Award Address

Reflections on 50 years of polymer chemistry*

I am greatly honoured to receive the prestigious Herman F. Mark Award for my contributions to polymer chemistry. Although I have received several other major awards, it is especially gratifying to receive the highest award of the Division of Polymer Chemistry, since I have been intimately involved for the last 18 years in the operations of this Division. This award is a very special one since it is named after Professor Mark, one of the greatest polymer pioneers and a truly remarkable and gracious individual. I was fortunate enough to have known Professor Mark and also honoured to have been chairman of the Biennial at which he received this award.

The prestige and honour of receiving this award is indicated by the eight outstanding polymer scientists that have received it to date. In order of receiving it, they are: Flory, Marvel, Huggins, Mark, Ferry, Overberger, Stockmayer and Szwarc. Truly a Who's Who of polymer science. Two of these awardees have received top science awards: Flory the Nobel Prize and Szwarc the Kyoto Prize. I am indeed most honoured to receive this award. Also, I am the first person to receive it for industrial contributions.

At this time, it is appropriate to review my career and contributions in a general way, especially since I came into polymer chemistry and research indirectly. In addition, I emphasize that my contributions were in the industrial arena where it is often difficult for a researcher to publish his findings in a timely manner, if at all. The difficulty increases with the importance of the work. Yet, industrial researchers have made great contributions to science and technology, many being largely unrecognized. Thus, I intend to acknowledge the work of this large group of creative industrial researchers.

My career reminds me of a comment made by J. Paul Getty when asked by some young people how to be successful. He responsed that there are three important requirements: (1) rise early (which I did); (2) work hard (which I also did); and (3) discover an oil well! This I did not do but I did discover some very important and useful polymer chemistry including some useful, new polymeric materials for which my company benefited financially, many-fold beyond the best oil well. I personally did not receive the financial benefit of an oil well but I did receive financial and other recognition from my company as well as other personal benefits such as intellectual stimulation, research freedom, and awards such as this one.

I became interested in chemistry in my high school years through a friend, Gordon Hoffman, who had a chemistry laboratory in his home. I became intrigued with the unique and pervading aspects of chemistry to all things. I set up a small laboratory in my parents' basement and spent much time before college doing experiments, and reading about chemistry. As with most budding chemists, I ran one experiment which could have had disastrous results. Contrary to the hydrogen–oxygen explosion often experienced by beginning experimentalists[1,2], we used an unusual approach. We decided to synthesize manganese metal based on the known reaction of manganese dioxide with aluminium metal. Thus, we heated a mixture of manganese dioxide powder with aluminium metal powder in a crucible with a Meeker burner. We were looking at it closely when the reaction occurred in a flash explosion, right in our faces and with unprotected eyes! Fortunately, neither of us was injured. The reaction was successful since the recovered crucible pieces were coated with manganese metal. The temperature had obviously exceeded the melting point of manganese (1244°C).

By my senior year in high school, I had a strong resolve to become a chemist. In fact, my life goal, as stated in the senior year book, was 'to be a good chemist'. This was in 1935, in a country still recovering from a very severe depression.

I wanted to go to college but was not sure that my family could afford it. However, my father suggested that I go to Stevens Institute of Technology, an Engineering School in Hoboken, NJ. He felt that I could learn chemistry there and costs could be minimized by my living at home, commuting every day to Hoboken (a 20 mile train ride to Jersey City, a subway ride to Hoboken and then a mile walk to Stevens). This I did through 4 years of college.

Although engineering was not a primary goal, I was very pleased to be able to go to college. Stevens was a good choice — an excellent school with the goal of providing a very broad-based, interdisciplinary engineering background (unique at this time) even though the final degree was 'Mechanical Engineer' for historical reasons. The Chemistry curriculum was excellent including an organic chemistry elective in the senior year. I actually did very well in my engineering courses and was elected to the honourary engineering fraternity, Tau Beta Pi. Indeed, a broad engineering background is excellent for a scientist as well as for conventional engineering posts and other positions of responsibility since it provides a practical view of the important areas of life, technical and economic as well as social.

