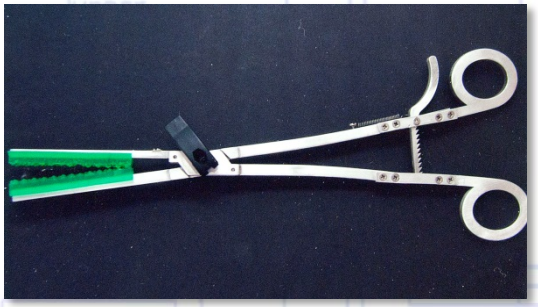
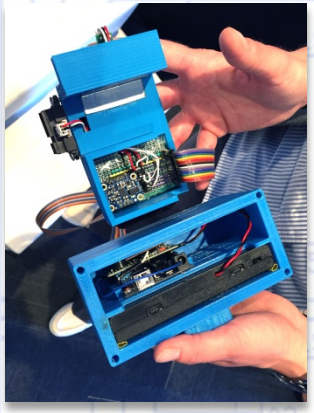
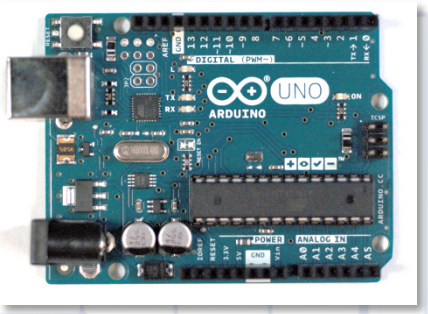
Introductory Medical Device Prototyping

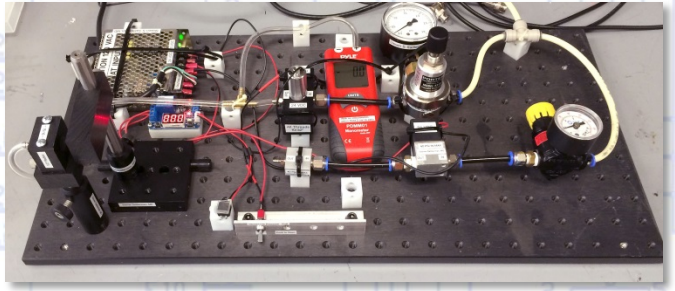
Medical Device Polymers

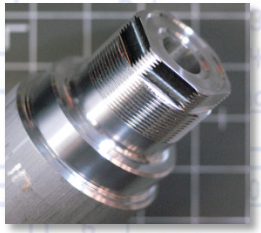
Prof. Steven S. Saliterman, http://saliterman.umn.edu/
Department of Biomedical Engineering, University of Minnesota









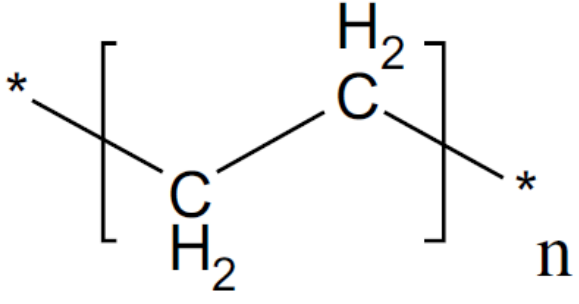


Medical Device Polymers

- **Polyolefins**
  - Polyethylene (PE)
  - Polypropylene (PP)
  - Cyclic Olefin Copolymers (COCs)
  - Polyvinyl Chloride (PVC)
- **Polystyrene/styrenics**
  - Polystyrene
  - Poly(acrylonitrile-co-butadiene-co-styrene) (ABS)
  - Polyacrylate (Acrylic, PMMA)
  - Polycarbonate (PC)
  - Polyurethanes
  - Polyformaldehyde (POM) (Delrin or Acetal)
- **Polyamides**
  - Polyamide (Nylon 6)
  - Poly(hexamethylene adipamide) (Nylon 66)
  - Polyether Block Amide (PEBA)
- **Polyesters**
  - Poly(butylene terephthalate) (PBT)
  - Poly(ethylene terephthalate) (PET, PETG)
- **High-Temp Thermoplastics**
  - Polysulfone (PSF)
  - Polyimide (PI) (Kapton)
  - Poly(ether ether-ketone) (PEEK)
- **Fluoropolymers**
  - Poly(tetrafluoroethylene) (PTFE) (Teflon), PVDF, FEP, ePTFE
- **Elastomers**
  - Silicones
  - Thermoplastic elastomers (TPE): TPA (polyamide TPE), TPC (copolyester TPA), TPO (olefinic TPE), TPS (styrenic TPE), TPU (urethane TPE), and TPV (vulcanized TPE).
- **Poly-p-xylylene (Parylene)**
- **Biopolymers**
  - Polylactic Acid (PLA)
  - Polyglycolic Acid (PGA)
- **Others** – PANI, PPy, PVAC, PEG

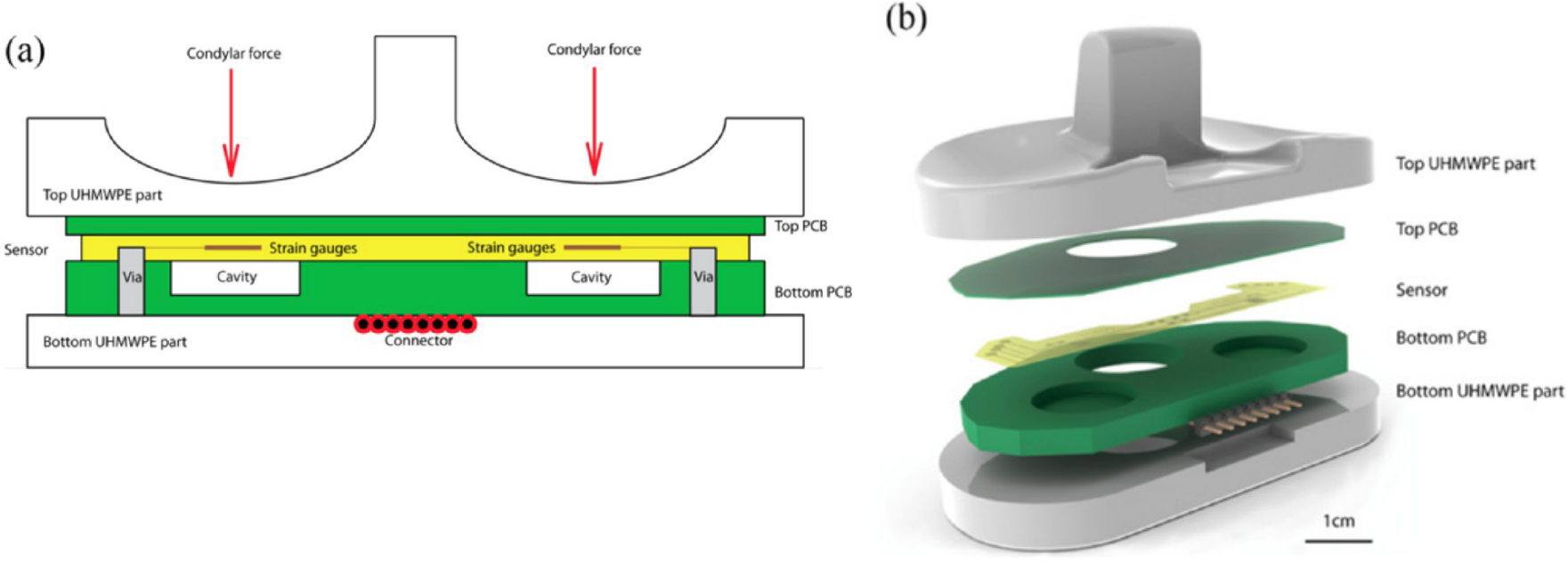
Polyethylene (PE)…

- Semi-crystalline material with good resistance to organic solvents, degreasing agents, and electrolytes.
  - It is resistance to wear, fatigue, and staining; and has low moisture absorption. PE is nontoxic and floats on water.
  - Graded as low density (LDPE), high density (HDPE) and ultra-high molecular weight (UHMWPE). The latter are self-lubricating, shatter resistance, machinable, and may be sterilized in steam



Boedeker Plastics Inc., 2004

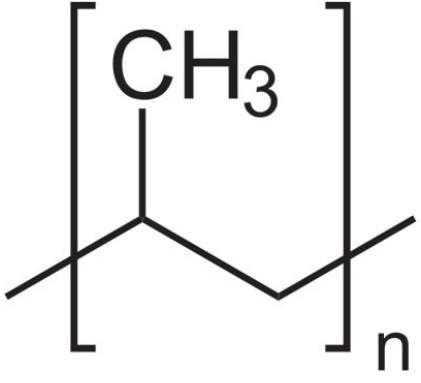
- Knee implant study device with stain gages made from UHMWPE.

