The role of Innovations in the growth of economy with particular reference to the Polymer Industry

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“Just remember one word…

Plastics.”

- From the motion picture The Graduate (1967)

- We have always lived in a polymer age

- The word “Polymer” is derived from the Greek *poly* and *meros,* meaning many and parts, respectively. There has always been an abundance of natural fibers and elastomers, but few plastics

- Early human extracted shellac from the excrement of small coccid insects *(Coccus Lacca)*

"Of all critical and strategic materials, rubber is the one which presents the greatest threat to the safety of our nation and the success of the Allied cause. If we fail to secure quickly a large new rubber supply our war effort and our domestic economy will collapse…. The rubber situation gives rise to our most critical problem."

- From the Baruch Committee Report to the President 1942

Adhesives

- How man made glue and natural gums have been replaced by synthetic adhesives based on PVA, urethanes, rubbers etc.

- How cyanoacrylates have made such a big difference?

- We even have adhesives for structural purposes. In war torn areas synthetic adhesives have been used.

Super-absorbent Polymers

How diapers and sanitary towels have made such a big difference to the quality of life?

Polymers arguably represents the most important class of materials today; their multiple and tunable attributes underpin expanding use across most advanced technology platform

In energy, sustainability, health care, security and informatics, defense and protection. In fact, more than any other class of materials, polymers, have the ability to serve in many different capacities, from major structural components (e.g. the upcoming Boeing 787 “Dreamliner” is 80% by volume carbon fiber reinforced thermoset) to high value-added ingredients on the scale of grams (e.g. lithography, drug delivery)

- Polymers already feature in numerous biomedical applications, including drug delivery systems (e.g. coated stents, transdermal patches, polymeric micelles and nanoparticles), artificial replacements (e.g. hip heart prostheses) and tissue engineering

“ I am inclined to think that the development of polymerization is perhaps the biggest thing chemistry has done, where it has had the biggest impact on everyday life”

- Lord Todd (b.1907), President of the Royal Society London

Polymers all around us

It certainly seemed so in 1957, when the Hula Hoop craze swept the nation (USA). The hoops were made of linear polyethylene

Wonders of Nature : Ambient Conditions

- Cellulose
- Natural Rubber
- Shellac
- Terpenes / Terpene Resin
- Silk

The broad field of macromolecular science has never been more vibrant. Driven by stunning fundamental advances in many fields, including

(i) polymerization methods

(ii) theory, simulation, and modeling,

(iii) understanding of new physical phenomena,

(iv) advances in characterization techniques, &

(v) harnessing of self assembly and biological strategies for producing complex multifunctional structures, research activity in the field continues to expand and attract practitioners from many other disciplines

- Innovative Processing for Nanostructured Materials
- Precision Fabrication in Three Dimensions
- Processing of Complex Organic/Inorganic Systems
- Low-Temperature, Environmentally Benign Processing
- *In Situ*, Real-Time Process Monitoring

Development of Interfacial Polycondensation
Use of Phase Transfer Catalyst (PTC)

Polycondesation through the reaction of bisphenols with phosgene, in an alkaline biphasic system using methylene chloride and PTC, was a significant advancement

Ion Exchange Resins

- How water is purified to have dissolved salts at ppb level?
- How Ca and Mg in saturated brine are reduced to ppb level?
- How P in nephrology patients is reduced with a resin based on polyallylamine cross linked with epichlorohydrin?
- How K in patients is reduced with a polymer of K styrene sulphonate?

More from less

- How Polystyrene blend with polyphenylene oxide (PPO) makes processing possible?
- How fillers help PP/PE/PVC?
- How FRP becomes more effective?
- How polyaramid fiber allows bullet proof chest to be made?

Nobel Prize Winners for Their Work with Synthetic Polymers

Scientist(s)	Year	Area
Hermann Staudinger	**1953**	Polymer hypothesis
Karl Ziegler and Giulio Natta	**1963**	Stereo-regulation of polymer structure
Paul Flory	**1974**	Organization of polymer chains
Bruce Merrifield	**1984**	Synthesis on a solid matrix
Pierre de Gennes	**1991**	Polymer structure and control at interface
A. J. Heeger, Alan Mac Diarmid, and H. Shirakawa	**2000**	Conductive Polymers

- Rubber gained worldwide importance with the invention of the air-filled or pneumatic tires by a Scotsman, John Dunlop, in 1888. He had a successful veterinarian practice in Belfast. In his off time he worked to improve the ride of his son's tricycle
- Leo Baekeland in 1907 announced in an American Chemical Society meeting the synthesis of the first truly synthetic polymeric material, later dubbed Bakelite
- Baekeland was born in Belgium in 1863, the son of an illiterate shoe repairman and a maid. He was bright and received his doctorate at the age of 20 with highest honors