My chemistry interests continued unabated throughout my college career. In my junior year, I had the opportunity to take on a senior project. Naturally, chemistry was my area of choice, especially organic chemistry for which I had acquired a strong interest even though I had not

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* Presented at the American Chemical Society, Division of Polymer Chemistry '17th Biennial Symposium on Advances in Polymerization and High Performance Polymeric Materials', 22–25 November 1992, Palm Springs, CA, USA

0032-3861/94/23/4933–07

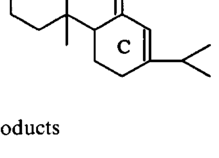
had a formal course. I approached Dr F. J. Pond, Head of the Chemistry Department, who allowed me to carry out organic synthesis laboratory work during the summer. Dr Pond spent a considerable amount of time tutoring me in organic chemistry during this period.

At the beginning of my senior year, Dr Pond gave me a research project in an organic area that he had worked on during his doctoral work in Germany in the early 1900s and in later years at Penn State.

By the middle of my senior year, I had become convinced that chemistry research was my area of future interest. I interviewed with a DuPont personnel man who visited Stevens looking for new employees. I expressed an interest in a research position. However, he advised me to continue my chemistry education and obtain a PhD degree. I discussed this with Dr Pond and he felt that an industrial research position for a few years might be a better approach. I agreed. At this point, he offered to recommend me to George Norman, who was a member of the Board of Directors of Hercules Powder Co. Subsequently, I was hired for a research position and started on 1 July, 1939. Shortly after arriving, Dr E. Ott assigned me to work with Dr H. M. Spurlin. Dr Spurlin was widely recognized as a polymer chemist and in particular for his work on cellulose and its derivatives. His efforts were being directed at that time towards the long-range interest of Hercules. Hercules had a very important interest in the rosin sizing of paper — the largest market for rosin, a major product of their Naval Stores operations based on recovering wood rosin and terpenes from Southern pine stumps which was acquired after World War I. The major component of wood rosin is abietic acid (a diterpene C_{20} carboxylic acid). This resin acid which contains two conjugated double bonds can be easily converted to more stable commercial products by hydrogenation and disproportionation (*Figure 1*).

Rosin sizing of paper has been practiced for over 185 years and basically consists of adding the sodium salt of rosin to the beaten, aqueous pulp slurry, adding aluminium sulfate to precipitate aluminium resinate which is retained in the paper during the water removal sheet making operation. After drying, the paper then has sufficient hydrophobic surface characteristics that it can be written or printed on with ink without any feathering of the ink such as happens on unsized paper. This process is a remarkable physical, chemical and colloidal phenomenon whereby as little as 1% or less aluminium resinate can change the hydrophilic surface characteristic of paper pulp (largely cellulose) to hydrophobic.

The mechanistic aspects of this process were not well established, particularly why the aluminium resinate adhered to the paper fibre in finely divided form to be retained during the paper forming process. An electrostatic retention mechanism had been proposed, i.e. that the aluminium resinate was positively charged and the paper fibre was negative, but was not unequivocally accepted and the details not clear. Dr Spurlin had proposed that this question could be settled by using electrophoresis studies on the paper and the size precipitate. He assigned this to me as my first research job. For 2 years I worked with Dr Spurlin on this task. We clearly proved that the electrostatic theory of size retention was correct and also delineated other important chemical aspects of rosin sizing. Some of the key factors that were revealed by this work are given in *Figure 2*.



Abietic acid

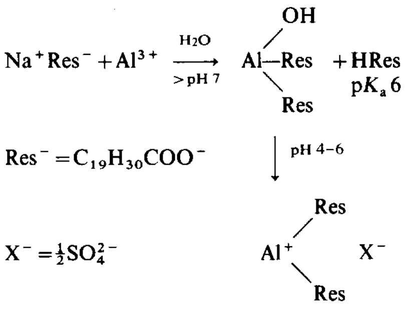
Derived commercial products
  Hydrogenated to:
    Dihydro-
    Tetrahydro-
  Disproportionated to:
    Dehydro- (C-ring aromatic) and dihydro-

Figure 1 Abietic acid and derived commercial products

The reaction of aluminium sulfate with the sodium salt of resin acids in water at pHs above 7 leads to a mixture of basic aluminium diresinate, which is a neutral, covalent compound plus 1 mol of free resin acid. When the pH is lowered to 4–6 (4.5 usually optimum for paper sizing), the basic aluminium diresinate becomes the positively charged $Al^{+}Res_2$ species. Since resin acids are very weak acids (pK_a 6), they are essentially neutral at the optimum pH so that the size precipitate has an overall positive charge, thereby explaining the source of the positive charge important for size retention. Although aluminium triresinate can be made in organic medium, it apparently is not stable in water, no doubt due to steric factors. After drying the paper we presume (although did not prove this) that the positive charge of the aluminium diresinate is destroyed in some way, perhaps by chemical binding to cellulose. A residual positive charge would no doubt be deleterious to the hydrophobicity of the size precipitate.

