Wallace Hume Carothers and the Birth of Rational Polymer Synthesis

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Wallace Hume Carothers holds a place of pride amongst the pantheons of twentieth-century chemists who transformed our way of thinking, and brought an entirely new perspective to a branch of science. Polymer science flourished in the years after Carothers as never before, and led to the creation of a new industry – vibrant, useful, and exciting. The greatness of Carothers lies in the profound, yet simple questions he asked, and the clarity and definitiveness with which he provided the answers. In a short working span of eleven years, he left behind an incredible legacy of achievements which ordinary mortals cannot even dream of accomplishing in several lifetimes. This article chronicles the life and times of Wallace Carothers, the men and the institutions that inspired him, his seminal contributions to polymer chemistry; the mood of melancholy that permeated his persona and which ultimately cost him his life.

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Wallace Carothers occupies a unique position in the history of chemistry, especially, polymer chemistry. His life was characterized by extraordinary intellect and prescience, shaped by a combination of people, environment, and circumstances. His personality remains an enigma even today; yet his monumental contributions have left an indelible mark on the science of large molecules [1]. It is often stated that eras are marked by certain cataclysmic events in history. The history of polymer science is marked by a period before and after Carothers. He laid the foundations of knowledge, both conceptual and practical, that led to the explosive growth of synthetic polymers – a class of man-made materials that were born in the early forties.

Keywords
Polymer science, polycondensation, polyesterifcation, polyesters, polyamides, nylons .

Wallace Hume Carothers was born on April 27, 1896, in the

Figure 1. Wallace Hume Carothers

Figure 2. Carothers in his laboratory.

small town of Burlington, Iowa, and spent his early years in Des Moines, Iowa. He attended a small community college in Tarkio, Missouri and took to chemistry. Influenced by his teacher, Dr Arthur Pardee, he proceeded to the University of Illinois, Urbana-Champaign in 1920 to pursue a higher degree in chemistry. Carothers was under severe financial stress, and the stipend paid by the University of Illinois was clearly insufficient. So he was tempted by the offer made by his former teacher, Dr Pardee (who had by then moved to the University of South Dakota) to join the University as an Instructor on a salary of US$ 2000 per year. For Carothers, this was a princely sum; so he made the move to the North Dakota University immediately after obtaining his Master's degree. It was here that Carothers showed his first flash of genius as an independent thinker [2].

To understand this period in the history of chemistry, we need to make a short digression.

Organic chemistry, at the turn of twentieth century was essentially a preparative science. Organic chemists were enamoured by their ability to synthesise diverse structures that were previously found only in Nature. Organic chemists deduced the structure of compounds based on synthetic steps sequentially performed on a molecule. However, they were neither interested nor worried about how the transformations took place in the first instance.

Physical chemistry on the contrary, was born at the beginning of the 1900s, and was defined narrowly as problems of dilute solutions and the study of chemical processes. Nernst, Ostwald, Arrhenius, and Van't Hoff dominated the field. The discipline was born out of a desire to confront the dominance of organic chemists of the day, and as an antithesis to organic chemistry, which dealt only with composition and structure. The objective of physical chemists was to study 'the science' behind 'the arrow' – the processes that determine chemical change. The goal was to shift chemistry from mere 'taxonomy' to 'analysis'. However, physical chemists rejected 'atomism', and any talk of atoms and molecules was almost heretic.

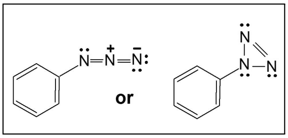

Figure 3. Linear *vs.* ring structure of diazobenzene-imide.

A landmark event occurred one hundred years ago when a seminal paper was submitted to the *Journal of American Chemical Society*. This paper changed the discipline forever. The researcher who wrote this paper simply entitled, "Atoms and Molecules", was Gilbert Newton Lewis and the paper appeared in volume 38, p.762, April 1916 issue of *JACS*. In this paper, Lewis enunciated the principle of a covalent bond, formed by sharing of a pair of electrons, and introduced the 'Lewis dot structure'. In one master stroke, Lewis's concept of a chemical bond united two branches of chemistry, namely, organic and inorganic, which were considered two distinct disciplines until then [3].