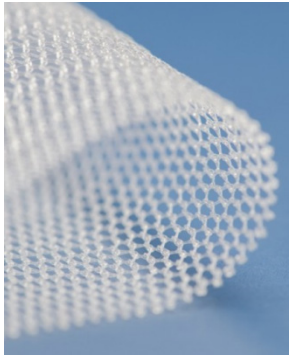


Forchelet, D.; Simoncini, M.; Arami, A.; Bertsch, A.; Meurville, E.; Aminian, K.; Ryser, P.; Renaud, P. Enclosed Electronic System for Force Measurements in Knee Implants. Sensors 2014, 14 (8), 15009−15021.

Polypropylene (PP)…

- Thermoplastic that is it is rugged, flexible and unusually resistant to many chemical solvents, bases and acids.
  - A relatively slippery "low energy surface" means that most adhesives will not stick to it.
  - Chain degradation may occur from UV light.

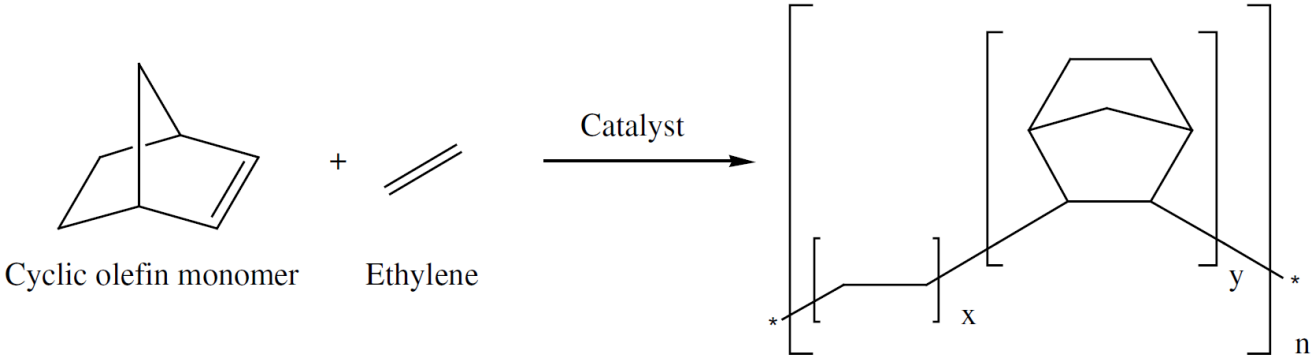




(Left) Image courtesy of Vitlab
(Right) Image courtesy of Pahacel

Cyclic Olefin Copolymers (COCs)…

- Highly transparent thermoplastics.
  - The incorporated ring structure gives COCs their stiffness, while its size prevents the molecules from becoming ordered enough to crystallize.
  - The total absence of crystallinity ensures very high transparency. Because the copolymers are olefinic, they have low densities, close to 1.0, resulting in a very high stiffness-to-weight ratio.
  - By adjusting the ratio of the co-monomers, COCs can be produced with a wide range of heat deflection temperatures.



Cyclic olefin monomer + Ethylene

Cyclic olefin copolymer

- Topas Advanced Polymers® produces a cyclic olefin copolymer elastomer for flexible applications that require high barrier properties, purity, and chemical resistance.

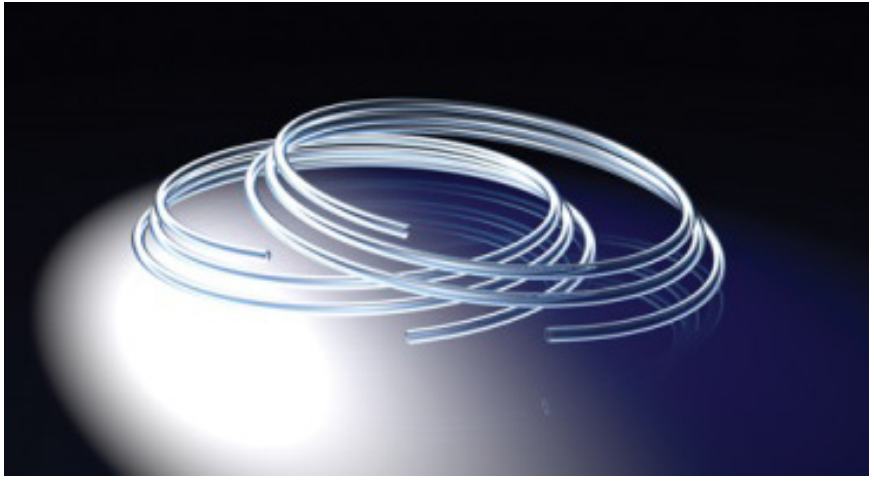


Image courtesy of Topas

Poly(vinyl chloride) (PVC)…

- Amorphous themoplastic that has excellent corrosion resistance.
  - It has a high strength-to-weight ratio, and is a good electrical and thermal insulator. It is easily machined, solvent cemented, and shaped.
  - The plasticizer employed in PVC may cause inflammatory response when used as an implantable material.

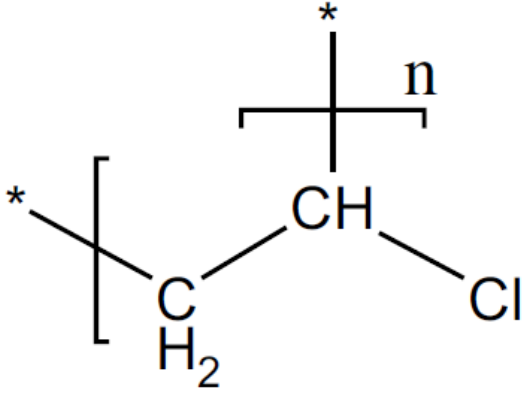
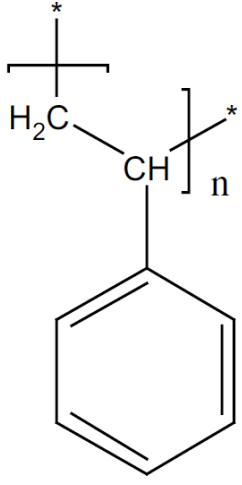


Image courtesy of Lubrizol.

Polystyrene (PS)…

- Amorphous transparent thermoplastic that may be processed by injection, blow molding, and vacuum molding.
  - It offers excellent electrical resistance and is resistant to alkalies, salts, lower alcohols, and weak acids.
  - FDA complaint for foods.



Boedeker Plastics Inc., 2004

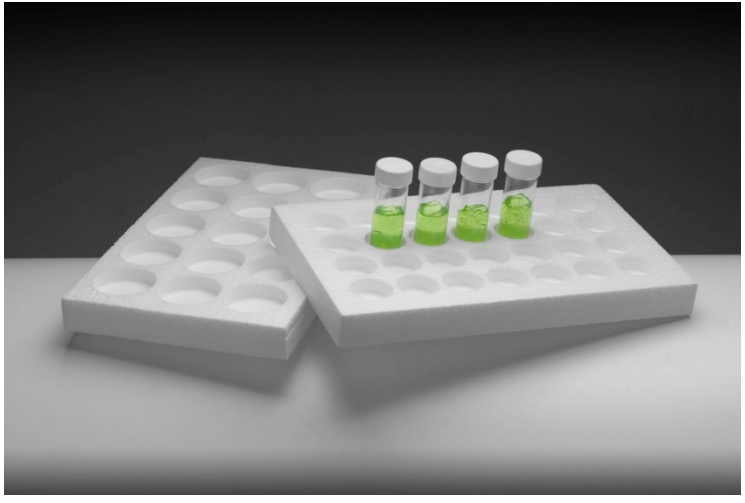
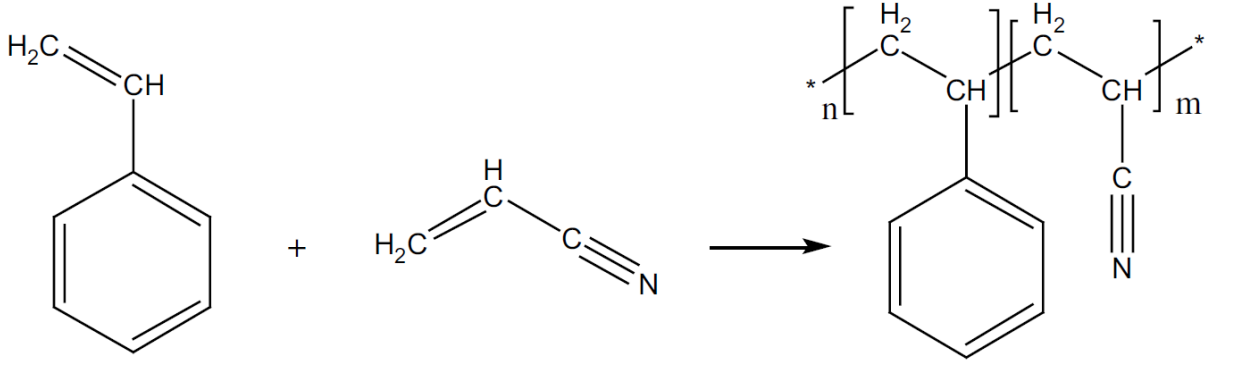


Image courtesy of Gmpolystyrene

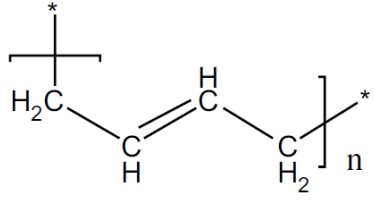
Image courtesy of Prosource Scientific

Poly(acrylonitrile-co-butadiene-co-styrene) (ABS)…



Styrene Acrylonitrile Poly(styrene-co-acrylonitrile) (SAN)

+



Polybutadiene

ABD is strong & light weight.