Cellulose is negatively charged under sizing conditions due to preferential anion adsorption and also due to the presence of water-soluble and water-insoluble polyuronic acids in the paper pulp. Uronic acid groups are the carboxyls formed by the oxidation of the primary hydroxyls in polysaccharides. The hemicellulose fraction of paper pulps contain such carboxyls which are quite

Size precipitate



$$Na^{+}Res^{-} + Al^{3+} \xrightarrow[>pH\ 7]{H_2O} Al(OH)(Res)_2 + HRes \quad pK_a\,6$$

$$\downarrow pH\ 4\text{–}6$$

$$Al^{+}(Res)_2 \quad X^{-}$$

$Res^{-} = C_{19}H_{30}COO^{-}$

$X^{-} = \frac{1}{2}SO_4^{2-}$

After drying, Al resinate may be chemically bound to cellulose and/or + charge destroyed

Cellulose negative charge

Due to:
  Anion adsorption
  Uronic acid groups, p$K_a \sim 3$
  All paper pulps contain anionic, water-soluble and water-insoluble polyuronic acids

Figure 2 Key factors in the rosin sizing of paper strong acids, pK_a ~3. Because of this higher acid strength, they form ionic compounds, thus leading to a negative charge under sizing conditions. As further proof of the electrostatic theory of size retention, we found that the water-soluble polyuronic acids from paper pulps when present in excess relative to the size precipitate are strongly adsorbed to give it a high negative charge. Polysaccharides containing uronic acid groups such as gum arabic, pectin and gum tragacanth behave in the same manner. The water-soluble polysaccharides may also provide a protective colloid action on the size precipitate because it exhibits a very strong coagulation tendency in the presence of the sulfate ion in paper sizing systems. Thus, it is clear that the rosin sizing of paper includes a unique combination of physical, chemical and colloidal phenomena. This work was ultimately published 25 years later[3] when Dr Spurlin received the Anselme Payen Award for his contributions to cellulose chemistry.

In 1942 I was assigned to an operating department to work on soil stabilization, a process very much like paper sizing. This was a new process developed during World War II to quickly develop aircraft landing strips in remote areas with minimal raw materials. In this process, a rosin soap was added to a wet soil, the soil compacted and then dried. The resultant soil became hydrophobic and resisted the usual detrimental effect of rain, thus making it useful for airplane landing strips. In 1944, I was transferred to the Sun Flower Ordinance Works in Lawrence, KS, to become an assistant shift supervisor in smokeless powder production. When the war ended in 1945, the Hercules Research Center requested my immediate return.

At this point, I was assigned to work on emulsion polymerization — my first polymer synthesis research activity. During the war, Hercules had developed disproportionated rosin soap (Dresinate 731) as a good emulsifier for the synthesis of styrene–butadiene rubber (SBR) by emulsion polymerization. Ordinary rosin soaps were not useful in this free radical polymerization because of the strong inhibition and retardant behaviour of the conjugated resin acids with many allylic hydrogens. This rosin-based emulsifier business was successful but there were still problems that had to be addressed such as the slower rate of polymerization with Dresinate 731 as compared with the competitive product, sodium stearate. I took over long range research in this area from Dr A. E. Drake. Early in this work I learned from Dr Drake about the self-sealing rubber liner technique which the rubber companies had developed for the SBR emulsion polymerization in pressure bottles, using hypodermic equipment to inject ingredients and remove product samples. I applied this to my research work and, indeed, this proved to be a very valuable aid to all of my subsequent research. This technique allowed many experiments (e.g. 10–20) to be run per day under controlled atmospheres (such as nitrogen) and low pressures (up to 0.34 MPa).

Early in this rubber programme I discovered and patented the superior redox emulsion polymerization system based on organic hydroperoxides, a small amount of iron pyrophosphate and reducing sugars which increased polymerization rates a phenomenal 50-fold with disproportionated rosin or fatty acid soaps and even gave good polymerization rates with ordinary rosin soaps. These organic hydroperoxide redox systems were ultimately discovered and developed by others for SBR manufacture at 5°C to make a superior SBR[4], which is now our largest volume synthetic rubber. These general systems are still being used today, albeit in somewhat modified form. This work led to my first research publication[5] and I was now embarked on a research career involving the discovery and development of new polymers.

