Chapter 10. Engineering and Specialty Polymers

provide outstanding properties when compared with the commodity thermoplastics

Advantages :

high thermal stability, excellent chemical resistance, low creep compliance,
high tensile, flexural, and impact strength

High prices : $1/lb for nylons, $20/lb for PI and PEEK

High strength-to-weight ratio :

replacements for metals in automotive and aerospace applications

Engineering plastics -- Polymers used in the manufacture of premium plastics products where T resistance, high impact strength, chemical resistance etc. are required.

Price range from $1/lb to $5/lb

: Aliphatic polyamides (nylon-6 and -6,6), ABS, acetal, PC, PSF, PPO, PPS, fluoroplastics(Teflon), engineering polyesters

TABLE 10.1 REPRESENTATIVE PROPERTIES OF IMPORTANT ENGINEERING THERMOPLASTICS

Property	ASTM	Nylon-6[a]	Nylon-6,6[a]	ABS[b]	PC	PPO	Acetal	PSF	PPS
Specific gravity	D792	1.12–1.14	1.13–1.15	1.03–1.06	1.20	1.06	1.42	1.24	1.34
Tensile strength, MPa[c]	D638	69	76	41–52	66	66	66–83	70	74
Tensile modulus, GPa[d]	D638	0.69	—	2.1–2.8	2.4	2.4	3.6	2.6	3.3
Elongation-to-break %	D638	300	300	5–25	110	20–60	25–75	50–100	3
Flexural strength MPa[d]	D790	34	42	76–90	93	93	97	106	138
Flexural modulus GPa[d]	D790	9.7	12–28	26–28	23	25–28	26–30	27	41
Impact strength notched Izod, J m^{-1}[e]	D265	160	112	160–320	854	96–267	69–123	160–320	11
Heat-deflection temperature, °C at 455 kPa (66 psi)	D648	150–185	180–240	102–107	138	137	124	150–175	137

[a] Moisture conditioned.

[b] Medium-impact grade.

[c] To convert MPa to psi, multiply by 145.

[d] To convert GPa to psi, multiply by 1.45×10^5.

[e] To convert J m^{-1} to lb$_f$ in.$^{-1}$, divide by 53.38.

Specialty plastics -- Polymers achieving high performance and finding limited but critical use (cost $50/lb or more)

Uses in aerospace composites, membranes, fire-retardant textile fabrics for fire fighters and race-car drivers, sutures & surgical implants

: PI, PEI, PAI, polybismaleimides, ionic polymers, polyphosphazenes, UHMWPE, poly(aryl ether ketones), polyarylates and related aromatic polyesters, polyacetylenes & other electrically conductive polymers

10.1 Engineering plastics

10.1.1 Polyamides

. Aliphatic polyamides :

nylon-6 & nylon-6,6 (most widely used engineering thermoplastics)
used as molded parts for automotive and other applications

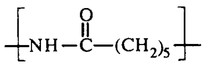
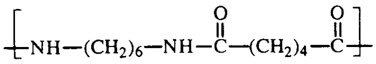
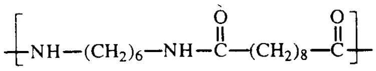
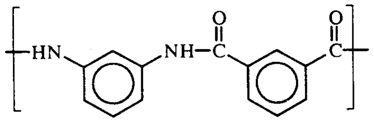
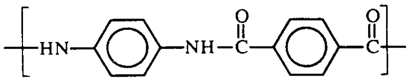
. Aromatic polyamides :

Nomex & Kevlar (fire-retardant fabric and tire cord)
outstanding high T resistance & high tensile strength

⇓

Excellent resistance to wear and abrasion, low coefficient of friction, good resilience, and high impact strength

TABLE 10.2 CHEMICAL STRUCTURES OF IMPORTANT POLYAMIDES

Monomer(s)	Polymer	Structure
Caprolactam	Poly(ε-caprolactam) (nylon-6)	 $\left[NH-\overset{\overset{O}{\|}}{C}-(CH_2)_5 \right]$
Hexamethylene diamine adipic acid	Poly(hexamethylene adipamide) (nylon-6,6)	 $\left[NH-(CH_2)_6-NH-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C} \right]$
Hexamethylene diamine sebasic acid	Poly(hexamethylene sebacamide) (nylon-6,10)	 $\left[NH-(CH_2)_6-NH-\overset{\overset{O}{\|}}{C}-(CH_2)_8-\overset{\overset{O}{\|}}{C} \right]$
Isophthaloyl chloride *m*-phenylenediamine	Poly(*m*-phenylene isophthalamide) (Nomex™)	
Terephthaloyl chloride *p*-phenylenediamine	Poly(*p*-phenylene terephthalamide) (Kevlar™)	

