

Polymers: a historical perspective

Robert Burford, FRSN

Emeritus Professor, School of Chemical Engineering, UNSW Sydney

Email: r.burford@unsw.edu.au

Abstract

This commissioned paper outlines the emergence of new forms of synthetics and plastics as our understanding of polymer chemistry has advanced.

Synopsis

Polymers have been ubiquitous since simple gaseous molecules began to form life-giving organic structures many millions of years ago. Today, we rely upon proteins comprising twenty amino acids, as well as DNA and RNA with many fewer nucleic acids. Similarly, many fibres and plants comprise carbohydrate polymers: we and other animals use these and protein-based polymers for our diet. Hence, organic earth's surface has an enormous diversity of naturally occurring polymers, sometimes called macromolecules.

Today, these continue to feed and clothe us, and much more, but the beginning of man-made materials might be considered to be the transition from entirely natural materials to either substitutes or modified macromolecules. This period might be classified as the “precursor age” of synthetic polymers. It originates from the early 19th century and is an exciting period of amateur science, entrepreneurship and considerable skulduggery. A theme that continues today is the replacement of conventional materials with improved or cheaper substitutes.

The second period relates to entirely synthetic polymers which have as raw materials small molecules that arise from processing of coal or oil. Aromatic compounds such as

phenols and styrene are “polymerised” to form thermosets,¹ including phenol formaldehyde “Bakelite” thermosets, but are also present in thermoplastics² including polystyrene and related materials such as styrene acrylonitrile (SAN) and ABS.³ The manufacture of Bakelite is often viewed as the birth of the synthetic polymer industry. The enormous growth both in diversity and volume of thermoplastics is a feature of the 20th century, dismissively called the “plastics age.” Again, important but sometimes serendipitous discoveries are a feature of this period, but the associated large-scale production introduced multinational corporations originating mainly in Europe, the US and Japan.

From the late 1930s, polymers based on ethylene and propylene, gases formed from “cracking”⁴ of naphtha or ethane/propane, have become commonplace. Their versatility and low cost have led to packaging and other single-use modes, which, in the absence of careful social behaviour, contribute markedly to unacceptable waste. This period of commoditisation is characterised by a transition from gleeful acceptance from the 1940s to the '60s to misgivings and apprehension in the 21st century.

³ Acrylonitrile butadiene styrene

The First Age of Polymers

The beginnings of human exploitation of natural polymers might date from the use of timber, including fire, many millennia ago. The use of natural fibres including various wools is another prehistoric example.

More recently, the creative application of an isolated polymer might start from the recreational use of coagulated rubber from *Hevea brasiliensis* by the Aztecs and others in Mesoamerica, as observed by Europeans in the 15th and 16th centuries.

The history of rubber is fascinating, as it combines great wealth with slavery, not just in South America, but in South East Asia and in Africa. This was convincingly broadcast by the late Professor Peter Mason (1979).

It is also documented extensively, for example in Stahl (1984) and Fenichell (1996). This latter text provides excellent case studies that are drawn upon elsewhere in this paper.

Here the emphasis is placed upon the deliberate manufacture of either new but modified materials that can be processed to take on desired forms, or, later, entirely new synthetic polymers (predominating in the Second Age). In many ways, however, synthetic polymers cannot match natural materials and this remains an aspiration.

The industrial age can be characterised not only by the harnessing of energy via the steam engine, but also the mass conversion of raw materials into refined or intricately produced products such as woven cotton and woollen garments. An examination of any technology museum will reveal a multiplicity of complex machines designed to value-add starting materials into consumer articles.

In this environment the opportunity for entrepreneurial inventors to make and sell new and desirable articles was compelling, and examples described below either replace scarce natural substances, or introduce new materials with novel properties. In this age, much work was conducted by energetic and creative, but somewhat uneducated, amateurs.

Although the primary focus in this paper is on plastics and to a lesser extent thermo-setting materials, the exploitation of natural rubber illustrates several common themes.

