

Chapter 9. Reactions of Vinyl Polymers

9-2. Functional group reaction

Chlorination

: decrease flammability & increase Tg

Chlorosulfonation

Fluorination

Aromatic substitution

Chloromethylation

9-3. Ring-forming reaction

: for greater rigidity, higher Tg, thermal stability

- 1). Carbon fiber or carbon nanotube
- 2). Ladder polymers

9-4. Crosslinking

for rubber & elastomer industries

- 1). Peroxide-initiated crosslinking
- 2). Vulcanization by sulfur
- 3). Radiation crosslinking
: Photon, electron, neutron or proton
but compete between degradation & crosslinking
- 4). Photochemical crosslinking (photocrosslinking)
: by UV or visible light
 - o incorporating photosensitizer
 - o incorporating groups for photocycloaddition or light-initiated polymerization
- 5). Crosslinking through labile functional group
: using difunctional or polyfunctional reagents
- 6). Ionic crosslinking
: gives elastomeric property & coating, adhesives due to high polarity

9-5. Block and graft copolymer

1). Block copolymer

- o AB block
- o ABA block : using telechelic polymer
- o AB block using living polymer or isopropyl-terminated polymer
- o vinyl monomer + initiator + oxygen
- o polystyrene + ethylene monomer

2). Graft copolymer

- o chain-transfer grafting : needs polymer, monomer & initiator
 - o grafting by activation of functional group
 - o two functional group : coreaction
 - o irradiation grafting : irradiation of monomer & polymer together
- : G value : number of free radicals per 100ev energy per g

9-6. Polymer degradation

1). Chemical degradation

- : oxygen mainly (speed up by heat or light)
- o order of resistance to oxidation
 - polyisobutylene > polyethylene > polypropylene
- o unsaturated polymers : fast oxidative degradation
- o allylic carbon : the most sensitive due to resonance-stabilized radical

2) Thermal degradation

- o nonchain scission : Durham route for preparation of polyacetylene
- o random chain scission : by homolytic cleavage
- o depropagation (unzipping)
 - : 1,1-disubstituted PMMA & poly(methylstyrene)

3). Degradation by radiation

- : compete with crosslinking
- : depends on radiation dose, polymer structure & temp.