* Nylon -- water sensitive (∵ hydrogen bonding of amide groups)
Water acts a plasticizer --> reduces tensile strength & modulus
Care must be taken to reduce water below 0.3% before melt processing.

nylon-6,6 : higher rigidity

nylon-6 : weather and thermally resistant, good barrier properties
(nylon-6 film is used for packaging of some oxygen-sensitive foods)

nylon-11 & nylon-12 : used for fuel lines and compressed-air brake tubing

* Aromatic polyamides (aramids)
-- developed to improve the heat and flammability resistance of nylons

Poly(m-phenylene isophthalamide) "Nomex" : decomposes about 370℃
highly heat resistant nylon,
obtained by solution or interfacial polym'n

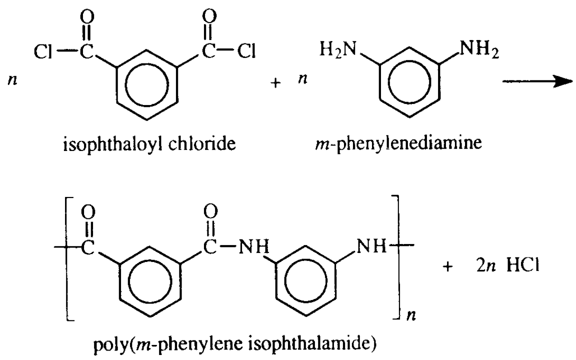


Figure 10.1. Synthesis of an aromatic polyamide, poly(*m*-phenylene isophthalamide) (Nomex™).

used as flame-resistant protective clothing & hot-gas filtration equipment
(substitute for asbestos),
stress & vibration damping material of the space shuttle

Poly(p-phenylene terephthalamide) "Kevlar" : decomposes above 500℃
higher strength & modulus than steel on equal-weight basis
(See Table 10.2)
used as a substitute for steel in belted radial tires,
bullet-resistant vests & other protective clothing,
skin covering for the first human-powered aircraft, *Gossamer Albatross*

10.1.2 ABS

high-impact, high-HDT grade of PS
Applications :
automotives, consumer products, business machines & telecommunications
By grafting SAN onto semicrosslinked particles of PBD
Typical formulation : < 15% butadiene, < 20% acrylonitrile
Rubber particles produced by bulk or suspension processes (0.5 - 5μm)
> those produced by emulsion methods (0.1 - 1μm)
Graft polym'n of SAN & PBD -- good interfacial adhesion

10.1.3 Polycarbonates

high impact strength, low moisture absorption, low combustibility,
good dimensional stability and high light transmittance
used as impact-resistant substitute for window glass ("Lexan"),
compact disks
Disadvantage :
limited chemical & scratch resistance, yellowing for long-term UV exposure
By polycondensation of bisphenol-A & phosgene (See Fig. 10.3)
--> HCl is liberated as by-product

cf) If sodium salt of bisphenol-A is used --> NaCl as by-product

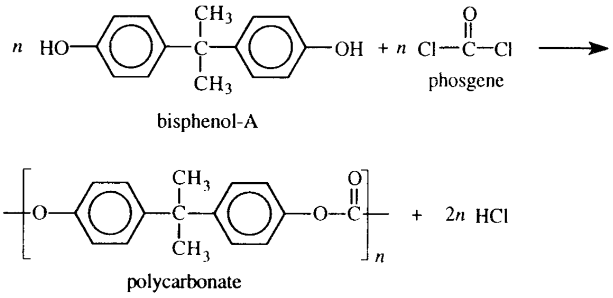
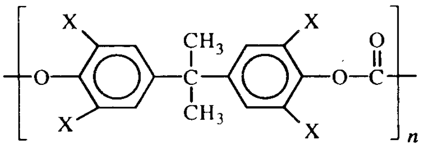


Figure 10.3. Synthesis of bisphenol-A polycarbonate by the polycondensation of bisphenol-A and phosgene.