Natural rubber was available from South America in the 18th century, and those controlling the plantations and essentially slave labour were becoming enviably wealthy. Opera houses, trams, electricity and much else was built in the Amazon beside a decimated native population. Saplings of these “rubber trees” were smuggled from South America and the survivors propagated in Kew Gardens. These in turn became the forebears of the globally distributed rubber plantations: pest species replacing native trees.

The next chapter was the need to make synthetic rubber to overcome the difficulties in sea transport of natural rubber to the UK and the US. The project was one of the underappreciated technical achievements of WW2. When I worked at the Australian Synthetic Rubber Company in the 1970s, secret codes both for raw materials and products, a legacy of the war, were still being used!

The transformation from a soft flowing and impure material to one that might be more valuable and useful was beset with technical challenges. Such challenges had to be overcome with a combination of mechanical changes as well as chemical modifications.

Natural rubber comprises *cis* poly isoprene, with (as we now know) a molecular weight of about 10^6 atomic mass units. Such a high molecular weight makes the material hard to process (“tough as boots”) and with poor adhesion qualities, which limits its further deployment. This was addressed using a crude masticator known as the Hancock “pickle,” akin to a torture instrument with multiple arrays of intermeshing teeth. The modified rubber was a marked improvement on the naphtha-dissolved rubber used by Charles Macintosh in the 1820s to waterproof garments.

Soon after, Charles Goodyear sought to improve the properties of “India Rubber” (named from the Caribbean Indies and from the ability of the polymer to erase pencil markings) with essentially no knowledge of chemistry at all. He tried numerous experiments with little success over more than a decade, with Goodyear in and out of debtor’s courts and prisons. It was however the entirely accidental exposure of rubber latex to spilt sulphur on a stove that led to crosslinking, or vulcanisation, a technology still conducted today. Despite his 1844 patent, Goodyear died impoverished. This is a representative example of an important and enduring but accidental discovery.

A second important discovery was the modification of cellulose ester to render the material both transparent and malleable. The origins are fascinating and relevant. The Victorian era was largely decorated with ivory: piano keys, hairbrushes, knife handles and much else. Particularly challenging items were billiard balls, those having the best “click” made from the middle, clear grained section of Ceylonese elephants’ tusks. Such was the supply and demand problem that a reward of \$10,000 in gold was offered

for invention of a credible substitute. Gun cotton (cellulose nitrate) was already known. Admixtures in solvent (collodion) were developed by John Hyatt in the 1860s to encase wood pulp and bone mixtures. Ultimately a suitable substitute was realised and the prototype remains (although the prize was not awarded), but Hyatt’s main discovery was to follow.

This was the addition of camphor to nitrocellulose to make the material malleable, and millable into a thin coherent mass. This product — celluloid — patented in 1869, became the key product of the American Celanese Corporation, and celluloid formed the basis of photographic film technology and greatly affected both the photographic and movie industries. Hyatt himself left to begin the hotel company that bears his name to the present time.

In assisting the Powerhouse Museum conservation team in Sydney, I’ve had the opportunity to learn of the polymers available from about 1880 to the 1940s (from the Penfold collection,⁵ amassed on a global tour) and to the present time. A surprisingly small number of polymer families existed, but in a diversity of manifestations. Many forms of ivory substitutes were available, sometimes with casein (milk protein) derived polymers. Celluloid materials, either cellulose nitrate or acetate, were also well represented. The former are dangerously unstable, whilst the acetate also loses acetic acid to leave brittle cellulosic residues. This is a major concern

⁵ During the period 1929–55, the Powerhouse Museum director Arthur de Raymond Penfold became fascinated by plastics, the new material, and stated: “The way they stirred the imagination of the public is as much a marvel as the wizardry of the modern organic chemist who gave us the great invention.” (Taylor 2010)

for the movie industry, with many endangered cellulose acetate films still at risk.

