Macromolecular Science Turns 100

by Christine K. Luscombe and Gregory T. Russell

Being 100 years since the birth of macromolecular science, 2020 was meant to be the "Year of Polymers," but instead it turned into the year of the pandemic. Actually the two are not unrelated—most PPE is made of polymer, and without it the health-care response to COVID-19 would have looked completely different and been far more treacherous. But that's another story, one with which the IUPAC Polymer Division is engaging [1]. Here is the story behind the centenary year that wasn't. It all centers on Hermann Staudinger, who changed everything in 1920.

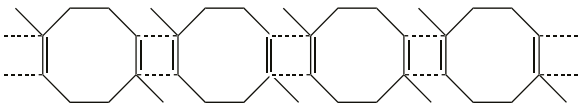
Who was Staudinger and what is the significance of 2020?

Hermann Staudinger circa. 1950.

Hermann Staudinger was a German organic chemist who won the 1953 Nobel Prize in Chemistry. He was born in Worms in 1881 [2-4], where his interest in science began, encouraged by his father, who was a high school teacher and neo-Kantian philosopher! While initially Hermann studied botany at the University of Halle, he quickly shifted his focus to chemistry, progressing via Darmstadt and Munich to obtaining a PhD in organic chemistry in Halle in 1903, where his work on the addition of malonates to unsaturated compounds foreshadowed the interest through which he was to obtain scientific immortality. After Halle he became an assistant to Johannes Thiele at Strasbourg, receiving his habilitation in 1907 for work on ketene chemistry. He then became an assistant professor at Karlsruhe, before succeeding the future Nobel laureate Richard Willstätter at ETH Zürich in 1912. His final move was to Freiburg in 1926, where he remained for the rest of his days. The geography of his life seems well described by the phrase "a river runs through it", for aside from his years as a student, he was always very close to the Upper Rhine.

During the early years of his academic career, Staudinger's research focused on small molecule chemistry, publishing 215 papers and becoming internationally recognized. But starting in 1917 he turned towards rather larger molecules. Specifically, his interest was piqued by rubber, of obvious importance at that difficult time. In the 19th century, polymers were used for commercial purposes but their structure was misunderstood. For example, Charles Goodyear had discovered vulcanization of natural rubber in 1839 to give birth to the rubber industry. By the end of the 19th century, nitrocellulose and celluloid were used as thermoplastics. In 1907, Baekeland developed a phenolic thermoset resin trademarked as Baekelite. These commercial successes occurred without knowledge of the molecular architecture of polymeric materials, and the properties of polymers were described using colloidal theory, where the measured high molecular weights were thought to be caused by the aggregation of small molecules into colloids. An example of the thinking at the time is presented below, which shows a proposed structure for natural rubber, suggested to be composed of dimethylcyclooctadiene units polymerized by self-assembly involving noncovalent interactions between double bonds on neighboring molecules [2].

Staudinger rejected such notions. In 1920, from his base in Zürich (not Freiburg!), he published a paper simply entitled "Über Polymerisation" [6]—next page. This is regarded as marking the birth of macromolecular science, which is why 2020 was so significant. Remarkably, it was not until the eve of this centenary that there was an English translation [7] of the 1920 paper. It makes clear that the celebrated work was really just a discussion piece in which Staudinger presents his hypothesis that polymers are in fact long molecules comprised of units linked together by covalent bonds. As Mühlhaupt observed, "At this early time Staudinger did not present convincing experimental evidence for his hypothesis" [2]. Such was to come two years later, when Staudinger and Fritschi reported hydrogenating the double bonds of natural rubber and showing that it retained its mechanical properties even in the absence of the double bonds, thereby proving that non-covalent interactions between these double bonds (see below) could not be the reason behind the properties of rubber [8]. Furthermore, it is in this 1922 paper that the word *macromolecule* is used for the first time. Thus between these two papers one has the birth of the so-called *macromolecular hypothesis*, which more or less occupied Staudinger for the rest of his life.



