Kinetics of radicalic chain polymerization-2:

- **Radical Chain Polymerization**
  - Reaction Mechanism of Free Radical Chain Polymerization
  - Kinetics of Free Radical Chain Polymerization

REF: Lecture Notes In Chemistry 82 Principles of Polymer Design and Synthesis

Introduction to Polymerization Reactions

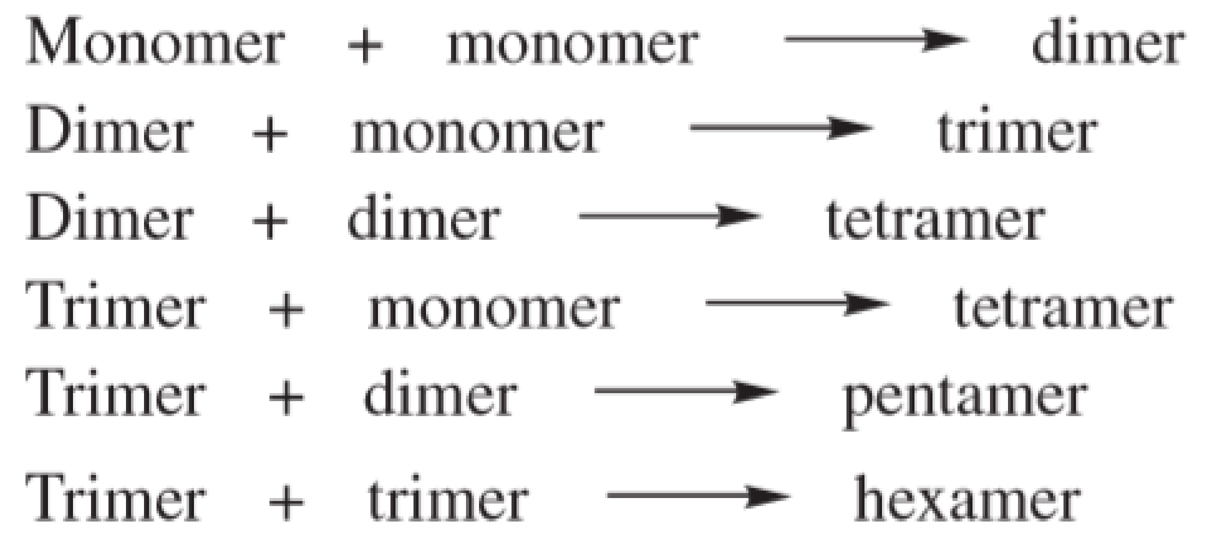
In addition to the structural and compositional differences between polymers, Flory [1953] stressed the very significant difference in the mechanism by which polymer molecules are built up.

Flory continued to use the terms condensation and addition in his discussions of polymerization mechanism, the more recent terminology classifies polymerizations into step and chain polymerizations.

Chain and step polymerizations have different features

- The typical step and chain polymerizations differ significantly in the relationship between polymer molecular weight and the percent conversion of monomer.

- The most important difference is in the identities of the species that can react with each other.
- Another difference is the manner in which polymer molecular size depends on the extent of conversion.
- Step polymerizations proceed by the stepwise reaction between the functional groups of reactants.
- The size of the polymer molecules increases at a relatively slow pace in step polymerizations.
- Step polymerizations proceeds from monomer to dimer, trimer, tetramer, pentamer, and so on



Monomer + monomer → dimer
Dimer + monomer → trimer
Dimer + dimer → tetramer
Trimer + monomer → tetramer
Trimer + dimer → pentamer
Trimer + trimer → hexamer