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Carothers in 1920, was fascinated by the concepts proposed by G N Lewis. His first foray as an independent researcher was to establish the chemical structure of diazobenzene-imide, a compound prepared by Emil Fischer in 1878. He established that the physical properties of diazobenzene-imide were similar to phenyl isocyanate. Based on this he concluded that diazobenzene-imide had a linear structure, and using Lewis's notation assigned the electronic structure (*Figure* 3). This resulted in his first scientific paper [4].

For reasons we still do not know, Carothers decided to return back to University of Illinois to pursue his doctoral degree under the supervision of the legendary Professor Roger Adams. One reason could be that teaching did not excite him. Records show that he was "careful and systematic, not brilliant" as a teacher. Dr Pardee, his mentor stated that he was not "interested in people" [5]. Carothers dreamed of his own private laboratory in New York, Berlin, Vienna or Paris, where he could pursue and test his ideas.

However, his return to Illinois turned out to be a propitious event. Professor Adams was to have a lasting influence on the scientific

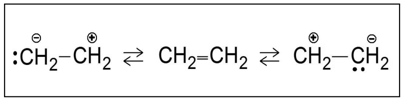

Figure 4. Lewis dot structure of ethylene.

Carothers attempted to provide an electronic structure to the simplest of unsaturated molecule – ethylene

career and personal life of Carothers. Adams asked Carothers to extend the important discovery that he had accidentally made – a unique platinum catalyst that was capable of hydrogenating olefins (called the Adams catalyst). Although he diligently pursued this work, he was clearly not too interested, since it lacked for him, any scientific rigour and was largely empirical. In his spare time, he continued his deep study of Lewis's theories and wrote a paper entitled, "The Double Bond" which appeared in 1924 [6]. He attempted to provide an electronic structure to the simplest of unsaturated molecules – ethylene (*Figure* 4). The proposal that electrons were polarized in ethylene was based on the chemical reactivity of double bonds, which organic chemists exploited. Carothers was attempting to reconcile chemical reactivity with the emerging concepts of the electronic structure of organic molecules. Carothers depiction of ethylene was certainly not right. However, we now know that a double bond in ethylene is capable of being polarized under the influence of an electronically charged species, being a radical, anion or a cation – a reaction that became the basis of polymerization of ethylene to polyethylene.

Carothers completed his PhD in 1924. Adam's admiration for Carothers grew as he found him excelling in physics, mathematics, physical chemistry, as well as organic chemistry. Such a combination of interests was unusual for a young man of his age. Carothers continued in Illinois for another two years. He delved deep into the burgeoning chemical literature from Germany, aided by his ability to read and write German. He was fascinated by the emerging theory of organic chemistry that enabled a rational understanding of why chemical reactions occurred. He was clearly not interested in mere synthesis of organic compounds but wanted to understand why and how chemical bonds form.

It was during his stay in Illinois that his mentors noticed his mood swings. Carothers yearned for success and a course of research where he could put to use his chemical intuition . However, his mental depression and melancholic thoughts sapped him of any positive energy. As Carl Marvel, his colleague at Illinois, would observe many years later, Carothers was a "complex man – shy, inquisitive, intellectually bright, quick, self-demanding, and an overachiever; pleasant, but at times despondent [7]."

At DuPont, Carothers asked a very fundamental question. Why has no one been able to synthesize a polymer of molecular weight greater than 4200, a record established by Emil Fischer for the synthesis of protein like polypeptides?

Roger Adams recommended Carothers to James Conant, who was then building a modern, research focussed chemistry department at Harvard. Conant envisioned a department where senior professors spent most of their time only on research. He was influenced by the academic excellence of German professors, and wished to recreate this ambience in the US. Instructors were hired to do the teaching of introductory chemistry. Carothers was offered the position of an Instructor at Harvard.