Other PC having general structure of



where X = Halogen, especially Br, or CH_3

ex) tetramethylbisphenol-A polycarbonate (TMPC), X=CH_3

: higher HDT, better hydrolytic stability than PC, but low impact resistance

--> improved through blending with HIPS, ABS, or MBS

10.1.4 Modified poly(phenylene oxide)

poly(2,6-dimethyl 1,4-phenylene oxide) "PPO" -- higher HDT than PC

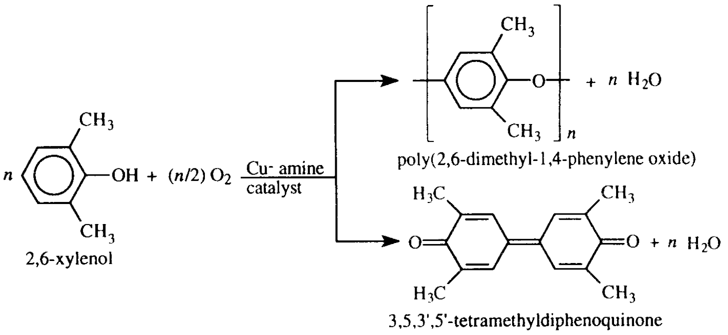


Figure 10.4. Oxidative-coupling polymerization of 2,6-xylenol. 3,5,3',5'-Tetramethyldiphenoquinone (DPQ) is a by-product of this polymerization. The concentration of DPQ impurity depends upon the choice of catalyst and conditions of the polymerization. For example, the yield of DPQ is about 3 wt % using a cupric formate and pyridine catalyst.

high impact strength, chemical stability to acids, low water absorption

Disadvantage : high T_g (≒ 214℃

=> susceptibility of methyl groups to thermal oxidation

=> problems for melt processing

Modified PPO "Noryl" -- to reduce processing T
by blending PPO with HIPS
Commercial resins of PPO & PA are available for improved thermal stability

10.1.5. Polyacetal

known as acetal, polyformaldehyde or polyoxymethylene(POM)
the first universal polymer (observed in the gas cloud of Halley's comet in 1987)
By anionic or cationic polym'n of formaldehyde or by ring opening polym'n

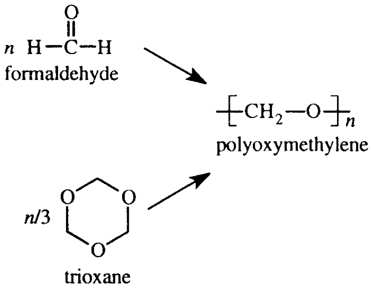


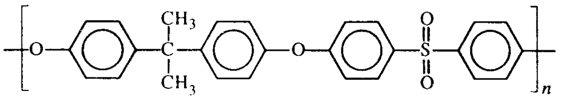
Figure 10.5. Two routes for the synthesis of polyoxymethylene.

high crystallinity & excellent chemical resistance (See Table 10.1 for properties)
==> automotive & electrical/electronic use
high dimensional stability
==> used as a replacement for metals in gears & machine parts
degraded by UV radiation --> color change, loss of toughness & tensile strength
==> stabilized by UV absorbers & HALS(hindered-amine light stabilizers)
carbon black & TiO_2 (effective for light & UV screening)
Acetal can be chemically recycled to monomers.

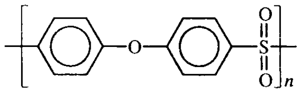
10.1.6 Polysulfones

high thermal, oxidative, hydrolytic stability & good resistance to acids, alkali & oils
high biocompatibility & ability to be sterilized ==> suitable for medical applications
high permeability & permselectivity ==> membrane polymers in gas separations

Polysulfone
(Udel™,
Ultrason A™)



Polyethersulfone
(Ultrason E™,
Victrex™)



Polyphenylsulfone
(Radel R™)

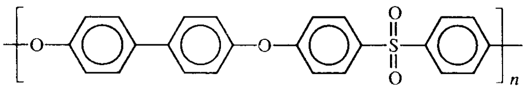


TABLE 10.4 REPRESENTATIVE PROPERTIES OF COMMERCIAL POLYSULFONES

Property	ASTM	PSF	PES	PPS
Specific gravity	D 1505	1.25	1.37	1.29
Tensile strength at yield, MPa[a]	D 638	70.3	84.1	71.7
Tensile modulus, GPa[b]	D 638	2.48	2.70	2.14
Elongation to break, %	D 638	50–100	40–80	60
Flexural strength, MPa[a]	D 790	106	129	85.5
Flexural modulus, GPA[b]	D 790	2.69	2.57	2.30
Impact strength (Notched Izod), J m^{-1} [c]	D 256	69	85	641
Heat-deflection temperature, °C at 455 kPa (66 psi)	D 648	174	203[d]	200–204

[a] To convert MPa to psi, multiply by 145.