- Shredded nitrocellulose could be mixed with camphor and heated under pressure to produce a tough white mass that retained its shape. This material, dubbed celluloid, could be made into the usual rubber-like products, as well as solid pieces like boxes, wipe clean lines, collars, cuffs, and ping-pong balls

- But celluloid was flammable, and did not stand up well in hot water. Those who wore celluloid denture could literally have their "teeth curled" when drinking a hot cup of coffee

- Poly(vinyl chloride) (PVC) was initially formed by Baumann in 1872; however, it awaited interest until 1926 when B.F. Goodrich discovered how to make sheets and adhesive from PVC-and the “vinyl-age” began
- Although polystyrene (PS) was probably first formed by Simon in 1839, it was almost 100 years later, in 1930, that the giant German company I.G. Farben placed PS on the market. PS-molded parts become commonplace
- Rohm and Haas bought out Plexiglass from a British firm in 1935 and began the production of clear plastic parts and goods, including replacements for glass as camera lenses, aircraft window, clock faces, and car taillights

Commercialization of Selected Polymers

Polymer	Year	Company
Bakelite	**1909**	General Bakelite Corp.
Rayon	**1910**	American Viscose Company
Poly(vinyl chloride)	**1927**	Goodrich
Styrene-butadiene copolymer	**1929**	I. G. Farben
Polystyrene	**1929/1930**	I. G. Farben and Dow
Neoprene	**1931**	DuPont
Poly(methyl methacrylate) (PMMA)	**1936**	Rhom & Haas

Conti….

Polymer	**Year**	**Company**
Nylon 6, 6	**1939/1940**	DuPont
Polyethylene (LDPE)	**1939**	ICI
Poly(dimethyl Siloxane)	**1943**	Dow Corning
Acrylic fiber	**1950**	DuPont
Poly(ethylene terephthalate)	**1953/1954**	DuPont / ICI
Polyurethane block copolymers (Spandex)	**1959**	DuPont
Poly(phenylene terephthalate)	**1960**	DuPont

1839

Charles Goodyear (1800-1860), American inventor

Began experiments on the hardening of rubber by heating it with sulfur. This process, which Goodyear called “vulcanization,” made hardly usable rubber gum into a major article of commerce. Independent experiments on vulcanization were carried out in Britain in the early 1840s by **Thomas Hancock** (1786-1865), who worked on the processing of rubber for over twenty years and may be fairly described as the first expert rubber technologist

1845

Christian Schönbein (1799-1868), German chemist

Prepared both nitrocellulose (cellulose dinitrate) and guncotton (cellulose trinitrate). **Theophile-Jules Pelouze** (1807-1867) had reported the reaction of cellulose with nitric acid in 1838, but SchÖnbein discovered the importance of adding sulfuric acid to nitric acid. He made article out of nitrocellulose but afterword concentrated, unsuccessfully, on the development of guncotton.

The first useful explosive from guncotton (cordite) was invented by the English chemist **Sir Frederick Abel** (1827- 1902) with **Sir James Dewar** (1842-1923) in 1889

1892

Charles Cross (1855-1935), **Edward Bevan** (1856-1991), and **Clayton Beadle** (1868-1917), British chemist

Developed viscose rayon. The British silk firm of Courtaulds, anxious to move out of the mourning crepe business, obtained the British rights to the viscose process of rayon manufacture and built a factory in Coventry in 1905. The American Viscose Company Courtaulds at Marcus Hook, Pennsylvania, in 1910, was for a decade one of the most profitable companies in America

1938

Roy Plunkett(b.1910), American chemist

With **Jack Rebok** (b. 1906) observed the formation of poly(tetrafluoroethylene) (PTFE) while working on the development of halogenated hydrocarbons as refrigerants for Kinetic Chemicals, a subsidiary of DuPont. DuPont started production of PTFE in 1943 to supply the Manhattan project with gaskets that would be resistant in the highly corrosive uranium hexafluoride Gas. After the war, PTFE was commercialized by DuPont as Teflon, and full scale production started in 1950. After years of relative obscurity, this polymer become well known as a low friction coating; the first nonstick pans appeared in 1960

For lack of Lac for Shellac

Shellac was made from a special resin secreted by the East Asian lacbug. The resin was harvested by scraping the hardened deposits from trees inhibited by the insets then processed. The search for a heap substitute for this material led Leo Baekeland (left) to Bakelite