In 1900, General Electric Company established the first organized industrial research and development laboratory in the US. AT&T followed this in 1911 (which later became Bell Labs). Thus began the hallowed tradition of scientific research and discovery that enabled the industry to bring many useful inventions to mankind. DuPont amassed a fortune, supplying explosives to the allied forces fighting in the First World War. Later the company ventured into manufacturing of automobiles (General Motors), dyestuff, paints, varnish, rayon and ammonia. DuPont was not known in its early days for its scientific acumen. Its success was based on enticing experienced foreign scientists, who had first-hand knowledge of technology, to join the company and duplicate much of the technology it practiced.

In 1926, dissatisfied with this strategy, Dr Charles Stine proposed to the company a programme of 'pure science or fundamental research'. His inspiration was General Electric, and he defined this activity as "work undertaken with the object of establishing or discovering scientific facts." He used an intriguing argument to expound the virtues of fundamental research and differentiate it from applied research – "applied research can succeed or fail, but fundamental research can only succeed because its only objective is to create new knowledge!"

Carothers convinced the scientific community through rational and unequivocal synthesis of high molecular weight materials that polymers are mere organic compounds linked by the same chemical bonds that characterize small molecules; and that polymers can be seen as extensions of ordinary structural theory.

After several failed attempts, Stine finally managed to get an approval from his management for creating such a programme. He built new laboratory facilities and named it appropriately as 'Purity Hall'. He began the task of hiring suitable scientists for pursuing the programme. Many leading scientists of the day were offered positions; this included, Roger Adams, Carl Marvel, Reynold Fuson, Henry Gilman, and Louis Fieser – each a legend in their respective areas. However, none of them were inclined to leave the secure and familiar environs of a university, and plunge into an uncertain future in the industry. Therefore, Stine decided to scout for "men of exceptional scientific promise but no established reputation, whose lines of research can largely be determined by us." Both Adams and Conant recommended Carothers to DuPont. Carothers was restless at Harvard and found his tasks constraining because he did not have enough opportunity to pursue research. His mind was full of ideas, but he felt that he needed "more than one pair of hands to get several things done." In the two years he stayed at Harvard, he published only one paper. So he was ready to move if someone promised him unfettered freedom to explore new ideas. DuPont made him such an offer, and Carothers decided to move. Conant commented on Carothers decision to leave as "Harvard's loss but chemistry's gain."

It was at the DuPont Experimental Station in Wilmington, Delaware, overlooking river Brandywine, beginning February 6, 1928, where Carothers would make his most outstanding discoveries. This was to be his home for the next nine years until his untimely death in April 1937. Moving from Harvard to DuPont was not without attendant pain. Carothers understood the respect that comes from being a faculty at Harvard. He called his job at DuPont as "industrial slavery." In 1929, he wrote to his friend Frances Spencer: "perhaps you know that I am now an industrial slave and clock puncher" [8]. He felt guilty that he traded academic respectability for money, limitless funds, and freedom to pursue his line of research. The cultural divide between industry and academia that Carothers felt, was palpable in his thoughts and words.

At DuPont, Carothers asked a very fundamental question. Why has no one been able to synthesize a polymer of molecular weight greater than 4200 g/mol, a record established by Emil Fischer for the synthesis of protein like polypeptides [9]. Following Staudinger's proposal of polymerization, there was a debate as to whether polymers were discrete molecular substances linked by covalent bonds or aggregated colloidal particles [10]. Carothers took a leaf out of the pages of organic chemistry, and asked whether it was possible to synthesize large molecules (polymers) from small molecules (monomers) using known organic chemical reactions, which will make the structure of polymer obvious and self-evident. He was also interested in understanding how the properties of such large molecules would depend on their constitution.