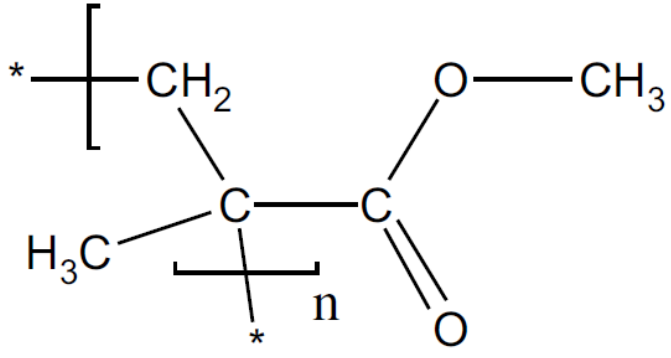
ABS
(SAN branches grafted into
the polybutadiene backbone)

- ABS-M30i works with 3D FDM Technology to build functional prototypes, tooling and production parts that can be gamma or EtO sterilized.

Image courtesy of Stratasys

Poly(methyl methacrylate) (PMMA) (Plexiglass)…

- Monofunctional monomer methyl methacrylate (MMA) and Poly(methyl methacrylate) (PMMA) (Plexiglass) (and mixtures with MMA)
  - Orthodontic appliances and bone “cement.”
  - Adhesives and bonding resins - 2-Hydroxyethyl Methacrylate (HEMA)
- Excellent optical properties, including UV stabilization, and resistance to moisture, detergents, cleaners, dilute inorganic acids, alkalies, and aliphatic hydrocarbons.
  - May be machined, heated, formed, and solvent cemented with clear joints.
  - Should not be used with chlorinated or aromatic hydrocarbons, esters, or ketones

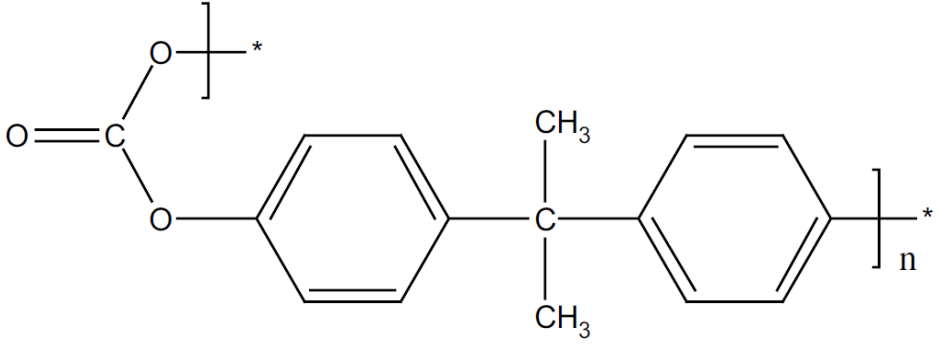


Boedeker Plastics Inc., 2004

Image courtesy of ePlastics, Ridout Plastics Co. Inc.

Poly(bisphenol A carbonate) (Polycarbonate)…

- Amorphous highly transparent thermoplastic with properties of high impact strength, low moisture adsorption, good heat resistance, good rigidity and electrical properties, and high creep.
  - PC is a good low frequency and high voltage insulator, making it suitable for electrical and electronic components.
  - PCs are graded by addition of various amounts of glass fibers. These increases tensile strength, stiffness, compressive strength, and lowers the thermal expansion coefficient.

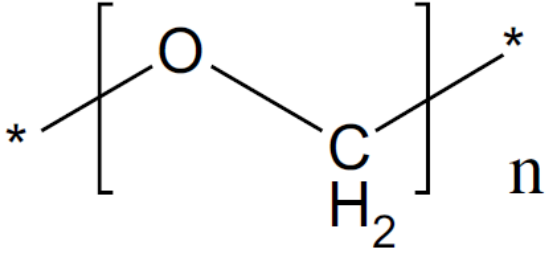


- LNP Lubricomp ® is a 30% carbon fiber reinforced PC resin from SABIC for replacing metal in scalpels and other components.

Image courtesy of SABIC

Polyformaldehyde (POM) (Delrin or Acetal)…

- Also known as polyoxymethylene.
  - High crystallinity and linear structure, and is resistant to thermal and oxidizing destruction.
  - It has high viscosity, hardness, rigidity, good temperature constancy and anti-frictional properties. It has replaced metals in a number of applications.
  - POM's solvent resistant properties and good dimensional stability enable it to be used in gear wheels, dry-run bearings, precision measuring devices, cameras, and microscopes.



- Prototype made from medical grade ABS, polycarbonate and Delrin.

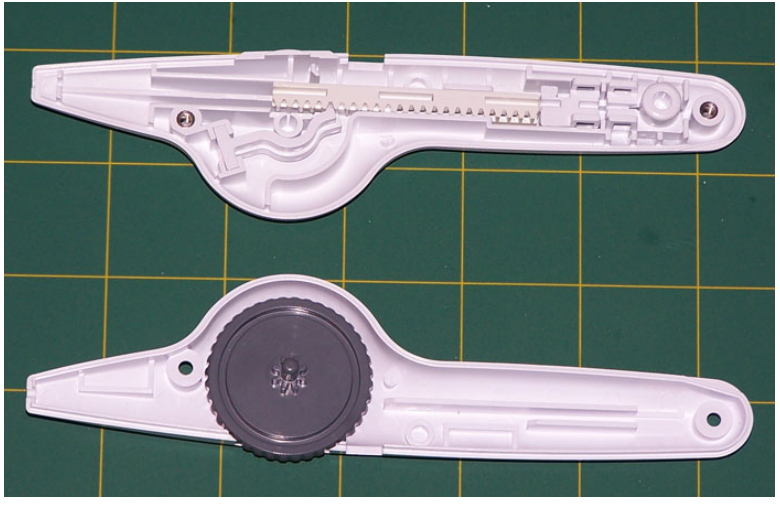
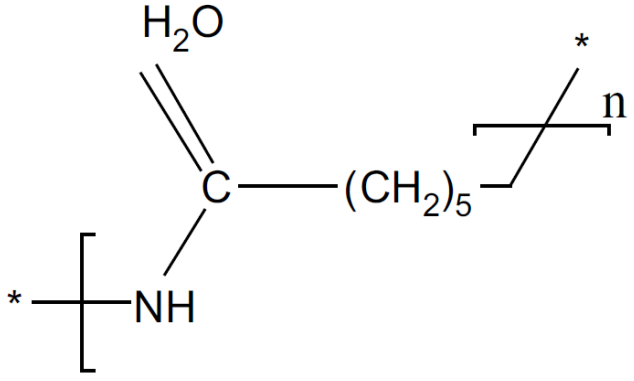


Image courtesy of Phoenix Proto.

Polyamide (Nylon 6)…

- Semi-crystalline thermoplastics with extremely good wear resistance, and are frequently used as replacements for bronze, brass, aluminum, steel, and other metals.
  - They are very light weight for their strength, have high impact resistance, high heat-distortion temperature, and are resistant to alkalies, dilute acids, and oxidizing agents.
  - Nylons are graded as being either unfilled or filled with molybdenum disulfide, oil, or both.



- Akulon® Polyamide 6 is being used in medical device packaging concepts.
  - It is a tough, strong thermoplastic that offers outstanding mechanical strength and barrier properties.

Image courtesy of DSM

Poly(hexamethylene adipamide) (Nylon 66)…

- Nylon 66 shares similar properties to Nylon 6, and is resistant to impact and abrasion, organic solvents, and petroleum products.
  - Polyamides can be processed by injection molding, extrusion, and blow molding.
  - Fibers may be created by a melt-spin process.