[b] To convert GPa to psi, multiply by 1.45×10^5.

[c] To convert J m^{-1} to lb_f $in.^{-1}$, divide by 53.38.

[d] Reported at 1.82 MPa (264 psi).

synthesized by condensation polym'n

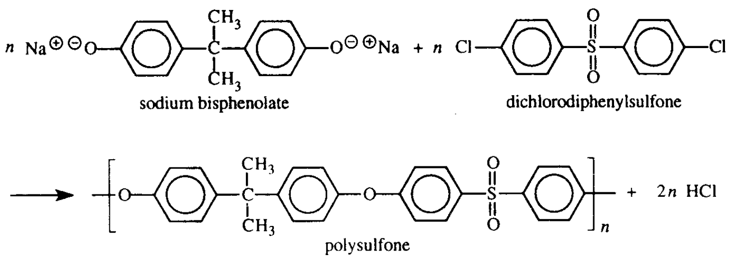


Figure 10.6. Polycondensation of bisphenol-A polysulfone.

widely used in automotive, aerospace, & medical industries

10.1.7 Poly(phenylene sulfide)

poly(p-phenylene sulfide) (PPS) or poly(thio-1,4-phenylene)

outstanding chemical resistance, good electrical properties, excellent flame retardance, low coefficient of friction, high transparency to microwave radiation

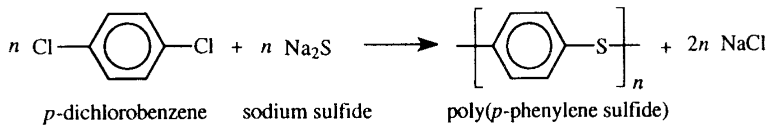


Figure 10.8. Synthesis of poly(p-phenylene sulfide).

highly crystalline, relatively high T_m (285℃ insoluble in organic solvents < 200℃

PPS coatings -- by spraying a slurry of PPS & heating the coated object > 370℃

Injection & compression molding(300~ 70℃ => crosslinking => insoluble product

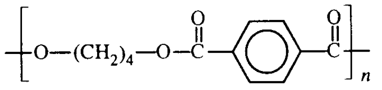
Applications -- cookware, bearings, pump parts for service in corrosive environments

10.1.8 Engineering polyesters

PET : used as a textile fiber, but poor surface quality & release properties of molded part (∵ low rate of crystallization of PET)

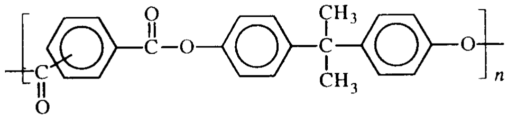
Modified grades of PET : beverage-bottle and molding applications

poly(butylene terephthalate) (PBT) : injection-molded parts for electrical & electronic use and for automotive markets



PET & PBT : high strength, rigidity & toughness, excellent dimensional stability, low coefficient of friction, abrasion resistance, and good resistance to chemicals, but moisture sensitive

All-aromatic polyester (polyarylate, PAR) : amorphous, high clarity, UV stability, high HDT(150<Tg<200℃ flame retardance, good electrical properties
-- solar collectors, lighting fixtures, safety devices, construction & transportation



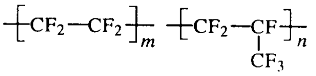
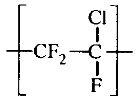
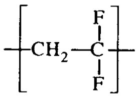
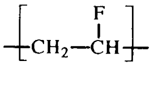
10.1.9 Fluoropolymers

polytetrafluoroethylene(PTFE or "Teflon") : by emulsion polymerization of TFE
-- highly dense (2.1-2.3g/cm^3), high T stability, low T flexibility, extremely low coefficient of friction, low dielectric constant, chemical inertness

Limited processability <-- extremely high crystallinity, high crystalline-melting T (T_m=327℃ <-- highly regular structure & MW

To improve melt processability, comonomers such as FEP are incorporated.