In general, Hercules gave me a fairly free hand to pursue areas that I felt were potentially important and interesting. Also, by this time I had taken some advanced chemistry courses in physical chemistry (under M. Kilpatrick at the University of Pennsylvania) and polymer chemistry (under E. O. Kraemer and H. M. Spurlin at the University of Delaware).

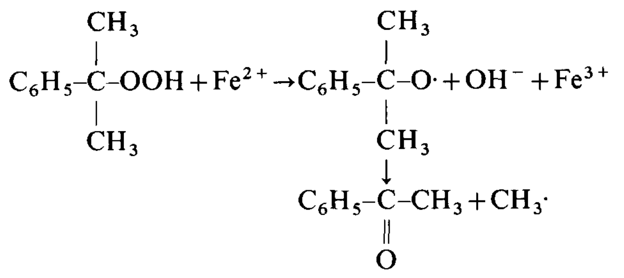
In the following, I will briefly highlight some of my research contributions, some of which have not been published except perhaps in patents, and also cite some of the 'near misses'.

As an extension of the SBR redox emulsion polymerization work, we studied SBR polymerization at -15°C in 75:25 water:CH_3OH medium since the rubber industry was interested in such systems to make an even better SBR and the rosin soap systems did not work well under these conditions. We developed hydroperoxide redox systems which did work well on rosin soaps. Because of the reduced chain transfer at this lower temperature, one could make very high molecular weight, soluble SBR which had some unique properties in adhesives. This work was not published but was disclosed to the rubber companies[6,7]. However, sub-zero SBR emulsion polymerization has not been developed commercially.

We sought other applications for our unique redox systems. A low temperature, low pressure system for making polyethylene was an attractive possibility and we developed redox systems in 95% t-butyl alcohol for polymerizing ethylene at 5°C, just below its critical temperature. Conversions were only a few per cent, molecular weight was low (at best 20 000) and the product brittle. However it was clearly a more linear polyethylene than the known commercial high temperature, high pressure product since the melting point was much higher. Thus, this product was linear polyethylene before it became available from the Ziegler and Phillips catalysts. In the course of this work, I had a concept which might accidentially have led to the Ziegler transition metal catalysts. However, lacking a key ingredient, I never tried it, thereby missing this very important discovery[4].

We did a fair amount of work in 1948 on the reactions of cumene hydroperoxide (CHP) to understand why our hydroperoxide redox systems were less affected by retarders and inhibitors. We found that CHP reacted with ferrous iron to preferentially reduce the OH end of the molecule [equation (1)], ultimately forming acetophenone and a methyl radical. In the actual redox system, the ferric iron is reduced back to ferrous iron by the reducing sugar so that little iron is required.

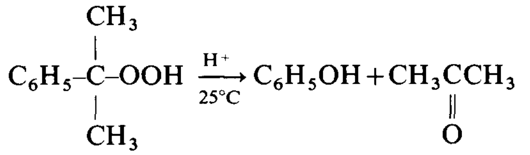
Presumably, the somewhat hindered and electronically favoured RO· free radical was more stable and thus less reactive to inhibitors, giving it a better chance to add to monomer and initiate polymerization as compared to the more reactive radicals from persulfate, hydrogen peroxide or benzoyl peroxide.



$$C_6H_5\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{-}OOH + Fe^{2+} \rightarrow C_6H_5\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{-}O\cdot + OH^- + Fe^{3+}$$

$$\downarrow$$

$$C_6H_5\text{-}\underset{\displaystyle O}{\underset{\|}{C}}\text{-}CH_3 + CH_3\cdot \qquad (1)$$



$$C_6H_5\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{-}OOH \xrightarrow[25^\circ C]{H^+} C_6H_5OH + CH_3\underset{\displaystyle O}{\underset{\|}{C}}CH_3 \qquad (2)$$

As an important offshoot of this work we discovered that CHP could be cleaved in organic media with many acid catalysts under very mild conditions to near quantitative yields of phenol and acetone. This general reaction [equation(2)] was reported by Hock and Lang[8] during World War II but under more severe conditions (aqueous H_2SO_4 at elevated temperature) and at lower yields. I was intrigued by our mild conditions and high analytical yields and continued to work on this facile cleavage. However, my immediate superior felt that I was wasting my time since CHP was 'too expensive for a phenol process'. CHP, of course, is prepared in high yield by the air oxidation of cumene. However, I pursued my convictions for about 2 months at which time the operating department recognized the importance of my work and took over the further development. Eventually, Hercules in co-operation with the Distillers Co. in the UK developed a new phenol process based on this reaction which Distillers, Hercules and others commercialized[4]. Today, >95% of the phenol in the world is made by this route ($\sim 5 \times 10^9$ kg per year). Since phenol is an important raw material for many polymers, low cost phenol is certainly a contribution to the polymer field.