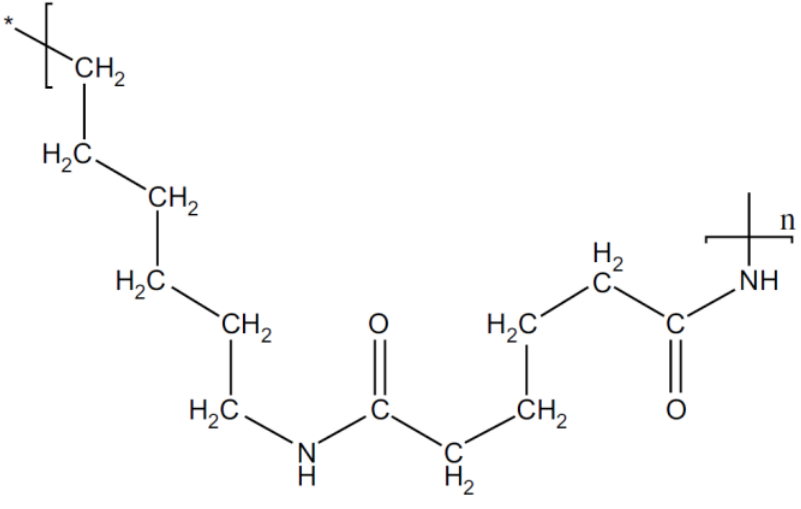


Image courtesy of Alibaba and Henan Jinhang

Polyether Block Amide (PEBA)…

- Copolymer of polyamide and polyethylene

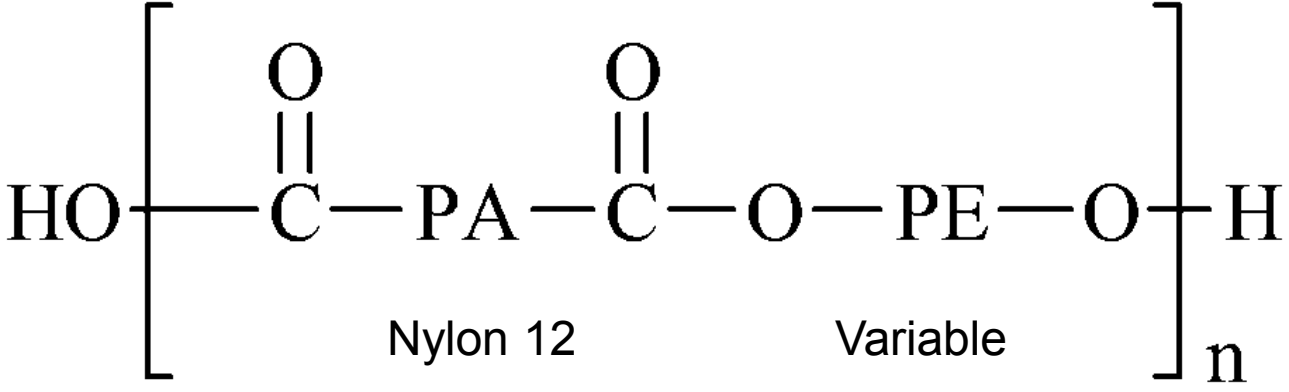


Image courtesy of RSC Advances

- Applications for Arkema Pebax® MED include catheters (angioplasty, stent-delivery, diagnostic, ablation…), balloons, tubes (peristaltic pumps, connecting tubes, colonoscopes, hearing aids…) and small-dimension molded parts.

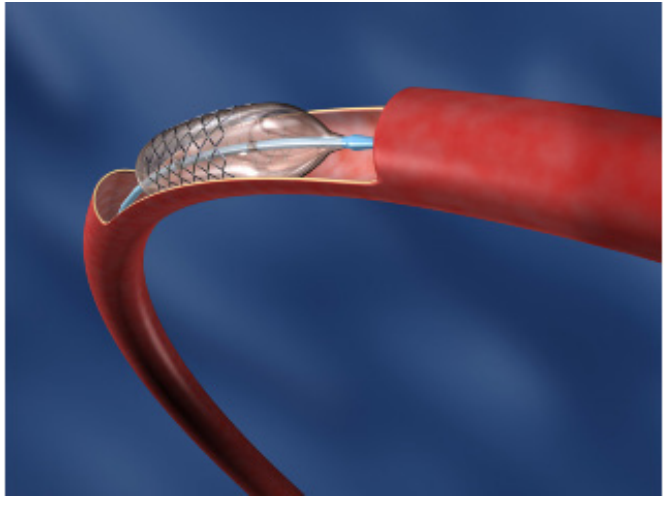
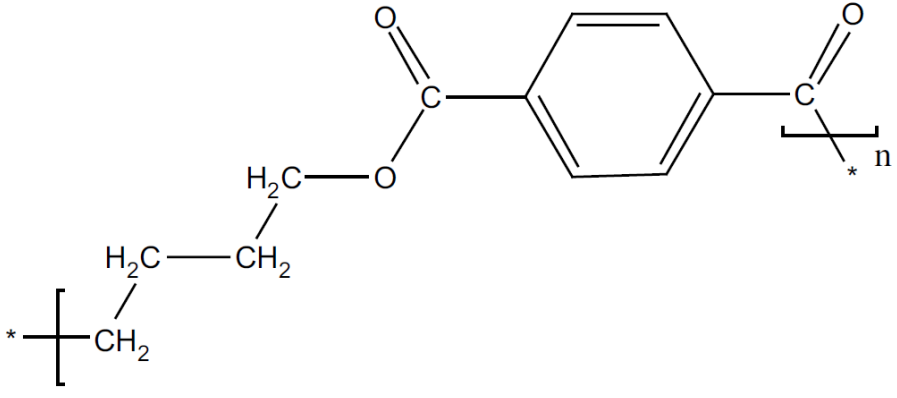


Image courtesy of Arkema

Poly(butylene terephthalate) (PBT)…

- PBT is a semi-crystalline thermoplastic with good impact resistance and toughness, low coefficient of friction and wear, and does not need lubrication.
  - It also is resistant to chemicals, chlorine, water, and steam. PBT is FDA and USDA compliant for food handling.

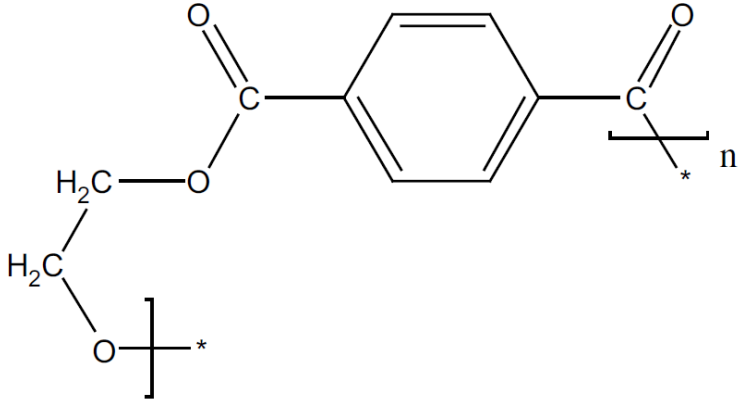


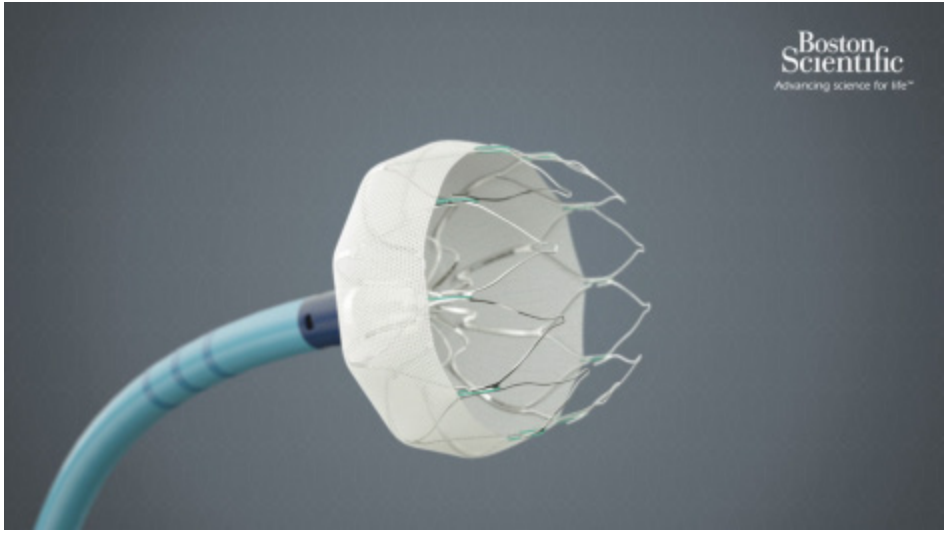
- BASF's Ultradur® B4520 PRO PBT for injection-molding.
  - Sterilized with ionizing gamma radiation or ethylene oxide
  - Can easily be printed on.
  - Broad chemical resistance to polar and non-polar solvents.
  - Low water/moisture absorption.
  - Ideal sliding, due to high friction and wear resistance (depending on the sliding partner).
  - Excellent heat aging behavior.

