Radiation Effects on Polymeric Systems

Polymerization

Mechanisms of Addition Polymerization

Monomer	Radical	Cationic	Anionic	Coordination
Ethylene	X	X	-	X
Propylene	-	-	-	X
Isobutylene	-	X	-	X
Styrene	X	X	X	X
Nitroethylene	-	-	X	-
Acrylates	X	-	X	X

Order of Reactivity in Free Radical Polymerization

Acrylates > Methacrylates > Vinyl > Allyl

Radiation Polymerization of Ethylene[1]

- Suggested as an economic process ~ 30 years ago (Brookhaven, Takasaki)
- Commercial plant plans shelved due to worker objections in USA

Radiation Polymerization of Ethylene[1]

Gas Composition[2]	Products	G Value
100% $CH_2=CH_2$	Polyethylene	131,684
	Acetylene	746
26.1% H_2; 73.9%$CH_2=CH_2$	Polyethylene	54,764
	Acetylene	31
	Ethane	7
	Butane	18
	Butene-1	16

[1] Lopata, Singh and Saunders, RadTech'90 NA, Chicago
[2] Initial irradiation conditions: Pressure, 32 MPa; Temperature, 30°C; Dose rate, 1.1 kGy/h

Concentration of Functional Groups Polyethylenes[a]

Functional Group	Functional Groups per 1000 Carbon Atoms							
	Radiation Polymerized					Commercial[1]		
	Oxygen Content		Density, kg/m^3			Density, kg/m^3		
	140 ppm	0.3 ppm	933	941	952	923[2]	960[3]	965[4]
C=O	0.464	-	-	-	-	-	-	-
RCH=CH_2	0.059	0.009	-	-	-	0.165	0.09	1.58
RCH=CHR'	0.092	0.039	0.06	0.06	0.09	0.04	0.02	0.02
RR'C=CH_2	0.130	0.081	-	-	-	0.25	0.06	0.08
CH_3	7.1	9.1	9	2	0	34	4.1	3.9
OH[5]	0.203	0.211	-	-	-	0.201	0.215	-

[1]Oxygen content unknown; [2] LDPE; [3] Ziegler; [4] Phillips; [5] Formed on exposure to air

[a] Lopata et al., 1990

Physical Properties - Polyethylenes

Property	Radiation Produced			Commercially Produced		
	Low Density	Low Density	High Density	Low Density Branched	Low Density Linear	High Density
Density kg/m^3	918	933	952	917-932	918-940	952-965
Melt Index g/10 min	17.1	102	7.4	3.5-0.15	-	17-0.35
Yield Strength MPa	10.3	15.7	14.7	-	-	22-30
Elongation %	520	600	600	100-650	100-965	10-1200
MW, M_n	-	22000	25000	27000[1]	-	52000[2]

[1] Density: 926/kgm^3; [2] Density: 952 kg/m^3; Lopata et al., 1990