TABLE 10.5 CHEMICAL STRUCTURES OF SOME IMPORTANT FLUOROPOLYMERS

Fluoropolymer	Repeating Unit
Polytetrafluoroethylene	$-[CF_2-CF_2]-$
Fluorinated ethylene–propylene copolymer (FEP)	 $-[CF_2-CF_2]_m-[CF_2-CF(CF_3)]_n-$
Polychlorotrifluoroethylene (CTFE)	 $-[CF_2-CClF]-$
Poly(vinylidene fluoride) (PVDF)	 $-[CH_2-CF_2]-$
Poly(vinyl fluoride) (PVF)	 $-[CH_2-CHF]-$

CTFE -- electrical insulators, gaskets and seals, and pump parts

PVDF -- coatings, gasket material, wire & cable insulation

PVF -- highly crystalline polymer (T_m=197℃ tough, flexible films with excellent films with excellent outdoor weatherability, good abrasion, stain resistance, --> protective coatings in building industry

Fluorinated polymers -- used as highly thermally & chemically resistant elastomers

10.2 Specialty polymers

Small but important markets in the aerospace, electronics & biomedical industries

10.2.1 Polyimides and related specialty polymers

High-T(T_g=385℃ solvent-resistant polymers

Uses : electronics, sleeve bearings, matrix component of graphite composites

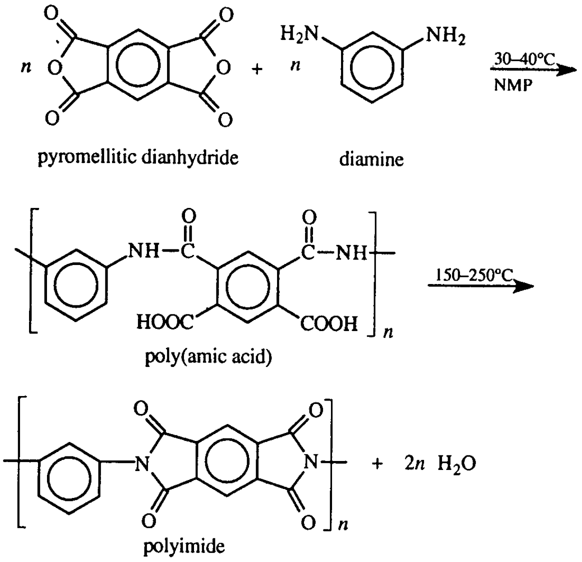


Figure 10.9. Polymerization of a polyimide.

Advantages : insoluble, infusible, high-T & oxidative stability,
good electrical insulation properties & radiation resistance

Disadvantages : limited shelf life of the precursor poly(amic acids),
structural weakness of the fully imidized product due to void formation as a result of water release in the curing process
==> Thermoplastic polyimides have become available.

10.2.2 Ionic polymers

contain up to 10-15mol% ionic content ==> *ionomers*

higher ionic content ==> *polyelectrolytes*

Applications : ion exchange resins, membranes, separators in chloralkaline electrolytes

Ionic sites -- pendant carboxylic or sulfonic acid groups

Typical nonionic polymer backbones -- PE, PS & PTFE

Microphase separation <--- incompatibility of ionic & nonionic segments

multiplets -- small aggregates consisting of only ionic material

clusters -- larger aggregates also including nonionic material

==> moderately strong, temporary, ionic crosslinks,

mechanical reinforcement(T_g, modulus, melt viscosity)

ex) "Surlyn A" : commercial ionomer (copolymer of ethylene & 15% of MMA)

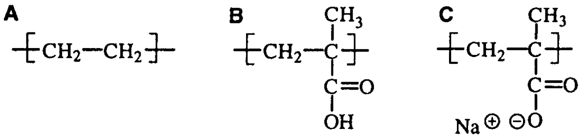


Figure 10.11. Comonomer units in Surlyn A. **A**. Ethylene. **B**. Methacrylic acid. **C**. Sodium salt of methacrylic acid.

10.2.3 Polyetheretherketones(PEEK)

partially(20-30%) crystalline, melt processed at elevated T

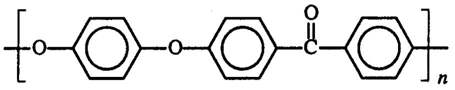
good abrasion resistance, low flammability & emission of smoke & toxic gases, low water absorption, resistance to hydrolysis, wear, radiation & high T steam

==> thermoplastic matrix for graphite composites(∵ olvent resistance, impact strength, thermal stability), solvent-resistant tubing for chromatography, wire & cable insulation for hostile environments, magnet wire coating