Image courtesy of BASF

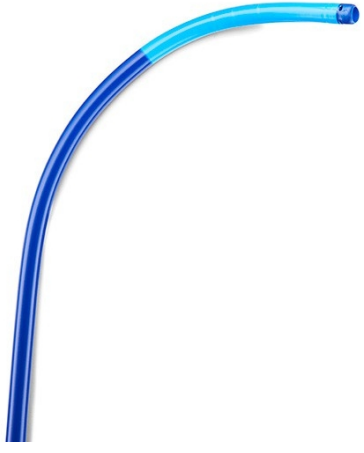
Poly(ethylene terephthalate) (PET)…

- PET is a semi-crystalline transparent thermoplastic with excellent wear resistance, low coefficient of friction, high strength, and resistance to moderate acid solutions.
  - It is resistant to chlorine-water sterilization, and is FDA and USDA compliant for food handling





The WATCHMAN® LAAC Device is a catheter-delivered heart implant designed to close the left atrial appendage (LAA). PET knit fabric mesh.

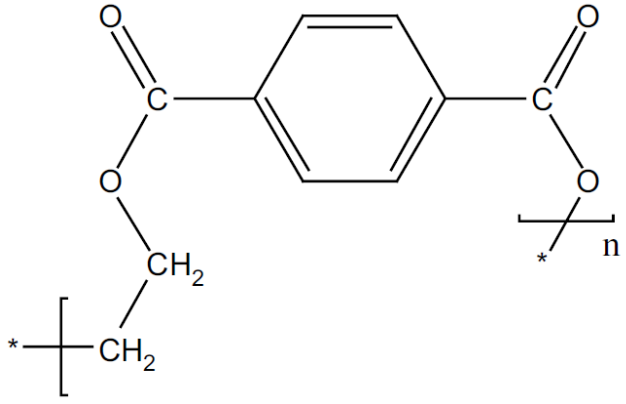


Access sheath is made from Polytetrafluoroethylene (PTFE) (Teflon)

Images courtesy Boston Scientific.

Poly(ethylene terephthalate glycol) (PETG)…

- Transparent copolyester with very high impact resistance.
  - Spectar is the brand name for extruded sheets.
  - It is a tough, clear, chemically resistant material that is FDA approved for food contact.
  - PETG may be machined, heated, vacuumed formed, and cut with conventional tools. It may be screen printed, painted, and hot stamped.



Boedeker Plastics Inc., 2004

- Bouton Optical® PETG (Polyethylene Terephthalate Glycol) Safety Visor.

Image courtesy of Bouton

Polysulfone (PSF)…

- Amorphous thermoplastic with high strength, high dimensional stability, and has high resistance to mineral acids, alkali, and salt solutions.
  - The resistance to detergents and hydrocarbon oils is good, even at elevated temperatures under moderate stress levels.
  - Not resistant to polar organic solvents such as ketones, chlorinated hydrocarbons, and aromatic hydrocarbons.

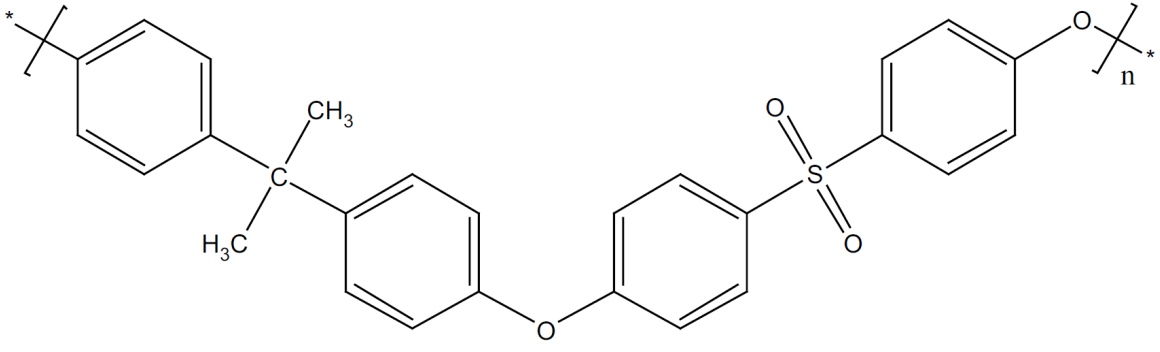


Image courtesy of Cole-Palmer

Polyimide (PI) (Kapton)…

- Polyimides are thermoplastic films with good dimensional stability and excellent chemical resistance.
  - They may be etched with RIE in oxygen and laser cut.
  - PI is especially useful in micromachined devices requiring flexible hinges and similar support structures, and for dielectric layers.

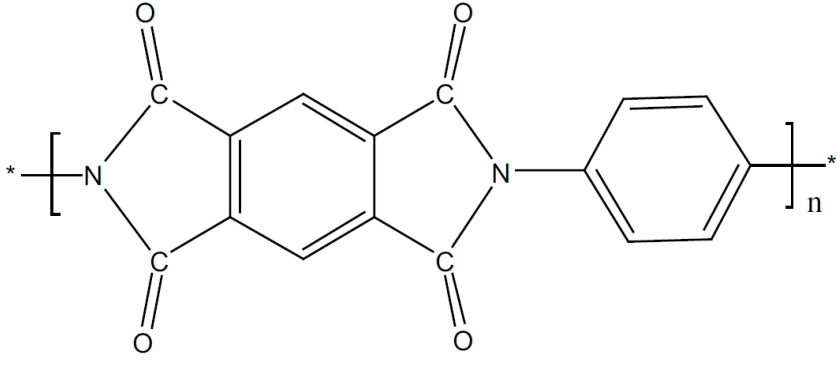
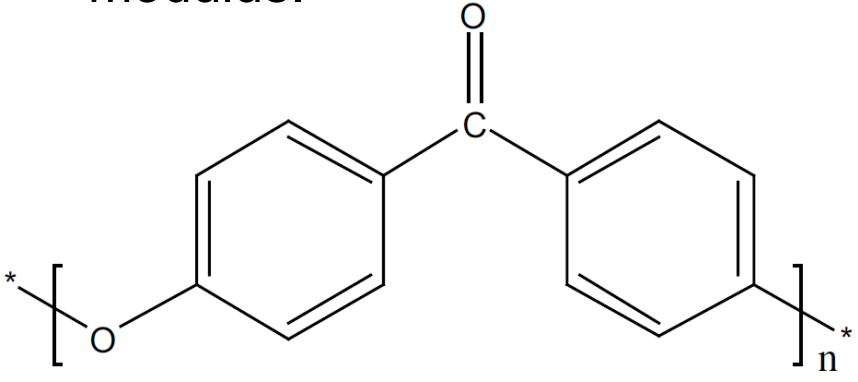


Image courtesy of Thomasnet.com

Poly(ether ether-ketone) (PEEK)…

- Semi-crystalline thermoplastic with excellent chemical resistance, very low moisture absorption, and is unaffected by continuous hot steam or water
  - Graded based on its filler. Unfilled PEEK is light brown or black and is FDA approved for contact with food. Glass filled (30%) PEEK reduces expansion and increases the flexural modulus.



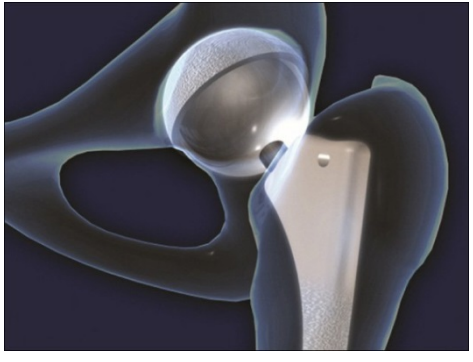


Image courtesy of Invibio.

Poly(tetrafluoroethylene) (PTFE) (Teflon)…

- High chemical resistance, low and high temperature capability, low friction, and is a good electrical and thermal insulator.
  - Various forms are used in vascular grafts, tubing, catheters, introducers, issue repair meshes, sutures, coatings and other implants.
  - It can not be melted; it must be compressed and sintered to form useful shapes.
  - PTFE is grade based on fillers, including glass fibers, carbon, graphite, molybdenum disulphide, and bronze

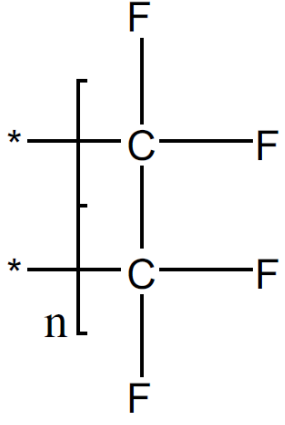
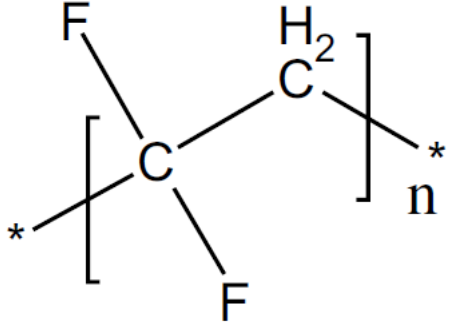
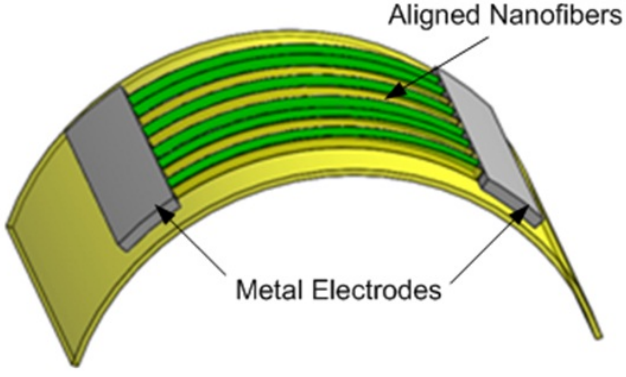