In less than a year after he moved to DuPont, Carothers began making seminal contributions. In 1929, he established the chemical equivalence of esterification and polyesterification, the former capable of forming one ester bond, whereas, the latter capable of forming many ester bonds simultaneously. He provided a more generalized definition of polymers as substances "whose structures may be represented by R-R-R-R- where -R- are bivalent radicals which in general are not capable of independent existence" [11]. He wrote 28 papers between 1929 and 1935, on the principles of polycondensation reactions and addressed a very profound question – if two bifunctional molecules, e.g., one a dibasic acid and one glycol or diamine react, two possibilities occur; the reaction can result in (1) a chain polymer of lower or higher molecular weight which still bears either a hydroxyl or carboxyl-terminal group, or (2) a smaller or larger ring which does not contain a reactive group. His early thoughts on polymerization chemistry and mechanisms were succinctly summarized in a review he authored in 1931 in *Chemical Reviews*, (Vol.8, 353) where he laid out the principles governing polycondensation reactions [12]. His definitive statement that "many naturally occurring macromolecular materials have a linear polymeric structure" is testimony to the sheer power of intuitive thought. In a matter of few years, he convinced the scientific community through rational and unequiv-

Box 1. Table of Contents, *Chem. Rev.,* Vol.8, 353, 1931.

IX. Polymerization

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ocal synthesis of high molecular weight materials that polymers are mere organic compounds linked by the same chemical bonds that characterize small molecules; and that polymers can be seen as extensions of ordinary structural theory "sufficient when used with some discrimination, to furnish a means of treating such substances in a rational fashion." Once and for all Carothers settled an argument, which Staudinger could not, for over a decade, since his seminal paper on polymerization.

In the meantime, a debate was brewing in DuPont regarding what good was coming out of all these efforts in Carothers's laboratory. The chemistry became clearer, but there were no useful polymers in the horizon. Carothers was still stuck in the Fischer's limit of molecular weight of 4500 g/mol! In another effort at DuPont, chemists had already made a new synthetic rubber from 2-chloro-1, 3-butadiene (chloroprene) called 'neoprene' by what Carothers called an 'addition polymerization' process. Although Carothers participated in this work, and wrote more that 20 papers on the subject, he was not really interested since this was distracting him from his fundamental quest. He termed the scientific work on chloroprene "abundant in quantity, but perhaps a little disappointing in quality.” [13]

Carothers equation, relates molecular weight or the degree of polymerization of fractional conversion of the reactants.

It was at this time that one of his colleagues, Julian Hill, gained access to a new distillation apparatus capable of removing volatiles from bulk samples at high temperatures and low pressures. Carothers already knew that factors limiting molecular weight in condensation reactions did not have to do with chemistry, but by the inability to remove all the water. If traces of water were present, it would simply reverse the reaction. Carothers also realized that each end of the growing polymer chain might also be a glycol component. Most of the time, scientists in Carothers’s lab used a 5 or 10 mol % excess of glycol over diacid. Hill started the reaction of a 16-carbon atom diacid with a 3-carbon atom diol (as usual 10% excess), and prepared a polyester of molecular weight 3300 g/mol . He then subjected this polyester to distillation at high temperatures and low pressures; and lo and behold, Hill and Carothers had produced a polyester of molecular weight 12000 g/mol, exceeding Fischer’s limit! This polymer could be drawn as thin lustrous filaments. Hill’s distillation apparatus had removed both water and glycol (condensation and transesterification) in one step. Carothers realized that to achieve high molecular weights, one needs to stoichiometrically balance the two reactive groups, namely the acid and the alcohol. This eventually led to the well-known Carothers equation, that relates molecular weight or the degree of polymerization to fractional conversion of the reactants (*Box* 2).

The year 1931 was an eventful year for Carothers. He best described it as, “there is so much to be done that there never seems to be times for such matters as going to the dentist or getting a new suit. My eyes and imagination enormously exceed my capacities.” He continues, “in spite of this, we have been enormously lucky in our research so far. We have not only a synthetic rubber but also something theoretically more original, a synthetic silk. If these two things can be nailed down, that will be enough for one lifetime.” These words, in my opinion, are the most understated words by a scientist in the history of science.