Proposed structure of natural rubber by Harries [5].

125. H. Staudinger: Über Polymerisation.

[Mitteilung aus dem Chem. Institut der Eidgen. Techn. Hochschule, Zürich.]

(Eingegangen am 13. März 1920.)

Vor einiger Zeit hat G. Schroeter[1]) interessante Ansichten über die Zusammensetzung von Polymerisationsprodukten, speziell über die Konstitution der polymeren Ketene veröffentlicht. Danach sollen diese Verbindungen Molekülverbindungen darstellen und sollen keine Cyclobutan-Derivate sein, wie früher angenommen wurde[2]); denn diese polymeren Ketene unterscheiden sich nach den Schroeterschen Untersuchungen in wesentlichen Punkten von Cyclobutan-Derivaten, die durch Synthese aus Aceton-dicarbonester-Derivaten zugänglich sind.

Title and opening paragraph of [6] – there was no fancy artwork in those days!

Isn't it obvious?

The macromolecular hypothesis – that of covalent linkages to give genuinely 'macro' molecules – seems so obvious now that it can be hard to grasp that it was enough of a paradigm shift to warrant a Nobel Prize. But consider the famous anecdote about Staudinger being told to forget his "grease chemistry," as well as friendly advice he received from Heinrich Wieland, himself a future Nobel Prize winner [2]: "*Dear colleague, abandon your idea of large molecules, organic molecules with molecular weights exceeding 5000 do not exist. Purify your products such as rubber, they will crystallize and turn out to be low molecular weight compounds.*" These stories show just how radical Staudinger's idea was at the time. While these days it is difficult to imagine how anyone would have rejected the notion of a macromolecule, it is worth noting that concepts of molecules and molecular structures were not well established a centenary ago. In a sense Staudinger should be regarded as the Galileo of macromolecular science—the person who took a revolutionary concept and turned it into a notion so obvious that one wonders how the alternative was ever entertained.

There are a number of curiosities about the 1920 paper. As already mentioned, despite its fame, it was only in 2019 that it was first translated from German into English [7], which in itself suggests just how quickly the central idea passed into accepted, obvious knowledge—few people felt the need to read about it! Similarly, the paper has been cited remarkably little—225 times as of April 2019, elevated to 378 by February 2021 courtesy of a centenary boost from historical interest rather than the scientific content *per se* [9]. These days such citation statistics would barely be sufficient to earn a faculty position, let alone a Nobel Prize! A final curiosity is an irony: as we pass 100 years of the macromolecular hypothesis, supramolecular chemistry looms ever larger on the landscape, it being chemistry that "examines the weaker and reversible non-covalent interactions between molecules" [10]. In other words, supramolecular chemistry involves molecular assemblies exactly of the nature that people thought "normal" macromolecules were pre-Staudinger. Accordingly, there is much debate as to whether or not supramolecular materials are polymers.

How has polymer chemistry evolved over the years?

This question may be answered by considering Nobel Prizes awarded for work in macromolecular science—see table below. It is important to remember that there is a lag time: what is seen on the stage in Stockholm usually reflects what was happening at the research coalface about 20 years earlier. Thus Staudinger's

Year	Winner(s)	Work
1953	Staudinger	"for discoveries in the field of *macromolecular chemistry*"
1963	Ziegler, Natta	"for discoveries in the field of the chemistry and technology of high polymers" (*coordination polymerization*)
1974	Flory	"for his fundamental work, both theoretical and experimental, in the *physical chemistry of macromolecules*"
1991	de Gennes	"for discovering that methods developed for studying *order phenomena* in simple systems can be generalized to more complex forms of matter, in particular to polymers"
2000	Heeger, MacDiarmid, Shirakawa	"for discovery and development of *conductive polymers*"
2002	Fenn, Tanaka, Wüthrich	"for development of methods for identification and structure analyses of macromolecules ... for development of soft desorption ionisation *methods for mass spectrometric analyses of macromolecules*"
2005	Chauvin, Grubbs, Schrock	"for the development of the *metathesis* method in organic synthesis" (in particular polymerization)