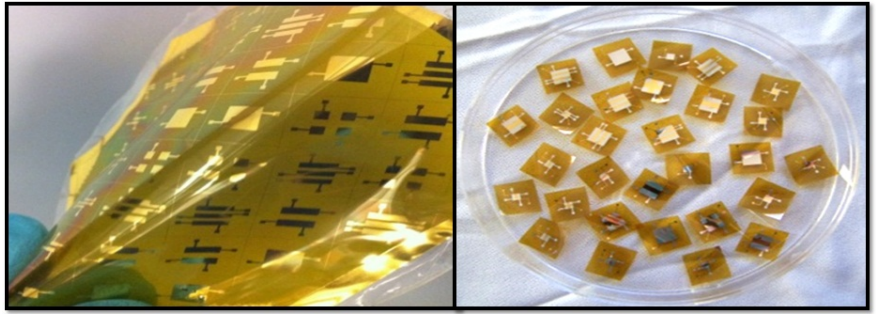
Image courtesy of Precision Coating Boedeker Plastics Inc., 2004

Poly(vinylidene fluoride) (PVDF)…

- PVDF is a high molecular weight, semi-crystalline thermoplastic with good thermal stability, high tensile strength and impact resistance, and is soluble in highly polar solvents.
  - Used to make piezoelectric films that produce voltage or charge proportional in both amplitude and frequency to applied dynamic strain. Piezo films also change dimensions in response to applied voltage, again in direct proportion to the amplitude and frequency of the applied voltage. This makes them ideal for transducers.





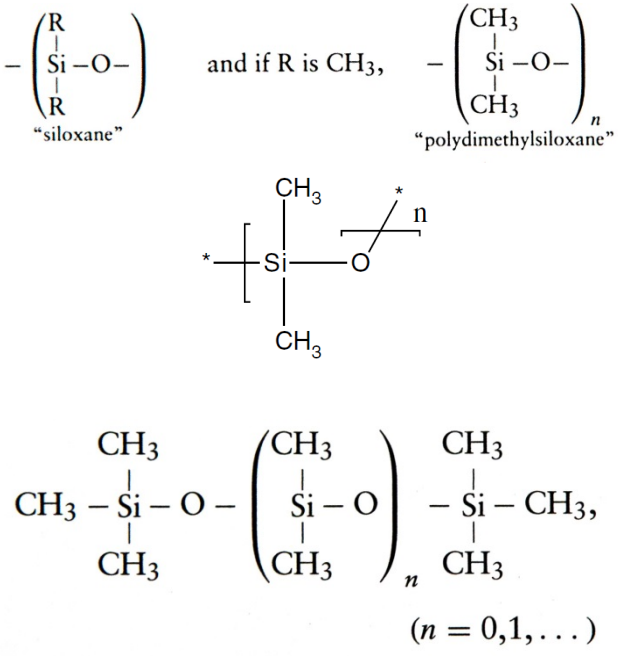


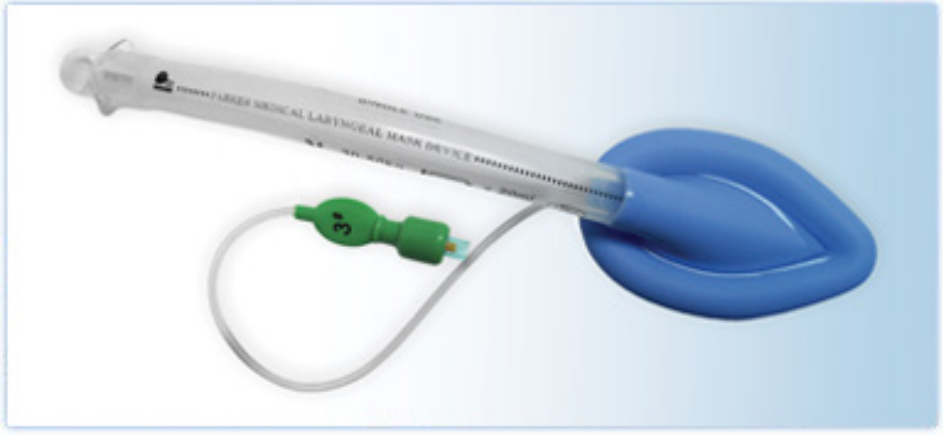
- Zhang Research Group® created nanostructures by electrospinning PVDF-TrFE (poly(vinylidene difluoride-tetrafluoroethylene) fibers.
  - These have been tested for use as endovascular sensors.

Image courtesy of Zhang Research Group

Poly(dimethyl siloxane) (PDMS, Silicone)…

- Poly(dimethyl siloxane) and Trimethylsilyloxy end-blocked polydimethylsiloxanes.
  - Backbone of repeating silicon and oxygen bonds.
  - “Siloxane” is the basic repeating unit, and “R” can be substitute by methyl, phenyl, vinyl and trifluoropropyl groups.
  - Thermosetting material – typically mixed from “Part A and B” materials in specific ratios and cured.
  - Silicones have excellent biocompatibility and biodurability.
  - Flexible.
  - Lower tensile strength or tear resistance compared to polyurethanes.
  - Degrade in strongly acidic or basic environments.
  - Like all hydrophobic materials they become quickly coated with proteins when placed in tissue contact.
  - Silicone gels are used for breast, testicular and other soft tissue implants.
  - Silicone adhesives are used in bonding and soft skin adhesives to the skin.
  - Useful in mold making.



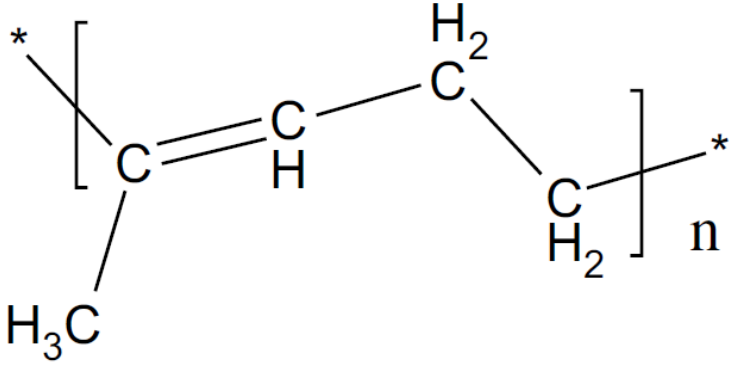


- Parker’s disposable silicone laryngeal mask device.
  - 100% medical-grade silicone device enables easy insertion and is designed to produce an effective seal.

Image courtesy of Parker.

Cis-1,4-polyisoprene…

- Used for synthetic rubber that does not contain proteins present in natural rubber or sulfur components used in vulcanization.
  - Dip-molded medical devices are at less risk for causing allergic reactions seen with natural rubber.



- Cariflex® polyisoprene medical stoppers and gloves.

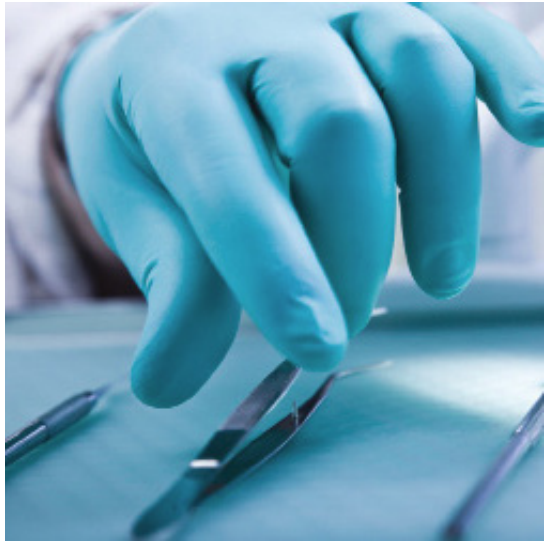
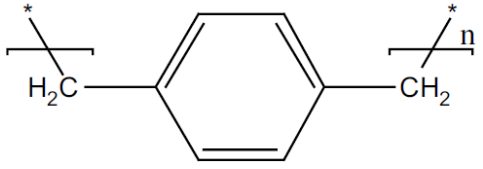


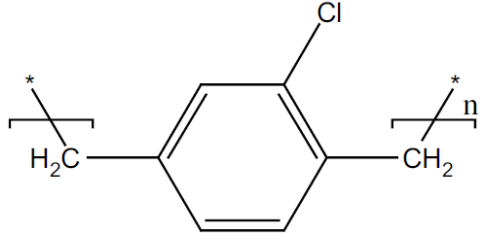
Image courtesy of Cariflex

Parylene…

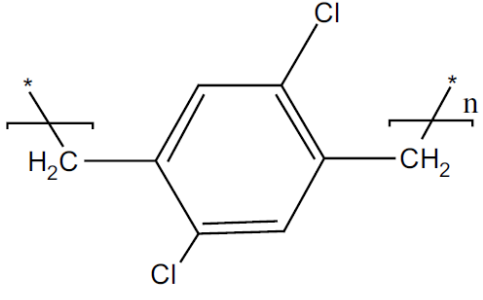
- Conformal coatings of several micrometers to several millimeters may be deposited.
  - Parylene N is a good dielectric, exhibiting very low dissipation factor, high dielectric strength, and a frequency independent dielectric constant.
  - Parylene C has very low permeability to moisture and corrosive gases, and is used for conformal insulation.
  - Parylene D has the added ability of withstanding high temperatures.