Another extensively represented polymer is Bakelite, phenol formaldehyde often filled with wood flour or fibres: the default material for telephones, piano rolls and much else. The Powerhouse Museum and similar institutions have vast collections of items made from Bakelite and similar thermosets. This historic material is notably still used for saucepan lids and handles, and allied thermosets are used in modern electronics including mobile phones. Hence even ancient polymers can be enduring.

Whilst celluloid became enormously successful through Eastman's Kodak business, a truly synthetic material was soon to emerge. Leo Baekeland⁶ had initially developed a superior film⁷ for Eastman for which he was extravagantly rewarded. Although the reaction between phenol and formaldehyde was known by Adolf Bayer in 1872, and casein, made from milk protein and formaldehyde, had also been invented in 1899 and is still used for buttons, the production of a valuable insulating material made using phenol and formaldehyde (Bakelite) was delayed until 1907.

Baekeland used high temperatures and pressure to overcome volatile gas formation that had rendered prior materials unsuitable. This is another example of persistence and sometimes counter-intuitive ideas that extend beyond the basic chemistry leading to successful invention. Similar reactors for these and Novolac⁸ resins are still provided

in quite recent textbooks, and kettles were employed in Australia until the 1970s.

Although liquid precursor mixtures were also made that could fill moulds, once heat and pressure were applied the solid made was permanent. Such a "thermoset" remains resistant to heat and stress, and Bakelite represents the first entirely synthetic polymer with no naturally occurring precursor. The synthetic plastic age had begun.

Early applications included electrical insulators (which continued being made after WW2), billiard balls (replacing celluloid) and lawn/carpet bowls (familiar to older readers!). In contrast to many earlier inventors, Baekeland was well educated and positioned to exploit and improve upon many other discoveries. Although not impoverished, he appears to have died lonely and eccentric.

The period from 1910 to the 1930s was an exciting time for the industrial discovery and manufacture of new polymers, including linear polymers such as polyvinyl chloride (PVC) or "vinyl" in 1926 and polystyrene in 1931 that could be truly plastic, that is, made into a fluid and be re-mouldable. Both these polymer types had antecedents, with for example polystyrene being known as the non-pungent solid form of styrene and called "metastyrene."

Nicholson's 1997 text explains that the term "polymerisation" was coined in 1870 to address the transformation of a molecule with one physical form to another quite different one but with the same empirical formula (polystyrene from styrene in 1866). This was done in the absence of polymerisation theory as known today.

It was also a fascinating time from an academic and theoretical perspective as the concept of what the molecular structure

⁶ The Belgian-American chemist Leo Baekeland developed Bakelite in Yonkers, New York, in 1907. The first issue of *Plastics* magazine, October 1925, featured Bakelite on its cover.

⁷ Velox photographic paper, in 1893.

⁸ Synthetic shellac.

of a polymer entailed was fiercely debated. Whilst Emil Fischer had carefully synthesised proteins with molecular weights up to 4200, according to Stahl's paper he did not formulate a detailed structure. There were other opinions supporting high molecular weight molecules, particularly with synthetic polyisoprene, but the conventional wisdom, which linked synthetic polymers with many naturally occurring systems, was of colloidal aggregates.

It was Hermann Staudinger who convincingly invented the term and concept of "macromolecules" in 1922, for which he was awarded the Nobel Prize in 1953, rather than the established associative model. He published papers starting from 1920 which remain rigorous today, relating initially to polystyrene and polyoxymethylene and then to many others.⁹ Again according to Stahl's record, Herman Mark, then an X-ray crystallographer and subsequently a pioneer in the forefront of polymer chemistry, mediated between the protagonists.

Such intense debate is not unusual. The availability of new information by neutron scattering added fire to the debate about chain alignment in crystallisable polymers, for which some supporters came to blows at a conference in the early 1980s! A key factor in science and medical Nobel Prize success is the unexpected nature of the research.