In 1887 Count Hilaire de Chardonnet (1839-1924) revealed his discovery of a method of spinning strands of cellulose nitrate into an artificial textile fiber These first fibers were highly flammable because of their nitrogen content a quality which prompted some to label the new material “mother-in-law silk”. The Frenchman solved the problem by treating his fibers with acid sulfide solutions and Chardonnet silk the first synthetic fiber, entered commercial production in 1890

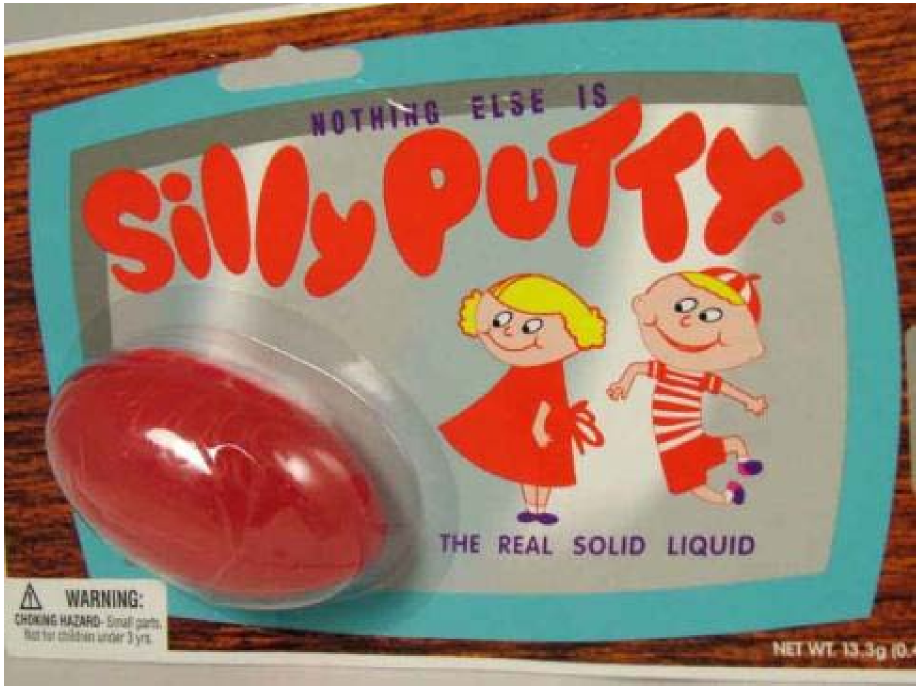
He can’t believe he ate the whole thing

The microorganism Alcaligenes eutrophus transforms sugar, ethyl alcohol, and carbon dioxide-hydrogen mixture into a special form of stored energy, a long chain polymer called PHB. Although W. R. Grace Company marketed the material in the 1950s, researchers at ICI have induced A. eutrophus to produce variants of the polymer for use in resins and films. It’s the smallest polymer factory yet