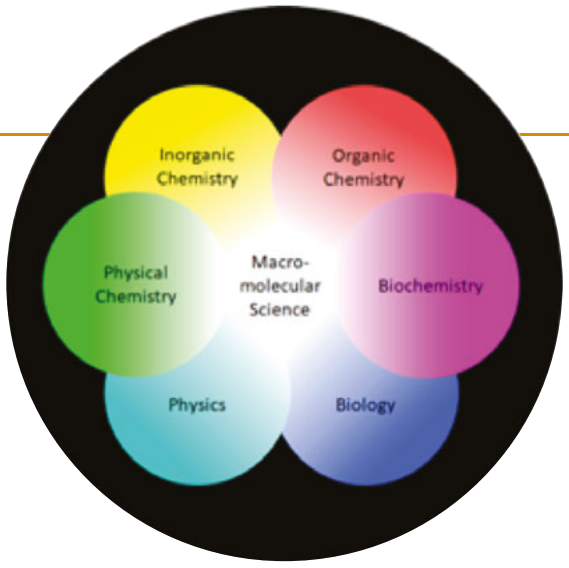
Nobel Prize winners in macromolecular science (all Chemistry [13] apart from Physics [14] in 1991).

prize in 1953 stems from organic chemistry being to the fore in the 1920s and 1930s, with Staudinger and W.H. Carothers (of DuPont) being the leading lights. By the 1940s through to the 1960s, polymer chemistry was largely a branch of physical chemistry, with Paul Flory the dominant figure, along with other giants such as G.V. Schulz, H. Mark and M. Szwarc. Indeed, IUPAC's *Commission on Macromolecules* was formed at this time as a branch of its Physical Chemistry Section [11], and Flory's 1953 textbook [12]—still the most celebrated in polymer science—largely consists of physical chemistry. This trajectory was taken even further in the 1970s, with the soft-matter physics of the dazzling de Gennes and his school taking a lot of the limelight. By the 1980s polymer science was spreading its wings and taking root in many different areas, as reflected in the flurry of Nobel Prizes around the turn of the century: materials chemistry (2000), instrumental chemistry (2002) and organic chemistry (2005) are all represented. Truth be told, macromolecular science has never strayed far from synthetic chemistry, with the Nobel Prize of Ziegler and Natta in the midst of all the above being a good example of this. The current period is certainly one in which the spirit of Staudinger has been recaptured and synthesis is dominant, with figures such as Krzysztof Matyaszewski, Mituso Sawamoto, Graeme Moad, Robert H. Grubbs, Craig Hawker, and Jean Fréchet leading the way. But really, it should be clear that macromolecular science has evolved to be broad and overlaps with all areas of chemistry. Furthermore it is intimately linked to other major scientific disciplines—the image above attempts to capture this [15].

The table on the previous page makes clear that Staudinger initiated a chain of Nobel Prizes being awarded in polymer science (or as Bob Grubbs puts it, the chemistry of the carbon-carbon double bond!) approximately every 10 years. Given that the last award was in 2005, one wonders if another Prize is due? It's a pity that the chance to make it 2020 was missed!

How has IUPAC been involved?

In what would seem to be pure coincidence, IUPAC was founded just one year prior to Staudinger's 1920 paper, so the two will forever celebrate the same landmarks in close succession. But it was not until the late 1940s, with the formation of IUPAC's *Commission on Macromolecules,* that explicit overlap of the two started [11]. In 1952 this body put out its first publication on systemized naming of macromolecules. It introduced, for example, the use of parentheses in source-based polymer names when the monomer consists of more than one word. In recognition of the



Macromolecular science started as organic chemistry but has spread its tentacles into all areas of chemistry and many areas of science. Reproduced with permission from Isr. J. Chem. 2020, 60, 9-19. Copyright 2020 WILEY.

