 46. Copyright 1950 American Chemical Society).

Mark had come over to Staudinger's view of long-chain molecules before his arrival at I. G. Farben (49). Meyer too supported the concept of long-chain, high molecular weight molecules, but the two men disagreed with Staudinger on some details. Based on their work, they ultimately developed a new theory that appeared to be a compromise between Staudinger's macromolecular model and the previous aggregate model. In their view, colloidal particles were not themselves macro-molecules, but rather were aggregates of long-chain molecules held together by "special micellar forces" (35, 48, 49). Thus, they held that the determined weights of colloid particles did not represent molecular weights, but "micellar weights" (49).

In both his published papers and personal correspondence, Staudinger opposed their work, leading to an often bitter debate between Staudinger and Meyer (35, 48, 49). According to Mark, he wrote Staudinger in November of 1928 in an attempt to keep the peace, saying that he was sorry to see that Staudinger was annoyed by Meyer's statements. The growing feud continued, however, until a journal editor finally ended it all by refusing to print their papers on the subject. Mark later recalled (35):

Even the champions of the long chain aspect did not agree with each other, as they easily could have done because instead of concentrating on the essential principle, they disagreed on specific details and, at certain occasion, they argued with each other more

vigorously than with the defenders of the association theory.

Throughout their joint work, Meyer and Mark did not use Staudinger's term macromolecule, but instead used the alternate descriptor *high polymer*. It has been proposed that this was in response to the dispute with Staudinger (30), but Meyer had first introduced the terms *hochpolymerer Verbindungen* (*high polymer compounds*) or *hochpolymerer Stoffe* (*high polymer materials*) in a paper submitted in the summer of 1928 (51). As this paper preceded both Meyer's joint papers with Mark and the ensuing conflict with Staudinger, this seems unlikely, although the conflict could have influenced their continued use, rather than giving Staudinger the satisfaction of using the term macromolecule.

The term high polymer was then reinforced and popularized through several books published by Meyer and Mark beginning in 1930 (52-54), particularly their critical two-volume *Hochpolymere Chemie* published between 1937 and 1940 (54). During the buildup to World War II, Mark emigrated first to Canada and then to the United States (50), where he continued to favor the use of high polymer over macromolecule, as illustrated by his multi-volume series *High Polymers and Related Substances*. As a result, the use of high polymers found acceptance in the United States, with the American Chemical Society organizing a High Polymer Forum in 1946, after which a formal Division of High Polymer Chemistry was founded in 1950 (30, 55). With little time, however, the descriptor "high" was dropped in common usage, thus resulting in the present synonymous usage of the terms polymer and macromolecule. Within this same time period, it should be noted that there was also an internal controversy over the general naming of the discipline (i.e., polymer science vs. macromolecular science) (30). Here, polymer science continues to be the more commonly used term.

Early Polymer Nomenclature

Although the discussion above has focused on the origin and evolution of the two primary terms polymer and macromolecule, it is also worthwhile to highlight some early practices in polymer nomenclature. Thus, while the overall family of materials could be identified as polymers or macromolecules, the names given to specific examples of this family was much less systematic.

The earliest known synthetic polymer, modern polyaniline, was first reported in 1834, but was not given a name until it was first commercialized as a cotton dye

in the 1860s. As such, it is perhaps not surprising that it was originally named *aniline black*, according to its source and color (18, 56). However, this name was still retained after its linear chain structure was determined in the early 20th century, with the name polyaniline not introduced until the 1960s (57).

In comparison, the first of the addition polymers, modern polystyrene, was first reported in 1839. As it was originally believed to be an oxidation product, it was originally called *Styroloxyd* (styrene oxide) (18). Further studies in 1845 by John Blyth and August Wilhelm Hofmann (1818-1892) showed that this was not the case, however, after which Hofmann renamed the material *Metastyrol* (metastyrene) (58). The prefix *meta*- had been introduced in 1833 by Thomas Graham as a way to denote a modification of an original compound (59). Thus, metastyrene would indicate a modified (i.e., polymerized) styrene.

The first to use the name *Polystyrol* (polystyrene) appears to have been Abraham Kronstein in 1902 (60). Even here, however, Kronstein is not using polystyrene in place of metastyrene, but is using it to differentiate one type of polystyrene from the more common form:

Berthelot's statement that the polymerization of styrene in hydrocarbon solution produces the same metastyrene as the heating of pure styrene is based on a mistake. The very fact that metastyrene is insoluble in hydrocarbons, while the product Berthelot obtained by heating styrene in a hydrocarbon solution is a soluble polystyrene, speaks for the diversity of these products.