This hydroperoxide and phenol chemistry was extended at that time to polymers. Thus high polymers from poly(*p*-isopropyl α-methyl styrene) and related isopropyl substituted aromatic polymers were oxidized to polymeric hydroperoxides which were used to make a wide variety of graft polymers via free radical polymerization and also acid cleaved to high molecular weight polyphenols (*Figure 3*). This work was covered by a number of composition of matter patents[9]. The polymeric hydroperoxide approach to graft polymers merits further work for possible utility, an area that has not been adequately explored and is related to the current emphasis on highly branched, dendritic polymers. High molecular weight linear polyphenols have been made recently by other methods and studied for electronic applications[10].

Up to this point much of our polymer studies were related to rosin, a major Hercules raw material. In addition to the emulsifier aspects, we and others at Hercules made a variety of polymers containing rosin-based monomers. One interesting area that I pursued consisted of making copolymers of N-hydroabietyl acrylamide. Specifically, we made water-soluble copolymers with acrylamide along with other comonomers to make products for some specific applications. Initial results were attractive and although a Hercules operating department extended the research, they decided not to pursue it or even patent it. The point I want to emphasize here is that we had probably prepared the first hydrophobically modified water-soluble polymers. In the last 10–20 years such polymers were found to have unique viscosifying effects and have been widely studied and commercialized. Unfortunately, we did not do any viscosity studies so did not recognize this important area of application.

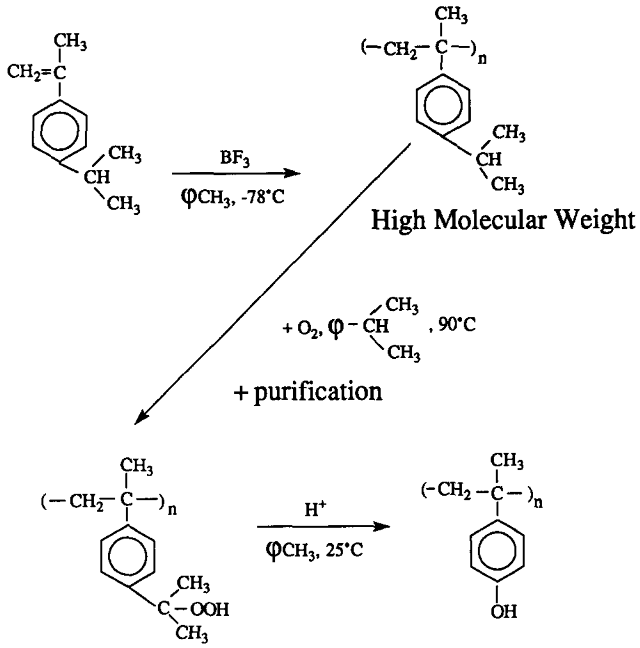


Figure 3 High molecular weight polymeric hydroperoxides and polyphenols

Hercules continued to have a strong interest in getting into the synthetic polymer field. When the Ziegler catalyst discovery on ethylene polymerization became available in 1954, Hercules licensed it. I was assigned to examine some of the longer range aspects and worked in this area for 2–3 years. Quickly, I independently discovered isotactic polypropylene, improved catalysts for making this new polymer as well as for linear polyethylene and the important hydrogen method of controlling molecular weight for polyolefins. The Hercules operating department developed a commercial process in collaboration with Hoechst for isotactic polypropylene. Hercules became the first US producer and ultimately the world's largest producer of isotactic polypropylene and a large producer of biaxially oriented film and of fibre[4], two of the largest market areas.

I went on to scout other possible applications for Ziegler type catalysts, particularly for polar monomers. On vinyl ethers we discovered a variety of new, unusual, non-Ziegler cationic co-ordination catalysts such as the reaction product of aluminium alkyls and alkoxides with sulfuric acid. These catalysts enabled us to polymerize vinyl ethers at room temperature to high molecular weight, isotactic polymers which were more stereoregular and higher melting than the prior art polymers of Schildknecht, which required polymerization at $-78°C$[4]. This lead, although pursued in some depth by Hercules on poly(methyl vinyl ether), was not commercialized.