The increasing awareness and adoption of the macromolecular concept aligns well with the amazing research by Wallace Carothers at DuPont. Many polymer discoveries are accidental, not only by amateur chemists but also by "the prepared minds" who see the value of the unexpected, including quite recent findings. Hence, the discoveries of

PVC in 1926, polyethylene in 1933, Teflon in 1938, metallocene catalysts and conducting polymers (including polyaniline) all entail lucky breakthroughs. The inspiring aspect of the polycondensation activities of Carothers was the intentional and systemic nature of that creative chemistry.

Carothers was associated with the development of polychloroprene in 1932 (DuPont trade name Neoprene) which has many properties superior to natural rubber, but Carothers is best known for polycondensation polymers, including polyesters and polyamides and nylon. Many of the fascinating commercial aspects of the latter are given in Chapter 6, "Nylon" in Fenichell (1996, pp. 19–22).

A concise (8-page) and authoritative online document from the American Chemical Society (2000)¹⁰ is also recommended. The ACS stated in 2000 that about half the industrial chemists in the US were working in polymer chemistry.

With hindsight it seems simple to take well-known reactions between dibasic¹¹ and diacid small molecules to make amides and esters. Indeed I used this to illustrate to undergraduate students, (with mixed success), the systematic nature of chemistry. A simple monoester reaction (ethyl acetate), followed by more complex reactions and then a di-ester reaction to form the polyethylene terephthate (PET, 1941) used in soft drink bottles followed. The di-amide reaction to give the DuPont nylon followed by 1935.

⁹ See "The Foundation of Polymer Science by Hermann Staudinger (1881-1965)"

¹⁰ Commemorative Booklet—The Establishment of Modern Polymer Science By Wallace H. Carothers (PDF)

¹¹ *Dibasic*: containing two carboxylic acid –COOH groups.

A key challenge was to increase molecular weight so that chains can entangle and not only offer adequate mechanical properties, but also to form fibres, and this requires extremely high conversion. According to the ACS article:

By the time DuPont started building its first plant in Seaford, Delaware, in 1938, more than 230 chemists and engineers had worked on the project at one time or another at a cost of \$27 million.

Both polyesters and polyamides remain successful moulded plastics and fibres, with PET in particular now a large volume, cheap commodity polymer.

Whilst nylon was indeed an amazing polymer, with 800,000 pairs of stockings sold on 15 May 1940 alone, and many parachutes saving lives when the US entered WW2 in 1941, there are other more sobering aspects. Carothers himself committed suicide in 1937, a year after his marriage. And to some extent the stockings were promoted on a lie, that they, unlike silk, were claimed not to run.

The Second Age of Polymers

If the Penfold collection of polymers is analysed, it becomes clear that only a small fraction in volume of those we are familiar with now are represented. During the 1940s, perusal of the newly published *Australian Plastics Journal* reveals from both papers and advertisements that available plastics were confined to cellulose, Perspex (poly methyl methacrylate, 1934), polystyrene, polyvinyl chloride and newly available polythene in 1933. The latter was by today's measure extremely expensive, a plastic bag costing about a day's salary. Synthetic rubbers and many thermosetting resins including urea and melamine formaldehyde compounds

were used in large volumes, and were also employed as laminates and coatings.

From the 1940s to the 1970s a very substantial expansion in industrial polymer manufacture occurred globally, including in Australia. PVC, polystyrene, synthetic rubber, polyethylene (PE) and polypropylene (PP, 1954) were all made, with several Australian plants being in the vanguard. The slurry process used by Shell for PP in Rosehill, NSW, and the Ziegler process for polybutadiene (invented in 1928) by the Australian Synthetic Rubber Co. were some of the first globally.

Today PE and PP are ubiquitous and represent well over half the volume of polymers made globally. This reflects the enormous growth in polymers based on ethylene and propylene, both gaseous intermediates, either from cracking of naphtha (a kerosene-like fraction from oil refining) or dehydrogenation cracking of saturated natural hydrocarbon gases.