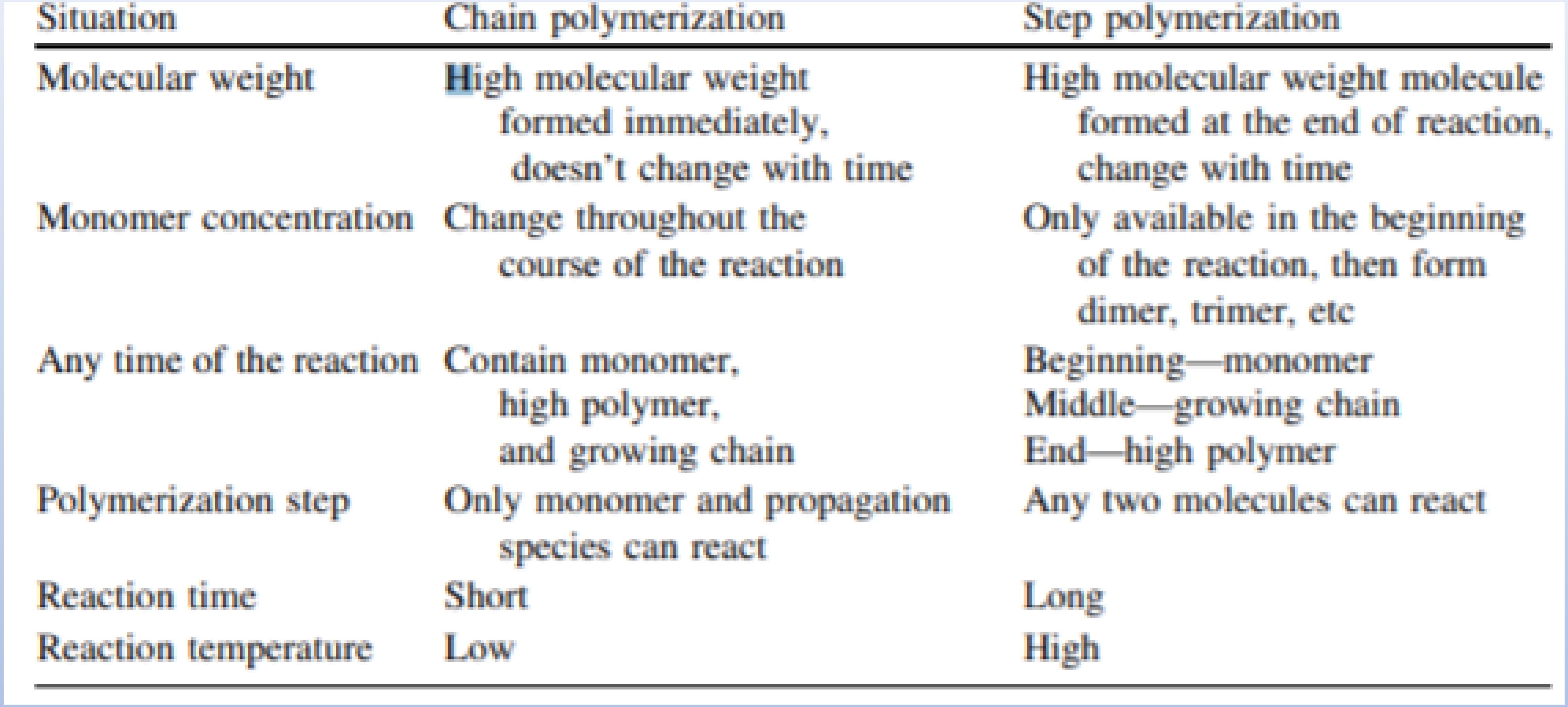
- In the chain polymerization, monomer does not react with monomer and the different-sized species such as dimer, trimer, tetramer, and n-mer do not react with each other.

- Step polymerization that distinguishes it from chain polymerization is that reaction occurs between any of the different-sized species present in the reaction system.

- The polymer in the chain polymerization growth by monomer reacting only with the reactive center.

- Polymer growth in the chain polymerization proceeds by the successive additions of hundreds or thousands or more monomer molecules.

Comparison of chain polymerization and step polymerization



Situation	Chain polymerization	Step polymerization
Molecular weight	High molecular weight formed immediately, doesn't change with time	High molecular weight molecule formed at the end of reaction, change with time
Monomer concentration	Change throughout the course of the reaction	Only available in the beginning of the reaction, then form dimer, trimer, etc
Any time of the reaction	Contain monomer, high polymer, and growing chain	Beginning—monomer Middle—growing chain End—high polymer
Polymerization step	Only monomer and propagation species can react	Any two molecules can react
Reaction time	Short	Long
Reaction temperature	Low	High