In spite of these fundamental advances, aliphatic polyesters proved

Box 2. Carothers Equation.

$$\mathrm{Dp_n} = \frac{(1+r)}{(1-r)+2r(1-p)},$$

where, r = Stoichiometric ratio of functional groups and p = fractional conversion.
When r = 1,

$$\mathrm{Dp_n} = \frac{1}{(1-p)}$$

p	**Dp_n**
0	1
0.9	10
0.95	20
0.99	100
1.00	∞

to be uninteresting materials in terms of its properties. So, Hill and Carothers turned their attention to the reaction of aliphatic diacids with diamines. Initially, they attempted the polymerization of 6-aminocaproic acid, and they obtained a small quantity of polymer and a cyclic lactam called 'caprolactam'. Carothers published this work with a definitive statement that "cyclic lactams do not polymerize under the conditions for the formation of a polyamide" [14]. This statement in print turned out to be fatal to DuPont. By 1937, I G Farben in Germany had found the reference in the literature to Carothers work and successfully polymerized caprolactam to a polyamide (now known as nylon-6). Similarly, Carothers had published the polymerization of phthalic acid with ethylene glycol to low molecular weight glassy polyester. J R Whinfield and J T Dickenson, at the laboratories of Calico Printers Association UK, replaced o-phthalic acid with terephthalic acid and obtained a linear polyester, poly (ethylene terephthalate)

(PET). ICI, UK developed this into a fiber, called 'terylene'. Ironically, DuPont had to obtain the license from ICI to introduce its own polyester fiber under the trade name 'dacron'. It is still a mystery how a person, as thorough and prescient as Carothers missed using terephthalic acid!

By 1932, the vision of a 'pure science' programme within DuPont was faltering. Five years and after many thousand dollars of expenditure, the fundamental scientific explorations had not yielded tangible results. The reputation of Dr Charles Stine, the original proponent of this idea of curiosity-driven, pure science research suffered damage. Dr Bolton, who was the Director of the Chemical Department, and a great believer of focused research directed towards the needs of the company (business driven research), was trying to cope with the challenges of the post economic depression era. He had high respect for Carothers' scientific acumen but felt that he was far too interested in publications. He once told Carothers, "if you could just get something with better properties, higher melting point, insolubility, tensile strength, you would have a new type of fiber. After all, you are dealing with polyamides, and wool is a polyamide." These words catapulted Carothers into action again. Carothers, by the end of 1933 had a feeling that he had said all that he had to say about condensation polymers. He had contributed to synthesis, explained the mechanism, and provided a general theory. He had developed a system of nomenclature and elucidated key relationships between structure and properties. He felt that he had climbed the mountain that he had set to, and that there was little more to accomplish. He was ready to write a history of polyamide fibers (which he did in 1935)!

Spurred by Bolton's challenge, Carothers in 1934, decided to make one more effort to find a polymer that had more desirable properties. He reasoned that use of additional methylene groups between acids and amines could reduce the melting point. He felt that a carefully purified ester of an amino acid could make the equilibrium more favourable for the preparation of a high molecular weight polyamide. This was demonstrated by the polymerization of the ethyl ester of amino nonanoic acid. Carothers called this 'polyamide-9'. Soon the group of Carothers set about preparing a vast library of polyamides from a variety of diacids and diamines containing 2 to 10 carbon atoms. There were as many as 80 potential candidates. On February 28, 1935, one of Carothers's co-workers performed the chemical reaction which will go on to create history. He reacted hexa-methylenediamine with adipic acid to create polyamide 6-6. When discovered, polyamide 5-10 was easier to spin as a fiber from its melt than polyamide 6-6. But Dr Bolton's prediction that benzene would become cheap and provide easy access to six carbon diacids and diamines won the argument, and all attention was diverted to the study of how to make polyamide 6-6 more easily processable. DuPont, commercially produced polyamide 6-6, under the trade name 'nylon'. As women's hemlines rose in the thirties, silk stockings were in greater demand but were very expensive. Nylon changed this as it could be woven into sheer hosiery. Dr Charles Stine introduced the product on October 24, 1938, in New York, to a forum of women's club members. On the first day they were available in the market (May 15, 1942), 800, 000 pairs of nylon stockings were sold (*Figure* 5). In 1941, nylon fibers were used to make the parachutes that helped the allied forces land on the beaches of Normandy on the D-Day, August 6, 1944, during the Second World War.