ever expanding importance of polymer chemistry and no doubt via impetus from the Nobel Prizes in 1953 and 1963 (see above), the *Macromolecular Division* of IUPAC was formed in 1967, just shy of the half-centuries of IUPAC and the macromolecular hypothesis. The first Division President was the Czech chemist Otto Wichterle, inventor of soft contact lenses. This formalized what continues to be a very strong and powerful relationship between IUPAC and macromolecular chemistry. For example, the *Commission on Macromolecular Nomenclature* of the Macromolecular Division was established in 1968, and it was immediately into its work, producing a series of major documents during the 1970s that shaped modern polymer language, including defining basic terms and structure-based nomenclature for regular single-strand polymers. The Commission remained prolific in the 1980s, during which were published recommendations relating to stereochemical definitions, terminology for molar masses in polymer science, structure-based nomenclature of inorganic and coordination polymers, and systematization of source-based nomenclature for copolymers. In 1991 the first edition of the Purple Book (the Compendium of Macromolecular Nomenclature) was published. The Division, through what is now known as the *Subcommittee on Polymer Terminology* (SPT), continues to publish regular recommendations that try to keep pace with the ever-increasing complexity of macromolecules being synthesized. This all represents IUPAC playing a vital role in the forward progress of macromolecular science.

The *Polymer Division* (PD), as Div. IV has been known since 2004, currently consists of four subcommittees: SPT, the Subcommittee on Modeling of Polymerization Kinetics and Processes, the Subcommittee on Polymer Education (SPEd), and the Subcommittee on Structure

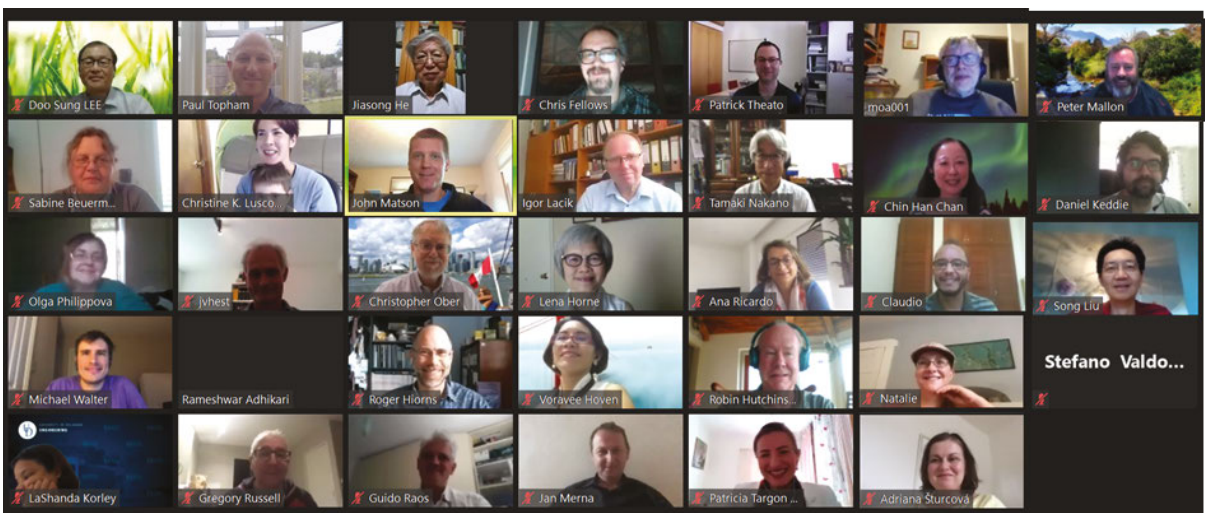
and Properties of Commercial Polymers. SPT is a very active group that develops terminological rules and definitions related to polymers. It also works closely with IUPAC Div. VIII (Chemical Nomenclature and Structure Representation) to provide recommendations on polymer nomenclature. The Subcommittee on Modeling and Polymerization Kinetics and Processes performs studies that aim to create uniform standards related to polymerization kinetics. While literature reports kinetic parameters related to polymerizations, these values frequently differ from group to group because of different assumptions that have been made. The Subcommittee addresses the situation through international collaboration. SPEd tries to provide support toward recurrent educational activities for students in underdeveloped countries. It organizes special symposia at the biannual MACRO conferences where speakers can share best practices on polymer education in their respective countries. We are also in the process of creating a freely available "syllabus" that provides guidance on the core chemistry content that should be covered in an undergraduate course on polymer science, together with sample questions illustrating each of the topics so that those who do not have easy access to textbooks can still learn basic polymer science. The Subcommittee on Structure and Properties of Commercial Polymers dedicates its work toward obtaining and reporting accurate information about mechanical properties of commercial polymers.