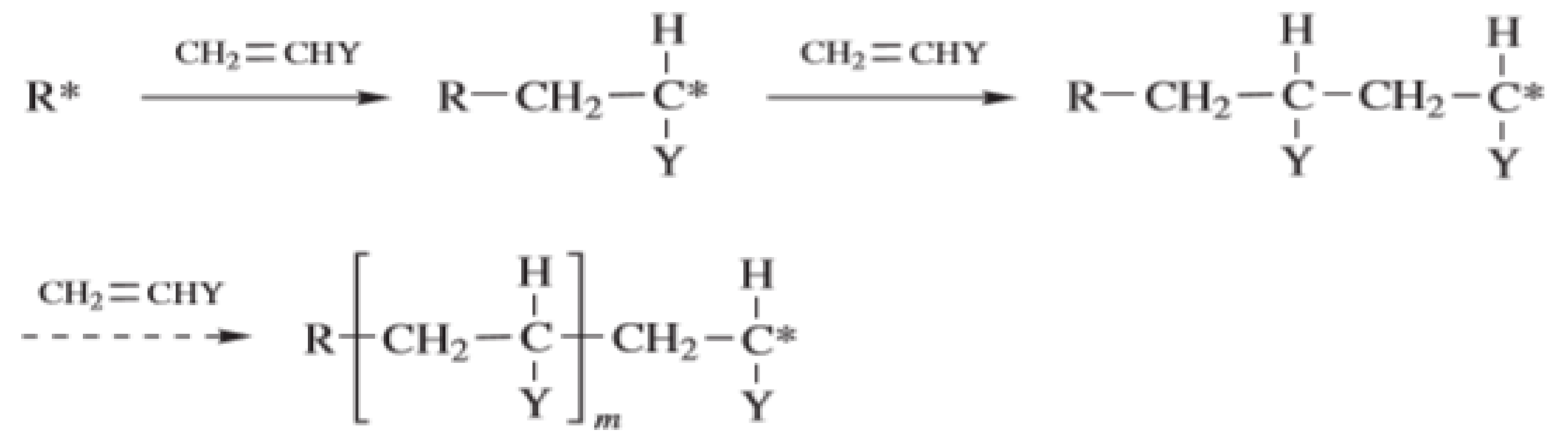
RADICAL CHAIN POLYMERIZATION

The polymerization of unsaturated monomers typically involves a chain reaction. In a chain polymerization, one act of initiation may lead to the polymerization of thousands of monomer molecules. The chain polymerization starts with an active center responsible for the growth of the chain which is associated with a single polymer molecule through the addition of many monomer units.

$$I \longrightarrow R^*$$

Thus polymeric molecules are formed from the beginning, and almost no intermediate species between monomer and high molecular weight polymer are found. Chain polymerization is initiated by a reactive species R* produced from an initiator I:

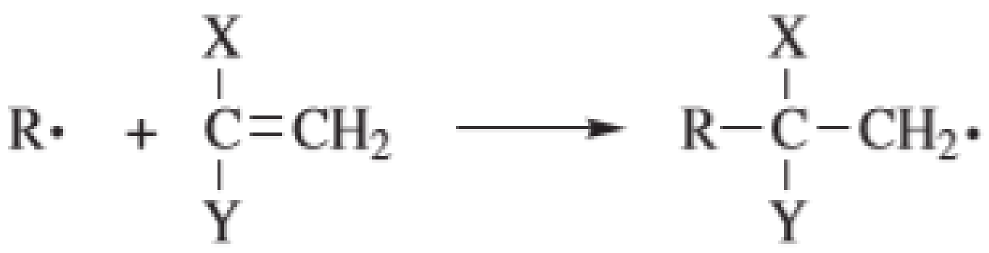
The reactive species, which may be a free radical, cation, or anion, adds to a monomer molecule by opening the p-bond to form a new radical, cation, or anion center. The process is repeated as many more monomer molecules are successively added to continuously propagate the reactive center as the following:



Polymer growth is terminated at some point by destruction of the reactive center by an appropriate reaction depending on the type of reactive center and the particular reaction conditions