The general resemblance of our new vinyl ether catalysts to the aluminium isopropoxide-$ZnCl_2$ systems that Price and Osgan had just discovered for propylene oxide (PO) polymerization led us to study some of our new vinyl ether catalysts and some of our improved Ziegler catalysts on epichlorohydrin (ECH). Initially we obtained a small amount of crystalline poly(epichlorohydrin) — a new polymer to us but later patented by Dow. Early in catalyst improvement studies we found some unusual organometallic catalysts from the reaction of triisobutyl aluminium ($i\text{-}Bu_3Al$) with water in less than stoichiometric amounts (0.5 to 1.0 H_2O/Al) so that the final product was an alkyl aluminoxane[4].

The catalyst based on $i\text{-}Bu_3Al$ polymerized ECH very readily at room temperature to high conversions, and high yields of high molecular weight amorphous poly(epichlorohydrin) — a new rubbery polymer[7]. We went on to improve these catalysts by adding a chelating agent such as acetyl acetone. This combination of aluminium alkyls with less than stoichiometric amounts of H_2O and acetyl acetone still represent the most versatile systems for epoxide and oxetane polymerization (*Figure 4*). We obtained composition matter patents on the catalysts and also on many high molecular weight polyepoxides which could not be made with prior art catalysts. Subsequently during the last 15 years the alkyl aluminoxanes were found by Kaminsky and others to be necessary for some unique transition metal catalyst systems for olefin polymerization[4]. This is still a highly active field. These catalysts were also found of value by others for the ring opening polymerization of cyclic lactones such as β-butyrolactone[4].

Two product areas stood out as promising from our extensive studies on many epoxides, i.e. two elastomers, particularly amorphous poly(epichlorohydrin) as a speciality elastomer and copolymers of PO with small amounts of an unsaturated epoxide such as allyl glycidyl ether as a more general purpose type elastomer (*Table 1*).

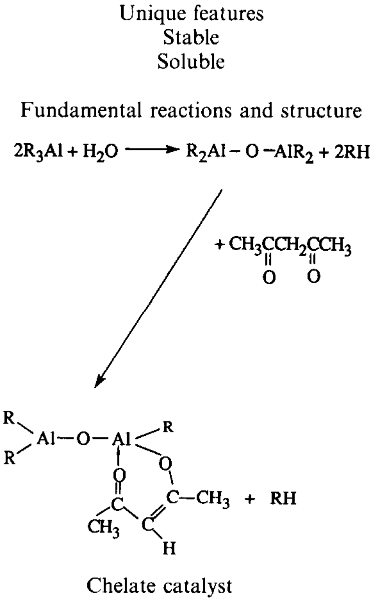


Figure 4 Aluminium alkyls with water catalysts

Table 1 Elastomers from monosubstituted epoxides[7]

	Amorphous	Crystalline m.p. (°C)
$-CH_2-\underset{CH_2Cl}{\underset{\mid}{CH}}-O-$	Solvent-resistant rubbers	120
$-CH_2-\underset{CH_2Cl}{\underset{\mid}{CH}}-O-CH_2-CH_2O-$		–
$-CH_2-\underset{CH_3}{\underset{\mid}{CH}}-O-CH_2-\underset{O-CH_2-CH=CH_2}{\underset{\mid}{\underset{CH_2}{\underset{\mid}{CH}}}}-O-$	S-vulcanizable rubber	–