TABLE 10.7 TYPICAL PROPERTIES OF PEEK

Property	Value
T_g (°C)	143
Heat-deflection temperature, °C at 1.82 MPa (264 psi)	148
T_m (°C)	334
Crystallinity, %	
typical	20–30
maximum	48
Heat of fusion, ΔH_f (J g^{-1})	130–161
Density (g cm^{-3})	
amorphous	1.265
crystalline	1.320
Water absorption, % over 24 h and 40% RH	0.15
Solubility parameter (cal/cm^3)$^{1/2}$	9.5
Tensile strength (MPa) at 23°C	91.0
Elongation at 23°C, %	150
Flexural modulus at 23°C, GPa	3.89
Impact strength, Charpy (J m^{-1})	1388

ex) "Victrex"



10.2.6 Liquid crystalline polymers(LCP)

Polymers containing long rigid units form anisotropic ordered solutions above some minimum conc. depending on T & aspect ratio(length/diameter ratio) x

Threshold volume fraction ϕ (from Flory's lattice theory)

$$\phi = \frac{8}{x}\left[1-\frac{2}{x}\right] \approx \frac{8}{x}$$

mesogens -- rigid units of LCP

lyotropic LCP -- LCP that forms liquid-crystal organization in solution

thermotropic LCP -- LCP that forms from the melt

Three recognized forms :

smectic state -- most ordered structure (observed only for thermotropic polymer)
(all the mesogens are arranged in a parallel & lateral order)

nematic state -- more common for polymers
(parallel but not lateral order)

cholesteric state -- oriented parallel but the directions vary from layers

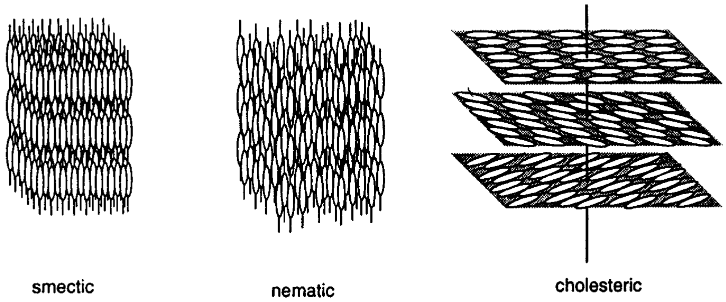
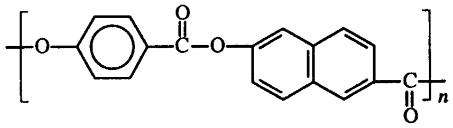


Figure 10.15. Representation of three principal liquid-crystal structures: smectic, nematic, and cholesteric. [Adapted from R. W. Lenz and J.-I. Jin, *Polymer News*, **11**, 200 (1986), with permission of the publisher.]

ex) "Vectra" (Liquid-crystal polyesters)



high dimensional stability, barrier properties, high thermal stability, high modulus & strength, high chemical & solvent resistance

Applications : electronic components(memory modules), aerospace applications,
filaments (limited use due to high cost)

10.2.7 Conductive polymers

A number of polymers are electrically conductive or can be made to be conductive by doping with an electron donor or acceptor.

Applications : polymeric electrodes for lightweight batteries, electrochromic displays,
sensors, solar cells

Polyacetylene -- MW up to 1M can be prepared

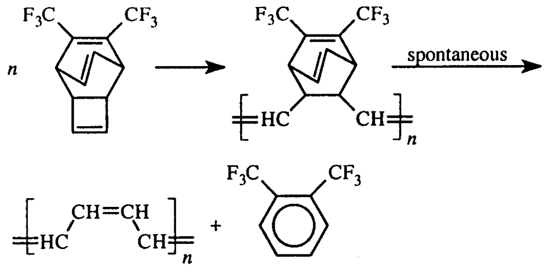


Figure 10.16. Synthesis of *cis*-polyacetylene by metathesis polymerization.

cis-isomer ($1.7\text{x}10^{-9}\text{Scm}^{-1}$) can be transformed to the more stable *trans*-isomer ($4.4\text{x}10^{-5}\text{Scm}^{-1}$) by heating of 200℃

Doping increases conductivity greatly.

==> Addition of AsF_5 increases conductivity to 400Scm^{-1}.

$-40 < T_g < 0$℃ & good thermal stability (decomposition T > 420℃

but easily oxidized

Other conductive polymers :

polyaniline, poly(p-phenylene), polypyrrole & polythiophene, etc.