Thus, the eventual replacement of metastyrene with the modern polystyrene continued to occur slowly.

While the evolution in naming for polystyrene seems like it should have become a blueprint for the naming of other polymers, this was not immediately the case. Rather, many polymers were still often described rather than given formal names. For example, another early addition polymer, polyvinyl chloride, was still referred to as polymerized vinyl chloride into the 1920s.

Copolymerization and Copolymers

As studies of polymeric materials advanced, so too did the complexity of some polymers being produced. With greater understanding of simple polymerizations and the nature of their products, a next logical step was the polymerization of mixtures of monomeric precursors. In modern practice, such polymerizations are known as *copolymerization*, the products of which are *copolymers*.

The first study of such a copolymerization has been credited to Willy Otto Herrmann in 1928 (61), who carried out the copolymerization of vinyl acetate with di- and tri-ethylene. However, as this is based upon his published memoirs in 1963, it is not clear what terms he actually used in 1928. Understanding of copolymerization progressed slowly, however, such that Georg Kränzlein (1881-1943) of I. G. Farben reported the novel observation in 1930 that (61):

copolymers are quite different from blends. Each monomer acts as a regulator on the other and they polymerize into each other.

As such, this may have been the first documented reference to the product of copolymerization as a copolymer.

The first academic study of copolymerization seems to have been reported that same year by Theodor Wagner-Jauregg, who investigated the copolymerization of maleic anhydride with either styrene or stilbene (62). Interestingly, he proposed to call such processes *heteropolymerization*:

For this type of addition reactions, the name additive hetero-polymerization is proposed, in contrast to additive homo-polymerization.

The fact that he proposed this new term, and does not even mention copolymerization, suggests that the term copolymerization was not widely recognized in 1930. By the 1940s, however, both of the terms copolymerization and copolymer were in regular use (63).

Oligomers and Limits of Size

Of course, a common point of argument is what exactly constitutes a high polymer or macromolecule? In addition, how should one refer to products that are not monomeric, but yet do not meet the criteria of macromolecules? As a solution, the term oligomer (from the Greek *oligo* "few" and *meros* "part") was ultimately introduced to describe low molecular weight products. The introduction of this term has been credited to the American polymer chemist Gaetano Frank D'Alenio (1909-1981, Figure 9) at General Electric Co's plastics laboratory in 1943. According to his coworker L. V. Larsen (64):

In 1943, Frank was preparing a laboratory manual for resins and plastics, which was published late in 1943. One day, several of us who worked with Frank were talking in his office about the proposed book and he remarked that, while there were the words "monomer" and "polymer" for polymerizable monomers, there was no corresponding simple word for "low molecular weight (or number) polymer."

I was familiar with the word “oligarchy,” and after looking up its etymology to be sure of the meaning of its prefix, I suggested to Frank that the word he wanted should be “oligomer,” and I believe he used it in print for the first time in his laboratory manual.



Figure 9. Gaetano Frank D'Alelio (1909-1981) (Courtesy of Smithsonian Institution Archives, Accession 90-105, Science Service Records, Image No. SIA2008-0803).

It has also been pointed out, however, that the German chemist Burckhardt Helferich (1887-1982) had used related, although more specialized, terms prior to 1943 (16). While at the University of Greifswald in 1930, he and his co-authors Eckart Bohn and Siegfried Winkler had used the term *oligosaccharide* to refer to carbohydrates composed of a small number of monosaccharides (i.e., monoses) (65):

For the simpler crystallized sugars that give two or more monoses on hydrolysis, there is so far no name that reflects their position between the monoses and the polysaccharides (so-called for some time now with more general agreement). There is a need for such a name. The name oligo-saccharide is suggested for this.

Later, while at the University of Leipzig in 1940, Helferich and Horst Grunert, had similarly used the term *oligo-peptide* to refer to small sequences of amino acids (66).

Nevertheless, the more general term oligomer is not really seen in the chemical literature until the 1950s. In addition, while the introduction of oligomer has allowed suitable reference to species of limited repeat units, the point of demarcation between an oligomer and a polymer is still an ongoing debate amongst modern polymer chemists.

Conclusions

As can be seen from the above discussion, the word polymer has a long and complicated history, with multiple meanings and connotations over the years. As such, knowledge of its evolution is critical for those attempting to study the history of polymers prior to the mid-20th century. At the same time, it is interesting to see that all of the remaining terms commonly used in polymer science are relatively modern and were all introduced within the last century, all beginning with the introduction of Staudinger's macromolecule.

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