Parylene N

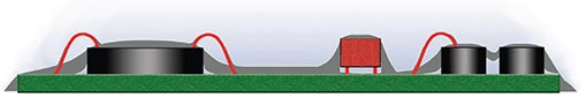


Parylene C



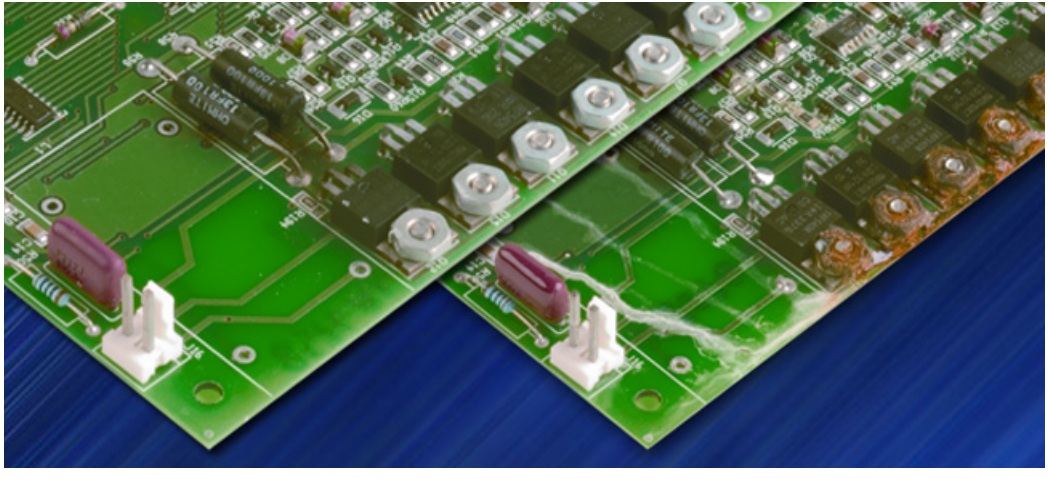
Parylene D

Liquid vs. Parylene Coating



Liquid Coating

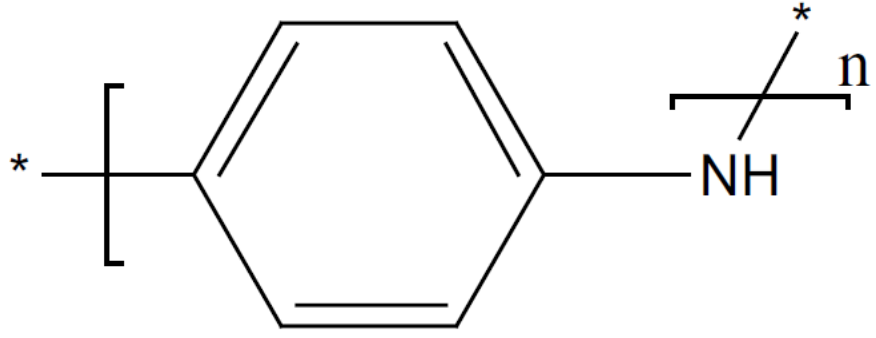
Parylene Coating



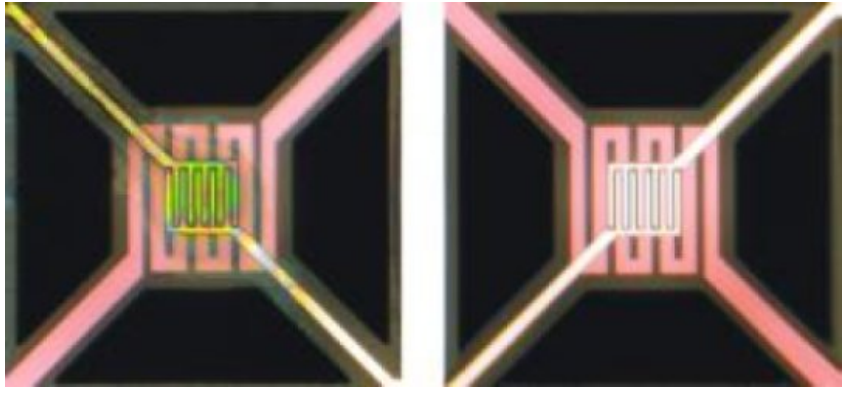
Images courtesy of Specialty Coating Systems

Polyaniline (PANI)…

- Polyaniline is a conductive polymer.
  - Conductivity results from a process of partial oxidation or reduction.
  - There are several forms that differ in chemical and physical properties.



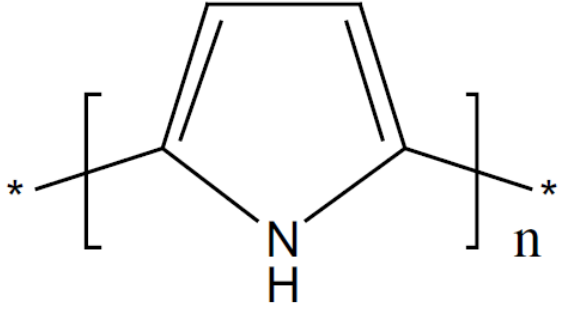
- Images of two NIST (National Institutes of Science) microheater devices, each about 100 micrometers wide.
  - On the left is a microheater coated with a conducting polymer, polyaniline, which is naturally green in color. On the right is an identical microheater with no coating.
  - The process produces a sponge-like coating that efficiently captures gaseous molecules.
  - As the microheaters cycle through a series of temperatures, changes in electrical resistance are used to detect toxic gases at part per billion levels



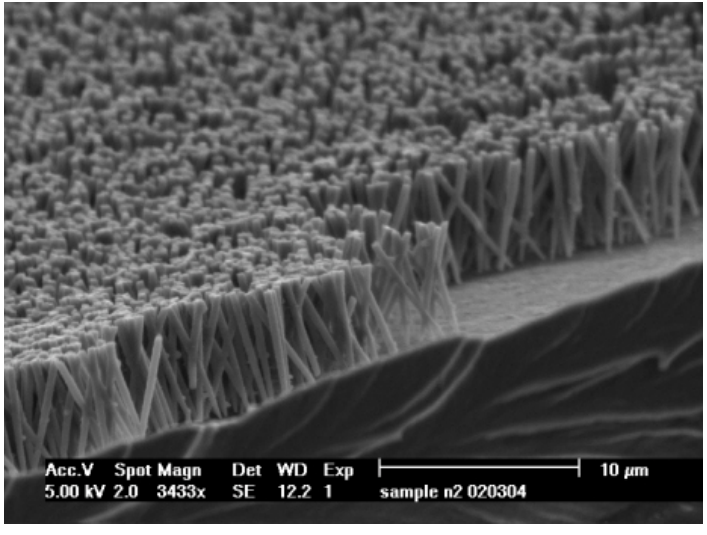
Science Daily, New gas sensors patterned with conducting polymer, 4/23/20015

Polypyrrole (PPy)…

- Polypyrrole is a conductive polymer like polyaniline.
  - Both of these materials may be useful for electrochemical sensors.
  - Used as a radar absorbing material – converting electromagnetic energy into heat.



- Scanning electron micrograph of 5.4 mm long polypyrrole nanotubes (grown 500 secondes in a template with 200 nm pores).



Pierre R. Marcoux*, László Forró, *XIXth International Winterschool on Electronic Properties of Novel Materials, Kirchberg (Autriche)*, **March 2004**.

Poly(vinyl acetate) (PVAC)…

- Polyvinyl ester – type of thermoplastic.
- Used primarily in adhesives (glue), both emulsion and hot-melt types.