As we enter the 2nd century of macromolecular science, the PD remains extremely active, arguably the most active within IUPAC given that it runs around 30 projects at any one time [16]—see the picture below for evidence of this activity!

How has the Staudinger centenary been recognized?

With 2019 being the International Year of the Periodic Table (not to mention the centenary of IUPAC!), it was not feasible to seek a UNESCO designation of "Year of Polymers" in 2020. Arguably this is in accord with the largely understated role of polymers in the modern world—it would only be if all polymers were removed that most people would realize just how ubiquitous and indispensable they have become in everyday life. But even without official recognition, there were still considerable plans for quiet acknowledgement of the Staudinger centenary within the scientific community. As one would expect, many of these events have had to be postponed due to the pandemic. For example, the ACS Spring 2020 National Meeting, entitled "Macromolecular Chemistry: The Second Century," was cancelled at the time and is now being held online over 5–30 April 2021, with live events 5–16 April. This time period is longer than the usual ACS meeting as each day will be much shorter so as to accommodate multiple time zones in this virtual era. A special ACS Division of Polymer Chemistry symposium, "Macromolecular Science at the Dawn of its Second Century," is being co-organized by Timothy Lodge, Krzystof Matyjaszewski and Peter Zarras [17].

Our IUPAC Polymer Division flagship conference, the IUPAC World Polymer Congress, a.k.a. IUPAC-MACRO meeting, is the largest biennial international multi-symposium conference dedicated to all aspects of polymer science and engineering. The 48th World Polymer Congress (MACRO 2020) had been scheduled for 5–9 July 2020 at Jeju Island, South Korea with PD Titular Member Doo Sung Lee as Congress Chair.



Screenshot of one of many Zoom meetings—including both of your authors!—that was held for SPT & PD in July 2020.

This has now been rescheduled to 16–20 May 2021, rebranded as MACRO 2020+, and will be a hybrid event where many scientists in South Korea are expected to attend in person while most international participants are expected to participate virtually [18].

Publishers have also had special initiatives to commemorate the centenary. For example, the Editor-in-Chief of the ACS journal *Macromolecules*, Marc Hillmyer, curated a series of editorials from leading polymer scientists to comment on *Macromolecules* papers that they thought had been particularly impactful or influential [19]. The editorials reflected the broad range of polymer science, highlighting work on block copolymers, discovery of RAFT, twisted crystals, kinetics of ATRP, random ionomers, non-radiative energy transfer studies of miscibility in polymer blends, hydrogels, branched polymers, syndiotactic polystyrene, spinodal decomposition, organocatalysis, polymer membranes, theory, living cationic and radical polymerizations, glass transition, polymer mechanochemistry, non-covalent interactions, polyion complexes, and tensile deformation mechanism in semicrystalline polymers. The breadth of these contributions highlights just how far polymer science has come in 100 years.

Both *Macromolecular Rapid Communications* and *Macromolecular Chemistry and Physics*, the latter founded by Hermann Staudinger, commemorated the event by having double special issues that were made freely available for the entire year. These special issues contained articles that represented various aspects of modern macromolecular chemistry ranging from synthesis to characterization and application.