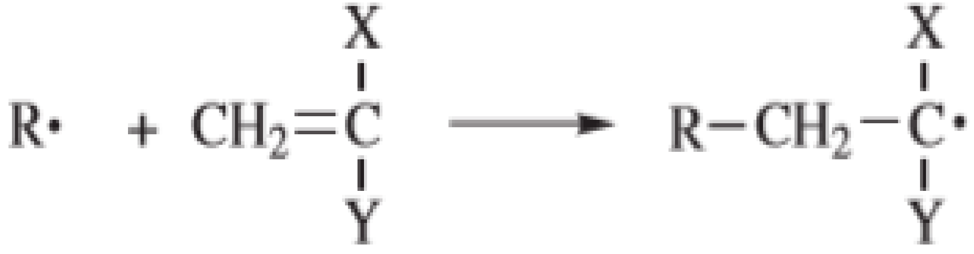
Chemical Structure of Monomer on the Structural Arrangement of Addition Polymers

There are two possible points of attachment on monosubstituted (X = H) or 1,1- disubstituted monomers for a propagating radical, either on carbon 1 to form I or on carbon 2 to form II as the following:



$$R\cdot + \overset{X}{\underset{Y}{C}}=CH_2 \longrightarrow R-\overset{X}{\underset{Y}{C}}-CH_2\cdot$$

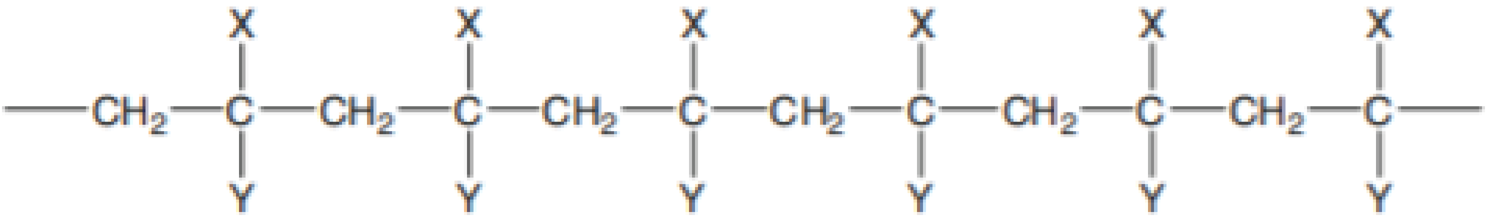
I



$$R\cdot + CH_2=\overset{X}{\underset{Y}{C}} \longrightarrow R-CH_2-\overset{X}{\underset{Y}{C}}\cdot$$

II

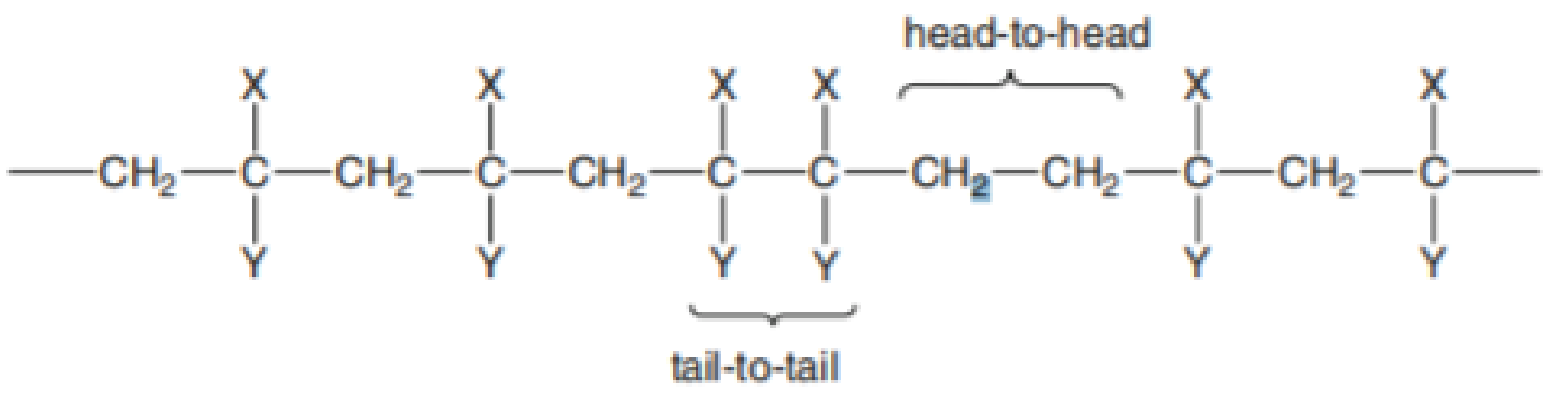
If each successive addition of monomer molecules to the propagating radical occurs in the same manner as I or II, the final polymer product will have an arrangement of monomer units in which the substituents are on alternate carbon atoms as shown in III:



$$-\mathrm{CH_2}-\underset{Y}{\overset{X}{C}}-\mathrm{CH_2}-\underset{Y}{\overset{X}{C}}-\mathrm{CH_2}-\underset{Y}{\overset{X}{C}}-\mathrm{CH_2}-\underset{Y}{\overset{X}{C}}-\mathrm{CH_2}-\underset{Y}{\overset{X}{C}}-\mathrm{CH_2}-\underset{Y}{\overset{X}{C}}-$$

III

This type of arrangement III is usually referred to as a head-to-tail (H–T) or 1,3-placement of monomer units. An inversion of this mode of addition, by the polymer chain propagating alternately via I and II, would lead to a polymer structure with a 1,2-placement of substituents at one or more places in the final polymer chain. The 1,2-placement is usually referred to as head-to-head (H– H) placement as shown in scheme I.

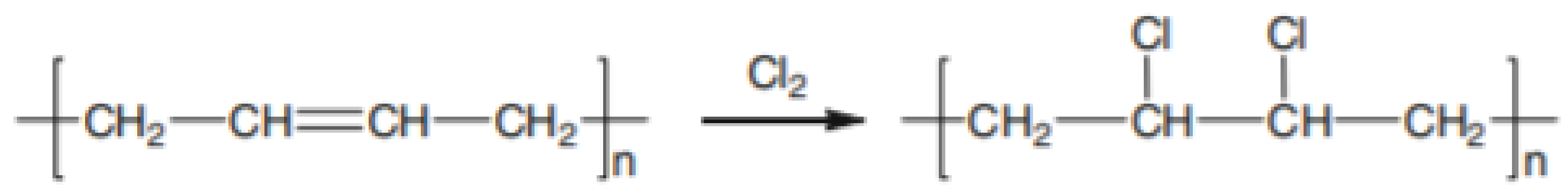


$$-CH_2-\overset{X}{\underset{Y}{C}}-CH_2-\overset{X}{\underset{Y}{C}}-CH_2-\underbrace{\overset{X}{\underset{Y}{C}}-\overset{X}{\underset{Y}{C}}}_{\text{tail-to-tail}}-\overbrace{CH_2-CH_2}^{\text{head-to-head}}-\overset{X}{\underset{Y}{C}}-CH_2-\overset{X}{\underset{Y}{C}}-$$

The head-to-tail placement is predominant, since successive propagations by I are favored on both steric and resonance grounds. The propagating radical (radical II) formed by attachment of a radical at carbon 2 is the more stable one. The radical II can be stabilized by the resonance effects of the X and Y substituents. The substituents cannot stabilize radical I, since they are not attached to the carbon.

The term isoregic has been used to indicate a polymer structure with exclusive head-to-tail placements. The terms syndioregic and aregic are used for polymer structures with alternating and random arrangements, respectively, of H–T and H–H placements

Some polymers consisting entirely of head-to-head (H–H) placements have been deliberately synthesized to determine if significant property differences exist compared to the head-to-tail polymers. The synthetic approach involves an appropriate choice of monomer for the particular H–H polymer. For example, H–H poly (vinyl chloride) was obtained by chlorination of 1,4-poly-1,3-butadiene in below equations.



$$\left[\!-CH_2-CH=CH-CH_2-\right]_n \xrightarrow{Cl_2} \left[\!-CH_2-\underset{}{\overset{Cl}{\overset{|}{C}H}}-\overset{Cl}{\overset{|}{C}H}-CH_2-\right]_n$$

H–H polystyrene was obtained by hydrogenation of 1,4-poly-2,3-diphenylbutadiene