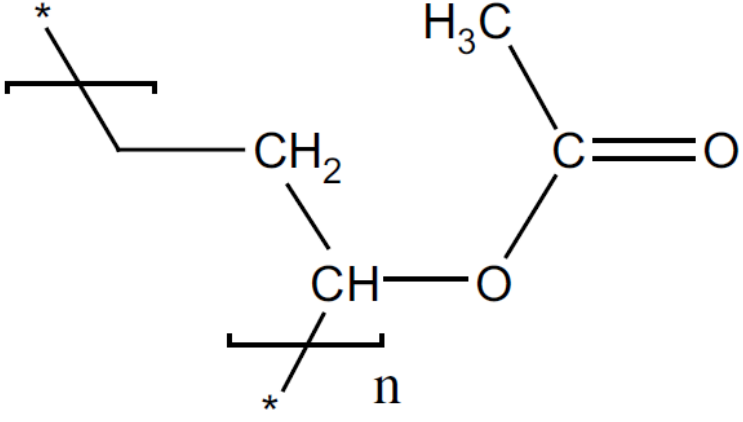
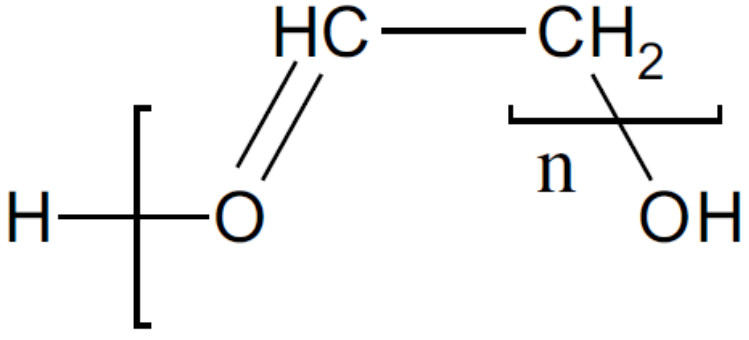


Image courtesy of Dakka

Poly(ethylene glycol) (PEG)…

- Biocompatible polymer with both clinical and research applications.
  - Commonly used in water for oral ingestion to cleanse the bowel in preparation for colonoscopy. Biodegradeable.
  - PEG and its copolymers [e.g., poly(ethylene glycol terephthalate)/ poly(butylene terephthalate) (PEGT/PBT)] have been used extensively in surface modification and tissue engineering.



Images courtesy of MiraLAX

Polymer Mechanical Properties…

Table 4. Comparison of Mechanical Properties of Commercially Available Polymers Used in Medical Implants and Devices[32,33]

	unit	bending strength (MPa)	compressive strength (MPa)	density (kg/m^3)	elongation (%)	fatigue failure (MPa)	friction coeficient	impact strength (J/cm)	shear modulus (MPa)	tensile strength (MPa)	yield strength (MPa)	Young's modulus (MPa)
PVDF	min	94		1780	20		0.34	1		50		2100
	max	94		1780	25		0.34	2		57		2900
HDPE	min	20		940	180	18	0.25	0.27	700	20		600
	max	45		965	1000	20	0.3	10.9	800	32		1400
LDPE	min	10		910	600		0.3		100	8	15	200
	max	40		928	650		0.5		350	12	20	400
PP-Copolymer	min	32	38	902	200	24	0.3	0.27	300	30		1100
	max	50	55	906	700	24	0.5	1.1	500	38		1550
PP-Homopolymer	min	20		902	500		0.3	0.27		25	17	800
	max	29		907	800		0.5	1		30	35	1300
PMMA	min	120	83	1170	2	11	0.54	0.16	1700	48		1800
	max	148	124	1200	10	12	0.54	0.27	1700	76		3100

Kuo, A.; Pu, Z. Polymer Data Handbook; Oxford University Press: Oxford, U.K., 1999.
MatBase: the free and independent online materials properties resource.
http://www.matbase.com/material-categories/natural-and-synthetic-polymers/.

Mechanical Properties (2)…

PTFE	min	5	7	2150	350	0.05	1.6	110	25		410
	max	6	8	2200	550	0.08	1.6	350	36		750
LCP	min	150		1070	1.2		0.53		120		10000
	max	300		1070	7		5.3		240		40000
PU thermoset	min			1100	500				20		
	max			1700	500				45		
PA11	min	55		1040	280	0.32		450	47		1100
	max	60		1050	280	0.38		500	47		1400
PA12	min	70		1010	120	0.3	0.5	300	35		1270
	max	85		1020	300	0.4	2	500	55		2600
PA46	min	150		1180	40	0.4		1200	100	30	1000
	max	150		1180	40	0.4		1200	100		3000

Kuo, A.; Pu, Z. Polymer Data Handbook; Oxford University Press: Oxford, U.K., 1999.
MatBase: the free and independent online materials properties resource.
http://www.matbase.com/material-categories/natural-and-synthetic-polymers/.

Mechanical Properties (3)…

PA6 cast	min	115		1135	10		0.36			55		700
	max	135		1155	350		0.43			85		3000
PA66	min	115	46	1130	12	22	0.25	0.48	1100	80		1700
	max	125	86	1150	300	22	0.42	1.5	1200	85		2000
PA6–3-T	min			1120	70					70		2000
	max			1120	150					84		2000
PI	min	100	165	1400	5	20	0.29	2.5		85	73	3100
	max	130	165	1430	7	20	0.29	5		90	73	3100
PDMS	min			970	430				0.203	2.24		360
	max			970	640				0.203	2.24		870
Parylene C	min			1.289	200		0.29			69	3200	2800
	max			1.289	200		0.29			69	3200	2800

Kuo, A.; Pu, Z. Polymer Data Handbook; Oxford University Press: Oxford, U.K., 1999.
MatBase: the free and independent online materials properties resource.
http://www.matbase.com/material-categories/natural-and-synthetic-polymers/.

Material Advantages and Disadvantages

Teo, AJT. Polymeric Biomaterials for Medical Implants and Devices. ACS Biomaterials Sci. Eng. 2016, 2, 454−472

Advantages and Disadvantages (2)…

Silicone[28, 49-54]	• Chemically Inert • Low toxicity • Good biocompatibility • Good electrical insulation, • Low thermal conductivity, • Thermal stability, • High gas permeability, • Hydrophobic.(context dependent) • PDMS ○ Clear ○ Non-flammable • Parylene ○ Good conformity ○ Able to provide thin layer of coatings (1-2μm) with low friction coefficient	• Long term effects not studied • High coefficient of friction • Soft (prone to damage during implantation) • Size and swelling • PDMS ○ Hydrophobic (context dependent) ○ Propensity for protein absorption ○ Possible contamination of cyclic silicone monomer • Parylene ○ Low mechanical strength, ○ Weak adhesion, ○ High moisture absorption rate ○ Low life-expectancy
Polyurethane [28, 50, 55]	• High durability, • High toughness, • Good biocompatibility and hemocompatibility • Good biostability • Low coefficient of friction • Low water permeability	• Environmental stress cracking • Degradation of the material in vivo • Metal ion oxidation
Polytetrafluoroethylene [50, 56]	• Chemically inert • Mechanically strong • Electrically inert • Hydrophobic	• Stiff • Susceptible to damage from traction when lead migrates • Has insulation microdefects
Polyamide (Nylon)[39-40,57-59]	• Causes minimal tissue reactivity • Has long-lasting tensile strength and high elasticity • Have temperature-varying electrical properties. • Moisture absorbent • Able to prevent bacterial transmission	• Moisture permeability • Poor heat sealability • High friction coefficient

Teo, AJT. Polymeric Biomaterials for Medical Implants and Devices. ACS Biomaterials Sci. Eng. 2016, 2, 454−472

Advantages and Disadvantages (3)…

Polyamide (Nylon)[39-40,57-59]	• Causes minimal tissue reactivity • Has long-lasting tensile strength and high elasticity • Have temperature-varying electrical properties. • Moisture absorbent • Able to prevent bacterial transmission	• Moisture permeability • Poor heat sealability • High friction coefficient
Polyimide [60-62]	• Good chemical resistance, • Good mechanical and electrical properties • Low creep • High tensile strength • Flexible, can be folded into compact module for restricted spaces • Constant dielectric constant over wide frequency range with low loss tangent • Stable over wide range of temperatures. • High heat resistance, • High light transmittance for a wide range of wavelengths • Certain polyimides are biocompatible upon interaction with blood	• High moisture absorption
Liquid Crystal Polymer [63-65]	• Chemically inert, • High mechanical strength and durability • Resistant to fire • Low moisture absorption • Able to fabricate thin layers • Flexible and easily conform to difficult shapes • Good MRI capability	• Composite film has poor adhesion to flexible substrates
CNT [66-67]	• Electrically conductive in specified orientation and insulative in another • Good mechanical and surface properties, • Mechanically strong with high tensile modulus and elastic modulus • Good bonding strength with metal substrates with good packing density	• Has concerns over cytotoxicity • weak against shearing between adjacent shells • easily compressed because of their hollow structure

Teo, AJT. Polymeric Biomaterials for Medical Implants and Devices. ACS Biomaterials Sci. Eng. 2016, 2, 454−472

Summary

- Concepts reviewed
  - Common medical device polymers
  - Polymer mechanical properties.
  - Material advantages and disadvantages.