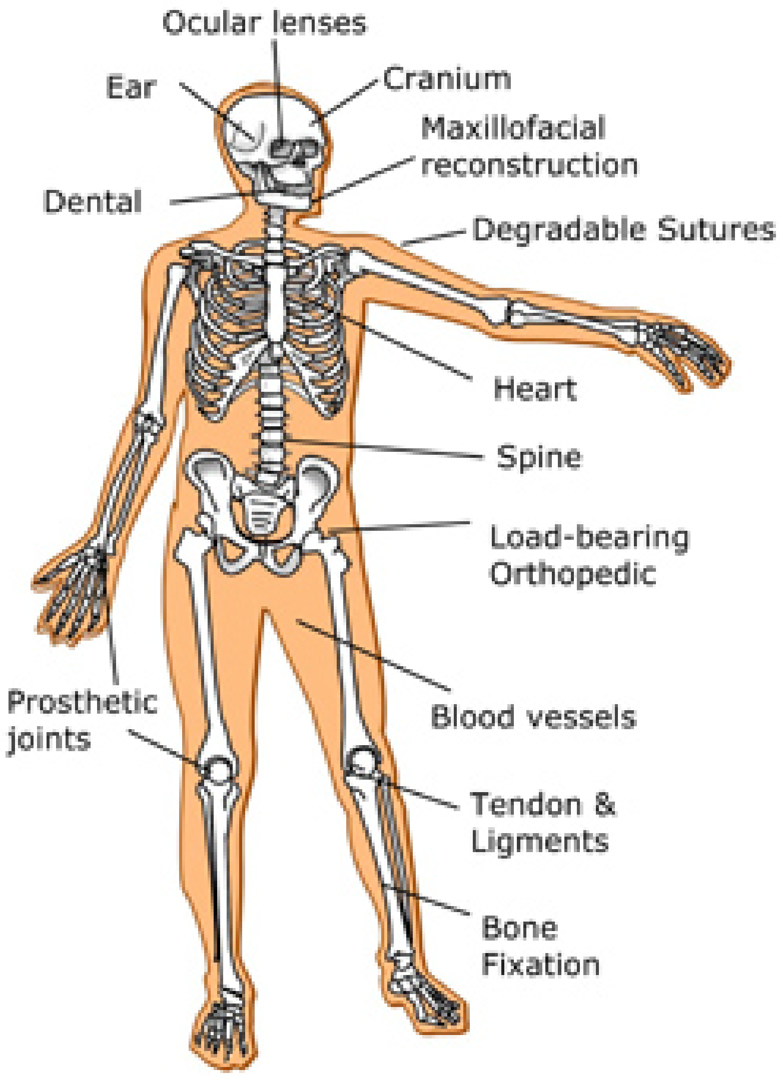
Stronger than a speeding bullet

Stephanie Kwolek, shown here with DuPont coworkers Herbert Blades, Paul Morgan, and Joseph Rivers, Jr. developed a special type of polyamide, the aramide Kevlar, which entered commercial production in the early 1970s. Aramid fibers are woven into bullet-proof vests and are now being integrated into structural components for aircraft

The "goofiest" discovery



Scientist at Dow Corning and General Electric developed silicones a family of polymers providing many applications and no small amount of fun



The six-million-dollar man?

Medicine has used versatile polymers as substitutes for skin and tendons, corneas and the human heart

Nylon's 75th Anniversary FETE

On Feb 28, 2010 at the Hagely museum & Library in Wilmington, the Delaware Academy of Chemical Sciences celebrated the 75th anniversary of the invention of nylon. On that date in 1935, organic chemist Gerard Berchet, a member of Wallace H. Carrothers' research group at the DuPont Experimental Station, prepared nylon 6,6 (a condensation copolymer made from equal parts of hexamethylenediamine and adipic acid), and a world-changing industry was born.

This synthetic fiber was first used to replace silk in women's hosiery. In world War II, nylon replaced silk in parachutes. After the war, DuPont increased nylon research and production, quickly expanding into products such as clothing, carpeting, tire cord, seat belts, sporting goods, and home furnishings.

Nylon becomes a major moneymaker and led DuPont to establish its textile fibers department, which introduced Dacron, Orlon, Lycra, and Kevlar. “These synthetic fibers changed our world in many ways and were a far cry from cotton, wool, and linen, the ‘natural’ ‘fibers,” says Allen A. Denio, organizer of the event, cofounder of the Delaware Academy, and councilor for the ACS Delaware Section.

Carothers was a highly respected organic chemist who earned his doctorate at the University of Illinois under Roger Adams in 1924. He continued his research there until 1926, when he accepted a position at Harvard University. He then moved to a new research lab, informed called “Purity Hall,” at the DuPont Experimental Station in 1928.

INNOVATORS

Connelly (From Left), Stemniski and Joseph X. Labovsky

Joseph X. Labovsky, 97, the last survivor of Carothers' research group, was the ceremony's guest of honor. Labovsky was hired as a laboratory assistant by Carothers, and they shared a love of Russian music and literature. "Joe had come to Wilmington at age 12 from the Ukraine. Carothers had helped him receive a college scholarship and was impressed by his great work ethic and laboratory skill," Denio says.

"DuPont should be recognized for hiring Dr. Carothers. He told them about his mental health problem involving episodes of deep depression, but he was hired anyway. During his employment he suffered periodic 'spells' when he would be absent, in some cases under hospital care. DuPont provided continuing support until his suicide in 1937," Denio says.

CELEBRATION

Stephanie L. Kwolek (left) and Denio

Stephanie L. Kwolek, who invented Kevlar as a research chemist in the textile fibers department at DuPont, was also honored at the event. The celebration was attended by DuPont Chief Innovation Officer Thomas M. Connelly Jr. and New Castel County Executive Christopher A. Coons, who presented a proclamation thanking Carothers and Labovsky for “their great contribution to society.”