What does the future hold?

As the new century for macromolecular sciences begins and we look to the future, the editors and advisory board members of *Macromolecular Chemistry and Physics* published a paper [20] sharing their views on the future of polymer science that addressed new synthetic methods, polymers with advanced properties and function, as well as sustainability. The IUPAC Polymer Division also wrote an essay reflecting upon the centenary [15], writing about the need to develop polymers that can ameliorate today's pressing problems related to climate emergency, sustainable development, and the preservation of the environment and human health. Given the ability of polymers to touch upon so many aspects of life, polymer science will remain a vigorous field that will attract scientists from all walks including but not limited to chemists, physicists, engineers, and those from the biological sciences. IUPAC can play a central in this regard by providing effective ways to communicate, attracting young scientists, and promoting a lively and intellectually exciting research area.

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Polymer Science Language to Publics through Arts

SciArts on occasion of 100th anniversary of understanding of polymer structure by Hermann Staudinger.

by Jan Merna, and Jan Pražan

SciArt Exhibition by http://janprazan.com and @Merna_ group endorsed by @IUPAC and @VSCHT developed in collaboration with @IUPACPolymer and celebrating Macromolecules Centenary and Staudinger opened on 30 Nov 2020 at UCTPrague under the patronage of UCT rector prof. Dr. RNDr. Pavel Matějka and IUPAC Polymer Division vice-president Dr. Igor Lacík.

Polymers are all around us since the evolution of life on Earth. Polymers made by Nature (natural polymers) are key for Earth life: nucleic acids (polynucleotides), proteins (polypetides) and polysacharides (like cellulose). We also use some of them in technical applications *e.g.* natural rubber (polyisoprene). Polymers made by men (synthetic polymers) only bit more than hundred years ago—(Bakelite 1909), become major class of materials after WWII and ensures quality of our lives.

People use currently ~400 millions tons of synthetic polymers per year worldwide, which by volume is more than the production of steel, making polymers No 1 material of today. Extensive range of polymers (plastics and rubbers) applications helps to save, harvest and store energy, protect food, clean and save water, protect other materials from corrosion (coatings) and save lives in biomedical applications (drug delivery systems, soft tissue implants) or in personal protective equipment (gloves and masks in fight against bacteria a viruses).

In 2020 we celebrate 100 years from Hermann Staudinger recognition of polymer structure, i.e. that these compounds are composed of giant molecules- macromolecules.

This *SciArts* projects aims to celebrate the anniversary by introducing selected basic terms in polymer science into broader chemical community and to publics. These terms are defined by scholars associated within IUPAC since 1949, when Czechoslovak chemist Otto Wichterle became the first president of IUPAC Polymer Division. IUPAC is major authority in defining of nomenclature and terminology—chemical language.

IUPAC terms are widely accepted and used by industry, in defining standards (ISO, DIN) and in legal documents created by governments, where clarity in communication between experts is essential to protect

intellectual property (patents) and avoid confusion which may lead to accidents with serious consequences (e.g. due to mistaken conversion of imperial units to metric systems orbital satellite was damaged causing billion dollar losses). IUPAC acts as global organization and creates partnerships with organization like UNESCO or OPCW, to promote access to chemistry education and sustainable chemical technologies.

Chemical language is highly precise and by principle abstract or difficult to understand on the first sight. The intention of this project is to familiarize selected principal terms of Polymer Science to broader chemical community and lay publics by their reformulation to common langue. To attract the initial interest of eager for knowledge readers and to stimulate taking the challenge to understand these abstract definitions, the form of abstract Art is used.

See https://pol.vscht.cz/sciart for more.

Jan Merna (www.merna.eu) is from the University of Chemistry and Technology Prague and serves on the IUPAC Polymer Division. Jan Pražan's work can be viewed at janprazan.com.