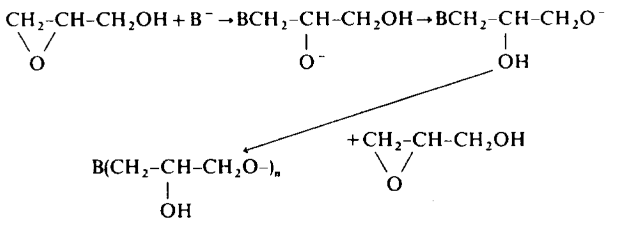
However, elastomers were a difficult sell at Hercules since we would be competing with our customers for rosin emulsifiers. A great deal of work was done on these products to improve their properties and outside contacts made. Finally Goodrich licensed the ECH elastomers which included copolymers. We helped Goodrich set up an interim facility as well as to continue work on solving a variety of problems perceived by Goodrich. The most important problem was the poor low temperature and dynamic properties of amorphous poly(epichlorohydrin). Copolymers were obviously the way to go. We had made and patented PO and ethylene oxide (EO) copolymers. Prior work on (ECH)-PO copolymers indicated some significant property deficiencies even though the copolymerization was a good one. We immediately recognized that ECH-EO might be the best candidate although EO was seven times more reactive than ECH. We developed a process for making this copolymer over the entire composition range and found that the 1:1 (mol/mol) ECH-EO copolymer was indeed an unusual one overcoming the low temperature deficiency of the homopolymer, giving good dynamic properties and with little sacrifice in some of the key advantages of the ECH elastomers, namely good oil resistance, good ozone resistance and heat resistance. As a result, the ECH elastomers were commercialized by Goodrich and later by Hercules and others. Currently they are being sold world-wide at about the 10×10^6 kg per year level. Most cars contain one or more parts made from these elastomers. The US producer is Zeon Chemicals, who in this modern world of acquisitions, took over both Goodrich and Hercules interests in the area[7]. As an interesting aside, the major plant for making these elastomers is inside a Hercules plant in Hattiesburg, MI and is owned and operated by Zeon Chemicals.

The PO elastomers are commercial but at lower volumes for speciality applications. These elastomers still need further improvements. Ultimately, improved products could be important large volume elastomers[7].

At this point in my career in 1966, my accomplishments were recognized by an honorary Doctorate of Engineering from the Stevens Institute of Technology.

An interesting area in which we did extensive work in my last 5 years at Hercules (1977–1982) was on a new approach to improved synthetic water-soluble polymers — an area of great interest to Hercules. The initial concept was to make synthetic rigid-chain water-soluble polymers — somewhat analogous to the unusual water-soluble polysaccharide, xanthan. In collaboration with other researchers at Hercules and later with Dr J. C. Salamone and his students, we made many such products, as typified by sulfonic acid substituted poly(phenylene terephthalamide) and aromatic polyimides. The products did give unusual viscosifying effects in water but were very salt sensitive. The salt deficiency was improved by making block copolymers containing EO blocks[11]. However, Hercules decided not to pursue these leads or even patent them. Dr Salamone and Dr A. C. Watterson[12] at the University of Massachusetts at Lowell and others continue to work in this area. Gieselman and Reynolds[13] at the University of Texas at Arlington have published on similar water-soluble polyelectrolytes from polybenzimidazole. Dang and Arnold have reported on a number of water-soluble rigid-rod polymers[14] and Marroco[15] has reported on water-soluble, substituted polyphenylenes. These products in general do not appear to have been well enough characterized to assess possible commercial merit. It does appear that water-soluble rigid chain polymers will eventually be developed which have commercial merit. This case is another example where the industrial researcher is at a disadvantage, i.e. not being able to pursue an area where he apparently was first and where the company interests were not long range enough to stay the course.

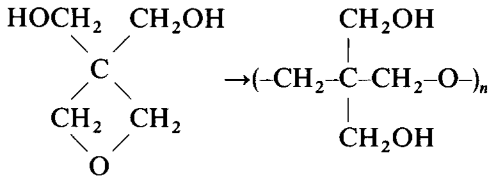
After I retired from Hercules at the end of 1982, I became a Visiting Professor of Chemistry at Arizona State University with the goal of pursuing some of my research leads, especially on hydroxypolyethers, some rather interesting analogues of the important polysaccharides. This work was supported by grants from NSF, ARO, PRF, DuPont and Hercules and led to three publications and three patents. In my prior Hercules work, interesting water-soluble high molecular weight polymers were made from glycidol (hydroxymethyl ethylene oxide)[16] and 1,2-bis(hydroxymethyl) ethylene oxide[17] — both atactic and isotactic. This was done with our epoxide catalysts after blocking the hydroxyl group with a trimethylsilyl group and then removing it after polymerization. In this same Hercules work, I discovered an interesting base catalyst rearrangement polymerization of glycidol to yield low molecular weight, water-soluble poly(3-hydroxyoxetane):



(3)

In the ASU work done in collaboration with Dr J. C. Mullis, a similar approach was used on some hydroxyoxetanes. Specifically, 3-hydroxyoxetane was polymerized to a high molecular weight, highly crystalline, atactic, water-soluble polymer melting at 165°C. This work confirmed that our low molecular weight polymer from the base-catalysed polymerization of glycidol was indeed poly(3-hydroxyoxetane). This polymer is interesting since it is related to poly(vinyl alcohol) (PVA) in that it has a CH_2O unit added to every chain unit. As in the case of PVA, it is highly crystalline even though it is atactic. This work also involved determining the unusual mechanism aspects of the spontaneous polymerization of 3-hydroxyoxetane to low polymer which had been reported in the literature. ^1H n.m.r. methods were developed to determine the tacticity of our products since PVA methods did not apply[4].