Their manufacture, however, has been challenging and adventurous. Low-density (LDPE) or branched polyethylene was and remains the result of extremely high pressure equipment that only became possible in the 1930s. When ICI scientists somewhat randomly explored how a mixture of benzaldehyde and ethylene would behave, they carefully noted that the ethylene hadn't magically disappeared but had formed a thin coating: polyethylene (or polythene); the beginnings in 1933 of a strategically important and subsequently lucrative industry.

Accounts by those involved vary somewhat, reducing the chance element, but remain vital historical records; for example, Raff & Allison (1956, Chapter 1) and McMillan (1979, pp. 10–14). Replicate experiments failed until the trace of an oxi-

dant in the benzaldehyde was realised to be the key to success in making LDPE. Again multiple fortuitous accidental incidents came into play.

This material was a valuable for it represented the first flexible insulator and was initially employed for submarine cables, but more crucially for radar.¹²

LDPE remains a significant global material today, despite its low modulus and melting point. It has a “softness” and transparency that makes it “user friendly,” and it continues to have an important place in packaging, where toughness can be equally important. LDPE, along with other polyolefins, is used extensively for single-use applications and is heavily represented in plastics waste streams.

A second and dramatic development was the discovery and use of catalysts to make both a new family of polyethenes (Karl Ziegler in 1953) with linear chains (high-density polyethylene HDPE) and polypropylenes (Giulio Natta) where the stereoregularity about each second backbone carbon is controlled.¹³ The history of this is detailed in McMillan’s book and much has been recorded in standard polymer science textbooks, in the Nobel Prize of 1963 Records, and in technical papers and magazines. HDPE and isotactic polypropylene comprise about half the volume of all polymers, reflecting their excellent mechanical and thermal properties and low cost. Their uses extend beyond single-use packaging to strong containers, hot water jugs, casings for irons, and, now, banknotes in many countries.

¹² During WW2 it was a state secret.

¹³ In 1963 Ziegler and Natta were awarded the Nobel Prize in Chemistry for their discoveries in the science and technology of polymers.

Their low density (less than water, even in bulk form) and high durability, especially when stabilised, contributes to their being a commonly found part of the waste stream both on land and in water.

It is perhaps difficult to believe the excitement and easy adoption of plastics in the 1950s and 1960s. However, conventional precursors made from ceramics and glass, as well as metals, were often heavy, brittle or liable to rust. There was also a fascination with the new and synthetic, and plastics did not have the connotations that they have today. Although the scene where Dustin Hoffman is advised, “I have only one word, Plastics” in the 1967 movie *The Graduate* might be viewed as somewhat cynical or ironic, it possibly just reflects a small turning point from popular consumer embrace.

Although research in biological macromolecules was being undertaken in Australian universities in the 1950s, synthetic polymers became a focus from the 1960s, with the establishment for example of the Polymer Division of the Royal Australian Chemical Institute and their annual Australian Polymer Symposia. These have not only attracted many famous international authorities, but also showcased top Australian academics, several becoming leading figures in subjects from emulsion polymerisation to newer types of synthesis (for example, RAFT, reversible addition-fragmentation chain transfer polymerisation) and much else.

CSIRO has had a very strong impact, examples being the shrink-proofing of wool using nanothickness coatings of polyurethane (invented in the 1930s), and the introduction of polymer banknotes in 1988.

Incidentally, Fenichel’s text (1996, p. 28) mentions that the Swiss editor of *Annalen*

der Physik und Chemie, J.C. Poggendorf, stated in 1846 in relation to nitrocellulose:

Your glass-like paper is splendid. I hope you can make it thick enough to use for window panes ... Might it not also make a good replacement for ordinary paper for bank notes?

The Hawke Government brought into being Cooperative Research Centres in 1991 to encourage a combination of research providers to assist Australian industry. The CRC for Polymers undertook many demanding challenges, ranging from agrifilms that degraded in a controlled way, to cables that endure fires.¹⁴

The Third Age: Is The Honeymoon Over?