Dilemma of an Innovator

Ideas may be considered revolutionary or pedestrian

Faces humiliation

Genius prefer homogeneity of individuals rather than heterogeneity of groups. We in the universities have the spiritual freedom to try new ideas

Small firms have therefore greater propensity to take risks

- **Sustainable innovation will require sweeping changes at all levels of society from the school room and the playground, to the boardroom and executive suites, to the hallways of New Delhi**

- **Knowledge for vision: Vision for Knowledge**

Chronological Developments of Commercial Polymers (up to 1982)

Before 1800	Cotton, flax, wool, and silk fibers; bitumens caulking materials; glass and hydraulic cements; leather and cellulose sheet (paper); natural rubber (*Hevea Brasiliensis*), gutta percha, balata, and shellac
1839	Vulcanization of rubber (Charles Goodyear)
1845	Cellulose ester (Schonbein)
1846	Nitration of cellulose (Schonbein)
1851	Ebonite (hard rubber; Nelson Goodyear)
1860	Molding of shellac and gutta percha
1868	Celluloid (plasticized cellulose nitrate; Hyatt)
1888	Pneumatic tires (Dunlop)
1889	Cellulose nitrate photographic films (Reinchenbach)

1890	Cuprammonia rayon fibers (Despeisses)
1892	Viscous rayon fibers (Cross, Bevan, and beadle)
1903	First tubeless tire (Litchfield of Goodyear Tire Co.)
1897	Poly(phenylene sulfide)
1901	Glyptal polyesters
1907	Phenol-formaldehyde resin (Bakelite; Baekeland)
1908	Cellulose acetate photographic films
1912	Regenerated Cellulose sheet (cellophane)
1913	Poly(vinyl acetate) (PVAc)
1914	Simultaneous interpenetrating network (SIN)
1920	Urea-formaldehyde resins
1923	Cellulose nitrate automobile lacquers

1924	Cellulose acetate fibers
1926	Alkyd polyester (Kienle)
1927	Poly(vinyl chloride) (PVC) wall covering
1927	Cellulose acetate sheet and rods
1927	Graft copolymers
1928	Nylon (Carothers; DuPont)
1929	Polysulfide synthetic elastomer (Thiokol; Patrick)
1929	Urea-formaldehyde resins
1930	Polyethylene (Friedrich/Marvel)
1931	Poly(methyl methacrylate) (PMMA) plastics
1931	Polychloroprene elastomer (Neoprene; Carothers)

1934	Epoxy resins (Schlack)
1935	Ethylcellulose
1936	Poly(vinyl acetate) (PVAc)
1936	Poly(vinyl butyral) (safety glass)
1937	Polystyrene (PS)
1937	Styrene-butadiene (Buna-S) and syrene-acrylonitrile (SAN) (Buna-N) copolymer elastomers
1939	Melamine-formaldehyde (MF) resins
1939	Nylon-6 (Schlack)
1939	Nitrile rubber (NR)
1940	**Isobutylene-isoprene elastomer (butyl rubber; Sparks and Thomas)**

1941	Low-density polyethylene (LDPE)
1941	Poly(ethylene terephthalate) (PET)
1942	Butyl rubber
1942	Unsaturated polyesters (Elis and Rust)
1943	Fluorocarbon resins (Teflon; Plunket)
1943	Silicones
1945	Styrene-butadiene rubber (SBR)
1946	Polysulfide rubber (Thiokol)
1948	Acrylonitrile-butadiene-styrene (ABS) copolymers
1949	Cyanoacrylate (Goodrich)
1950	Polyester fibers(Whinfield and Dickson)

1950	Polyacrylonitrile fibers
1952	Block copolymers
1953	High impact polystyrene (HIPS)
1953	Polycarbonates (Whinfield and Dickson)
1956	Poly(phenylene ether); poly(phenylene oxide) (PPO) (General Electric)
1957	High-density polyethylene (HDPE)
1957	Polypropylene
1957	Polycarbonate
1958	Poly(dihydroxymethycyclohexyl terephthate) (Kodel; Eastman Kodel)
1960	Ethylene-propylene monomer (EPM) elastomers

1961	Aromatic nylons (aramids) (Nomex; DuPont)
1962	Polyimide resins
1964	Poly(phenylene oxide)
1964	Ionomers
1965	Polysulfone
1965	Styrene-butadiene block copolymers
1966	Liquid crystals
1970	Poly(butylene terephthalate)
1974	Polyaetylene
1982	Polyetherimide (General Electric)
1991	Carbon nanotubes (Iijia; NEC Lab)

- **There is no innovation that is more important for the world than the development of young minds**