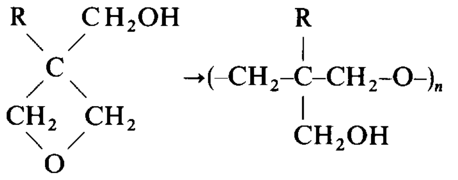
High molecular weight polymers were made from a family of 3,3-substituted oxetanes, namely 3,3-bis(hydroxymethyl)oxetane (BHMO) and 3-alkyl-3-hydroxymethyl oxetanes. The BHMO polymer is an interesting analogue of cellulose being highly crystalline and highly insoluble with a melting point of 315°C [equation (4)]. It is obviously more stable to hydrolysis and probably oxidation than cellulose and potentially more readily fabricated. Oriented fibres and films were made. The 3-alkyl-3-hydroxymethyl oxetane products where the alkyl is methyl, ethyl or n-propyl are atactic but are still crystalline with melting points in the range of 160–180°C but of course more soluble and more easily fabricated [equation (5)][4]. These polymers, especially the methyl form, offer another example like PVA where replacing a hydrogen on a crystalline polymer with a hydroxyl group does not prevent it from crystallizing even though atactic. These cases are of course, different from PVA since the hydroxyl is not on the main chain but on a methyl group attached to the main chain.



(4)

BHMO

PBHMO
(highly crystalline and
insoluble, m.p. 315°C)



(5)

R = Me, Et or n-Pr
(atactic, crystalline, m.p. 160–180°C)

Copolymerization in this family of 3,3-disubstituted oxetanes is essentially ideal. Surprisingly the copolymers are crystalline over the entire composition range with melting point varying linearly with composition. Thus, this is a new example of isomorphism in the polymer area where the copolymer units fit in the same crystal lattice as those of the homopolymers[4].

This unique family of 3,3-substituted oxetane polymers and copolymers merits considerable further study, in particular a detailed study of the mechanical properties and potential applications. A more stable analogue of cellulose which is easy to fabricate is an attractive possibility. In my view, there is still a large need for a hydrophilic fibre-like cellulose which is much more durable.

My experience in academia has been interesting. There are obviously positives and negatives compared to industry. Academic freedom is certainly important but this plus is negated rather seriously by the need to obtain substantial grant money to carry out any significant research programme. The peer review system used in assigning government grant funds is certainly defective. To think that a busy researcher can reliably evaluate a detailed grant proposal in a few hours (probably all the time that he can allocate) for an area that he or she may not be familiar with in detail is rather ludicrous. Also, each individual has his own rating prejudices — what one rates excellent may be only good to another. Needless to say the problem is exacerbated by the current recession, and the decreased availability of funds combined with an increasing need. One critical problem is the need for more individual research based on the fact that more important developments come out of such activity. However, much of the available government funds go to large special programmes such as centres of excellence, and special research programmes to a group of researchers such as the recently announced 'Grand Challenge' programme where $20 million is allocated to seven research groups on high risk programmes. Also, it appears desirable, if not necessary, to know the result of your research proposal before it is funded. This, of course, is completely contrary to the purpose of long range research. In my own limited experience I have seen numerous reviews where the reviewer did not properly read the proposal. We certainly should improve the system.

In conclusion, I am very appreciative and honoured to receive the prestigious Herman F. Mark Award. I have been most fortunate to be able to make my research contributions to polymer chemistry which, in my view, is the most important sub-discipline in chemistry. These contributions have, of course, depended importantly on many collaborators at Hercules and at ASU, a few of whom I have cited. Unfortunately, we are in very difficult times for science and technology due, in part, to the current world-wide recession which is due to a variety of complex factors. The most alarming aspects of the current situation are the decrease in long-term research by industry and the lack of adequate research funding for academia, which is a very important part of long-term research. Hopefully, when the world deals with its many important current problems and gets back on a better economic track, improved research priorities can be developed by industry, government and academia. In any event, it is our individual responsibilities to do what we can to facilitate this process.

E. J. Vandenberg
Department of Chemistry and Biochemistry,
Arizona State University,
Tempe, AZ 85287-1604, USA

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