The low-cost and continually improving properties of polymers, combined with growing affluence and increasing population, have all contributed to seeing an enormous volume of discarded polymer waste. Such outcomes should come as no surprise. As early as 1944, Fleck wrote:

Plastics have a very definite and very useful future ahead of them, but undesirable publicity and wrong design can blast that career.

More recently, in a prophetic 1989 address, Dr A. MacLachlan, then Senior V-P, Technology at Du Pont, stated:

One of the most important challenges for the future of the polymer industry is refining the processes used to make and form polymers and the methods used to dispose of them. Whilst it has been estimated that only 8% of the waste generated in the United States is synthetic polymers, their durability and visibility magnify the

problem in the eyes of the public. Attitudes towards plastic products are becoming more negative. This problem must be addressed. New technologies to minimize and recycle waste must be developed

If we do not have this mindset, we may find more and more environmental roadblocks appearing. In other words, we have to move from being problem creators to problem solvers. To the scientific community these are intriguing challenges. [MacLachlan, 1990].

The annual volume of plastics produced overtook all metals and glass several decades ago and continues to increase globally (although manufacturing has declined in Australia). High-volume, low-cost polymers continue to provide many solutions to societal challenges, from cataract lenses to lighter-weight motor vehicles and aircraft. Perhaps the affordability of many polymers has made them the subject of individual and industrial carelessness. A concise and thoughtful commentary was given by Paul Moritz in 2019.

Such waste issues have come to the forefront of politicians, media and the public, and already some remedies are emerging. Fully recyclable PET bottles are now available for beverages, and trends to thinner packaging are evident. However, much needs to be done, as identified by the Australian Packaging Covenant, including changes in public and corporate values. Clever technical solutions are inevitable, and in Australia this is already being encouraged by a Cooperative Research Centre for Plastics Recycling. Changes in social behaviour and a changing economic agenda both need consideration, and will take time.

¹⁴ Andradý & Neal (2009) paint a similar picture [Ed.]

References

- American Chemical Society, Division of the History of Chemistry and The Office of Communications (1999), *The Foundation of Polymer Science by Hermann Staudinger (1881–1965)*, Freiburg, Baden-Württemberg, ACS-GDCh.
- American Chemical Society, Division of the History of Chemistry and The Office of Communications (2000), *Commemorative Booklet—The Establishment of Modern Polymer Science By Wallace H. Carothers*, Wilmington, Delaware, ACS.
- Andrady, Anthony L., and Mike A. Neal (2009), “Applications and societal benefits of plastics,” *Philos Trans R Soc Lond B Biol Sci.* Jul 27; 364(1526): 1977–1984.
- Fenichell, Stephen (1996), *Plastic: The Making of a Synthetic Century*, HarperBusiness.
- Fleck, H. R. (1944), *Whither Plastics? The Possible Uses of Plastics in Industry Science and Art*, English Universities Press.
- MacLachlan, A. (1990), “Polymers: an industrial perspective,” *Chemtech*, 20, 590.
- McMillan, Frank M. (1979), *The Chain Straighteners: fruitful innovation, the discovery of linear and stereoregular synthetic polymers*, Macmillan Press, London.
- Mason, Peter (1979), *Cauchu, the weeping wood: a history of rubber*. ABC, Sydney.
- Moritz, Paul (2019), “Perhaps people, not plastics, are the problem,” *Chemistry in Australia*, Sept./Oct.
- Nicholson, J. W. (1997), *The Chemistry of Polymers*, 2nd ed., Royal Society of Chemistry, London.
- Raff, R. A. V., and J. B. Allison (1956), *Polyethylene*, Interscience, New York.
- Stahl, G. Allen (1984), “Development of a modern polymer theory.” *Chemtech*, 493-4 (August).
- Taylor, Erika (2010), *Conservator’s Corner: Investigating our plastics collection.* <https://maas.museum/inside-the-collection/2010/04/14/conservators-corner-investigating-our-plastics-collection-2/>