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Nylon-6 changed the fortune of DuPont and established it amongst the leading chemical companies of the world with a string of successive inventions that defined the post-war polymer industry.

By the end of 1933, Carothers was no longer in the hot seat of research at DuPont. He was torn between the desire to pursue questions of fundamental interests and the increasing demands by the company to align basic sciences with the specific business objectives of the company. Carothers wrote in 1933 "as far last year is concerned there is nothing of material importance to communicate. I still struggle along as a group leader, which is to say, a kind of a clerk." As the polyamide programme moved into development mode, Carothers disappeared from the laboratory for

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long periods of time, was admitted to psychiatric care and spent long weeks in a hospital in 1934. He even toyed with the thought of leaving DuPont for an academic career at the University of Chicago but did not make the final decision.

In recognition of his influence on the science that was emerging, a Faraday Society Discussion Meeting was held in Cambridge, UK in 1935 on the subject of 'Phenomenon of Polymerization and Condensation'. Carothers presented his work at this meeting [15]. In the concluding part of his lecture, Carothers laid out the visions of a new science that was yet to emerge. He asked, "why do Nature's amino acid monomers form polypeptides? In the laboratory, these monomers will smoothly cyclize to form diketopiperazines. But organisms, in contrast, make (linear) polymers that serve structure and function. How can this be?" He then speculated that "if the reaction is preceded by adsorption at an interface, as it might be biologically, the molecule is no longer free to assume its spatially probable configuration; and in any event, the (role) of surfaces on bifunctional reactions present an almost completely unexplored field." Carothers had alluded to the role of shape and surface as a template for facilitating unique selectivity in chemical reactions, a field that would witness explosive

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growth within the next decade, both in biology and in chemistry. On the recommendation of his mentor, Roger Adams, Carothers was elected to the membership of the US National Academy of Sciences in May 1936 – the first industrial scientist ever admitted to the Academy.

Ironically, the man who launched DuPont on the journey of science led discoveries, did not live to see the final accomplishments. Since his young days, Carothers suffered from chronic depression and mood swings. Many have talked about how he always had a bottle of cyanide in his pocket. In all fairness to him, he acknowledged this weakness. Upon being offered a position by DuPont, he chose to write to his future employers saying, "I suffer from neurotic spells of diminished capacity which might constitute a much more serious handicap there than here" [16]. Carothers suffered from melancholia and manic depression. In 1932 he wrote, "My nervousness, moroseness, and vacillations get worse as time goes on, and the frequent resort to drinking does not bring about any permanent improvement. No, I am not dead, but only moribund, feeling rather feeble, smelly and cockroach-like. Just why I do not know. I go through a dozen violent storms every day." He was back under psychiatric care in 1936. His unhappiness was compounded by the death of his sister Isobel in January 1937. He checked into a Philadelphia Hotel on the evening of April 28, 1937, one day after his forty-first birthday and committed suicide by drinking a cocktail of lemon juice laced with potassium cyanide.

Carothers married Helen Sweetman on February 21, 1936. Helen was a Patent Assistant at DuPont, and had known Carothers for many years in her professional capacity. His daughter Jane was born posthumously on November 27, 1937.

The first Nobel Prize in the area of polymer science was awarded to Hermann Staudinger in 1953. Carothers would have been fifty-seven that year, and would have certainly made that historic journey to Stockholm if he had been alive.

Suggested Reading

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