

$\bar{X}_W$   $p = 0.99, X_w = 199$   
 $p = 0.95, X_n = 20$

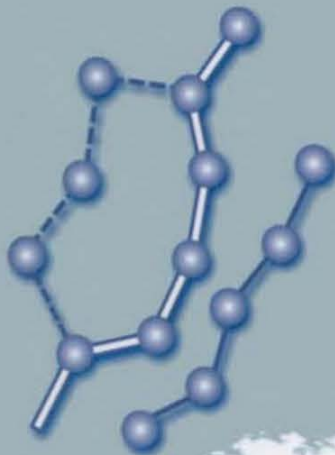
THE ELEMENTS OF

# Polymer Science and Engineering

Second Edition

An Introductory Text  
and Reference for  
Engineers and Chemists

**ALFRED RUDIN**



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**Alfred Rudin**  
University of Waterloo



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## Chapter 4

# *Effects of Polymer Isomerism and Conformational Changes*

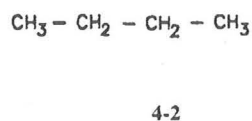
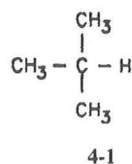
*With a name like yours, you might be any shape, almost.*  
—Lewis Carroll, *Through the Looking Glass*

Three types of isomerism are important in macromolecular species. These involve constitutional, configurational, and conformational variations. These terms are defined and illustrated. Their usage in macromolecular science is very much the same as in micromolecular chemistry.

### 4.1 CONSTITUTIONAL ISOMERISM

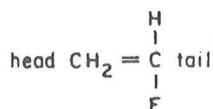
The constitution of a molecule specifies which atoms in the molecule are linked together and with what types of bonds.

Isobutane (4-1) and *n*-butane (4-2) are familiar examples of constitutional isomers. Each has the molecular formula C<sub>4</sub>H<sub>10</sub> but the C and H atoms are joined differently in these two molecules. In polymers the major types of constitutional differences involve positional isomerism and branching.



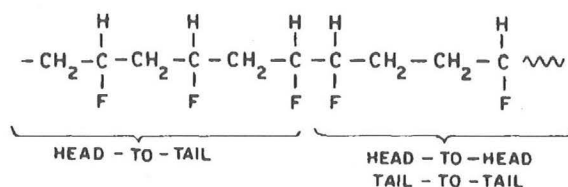
## 4.1.1 Positional Isomerism

Vinyl and vinylidene monomers are basically unsymmetrical because the two ends of the double bond are distinguishable (ethylene and tetrafluorethylene are exceptions). One C of the double bond can be arbitrarily labeled the head and the other the tail of the monomer, as shown in the formula for vinyl fluoride (4-3).



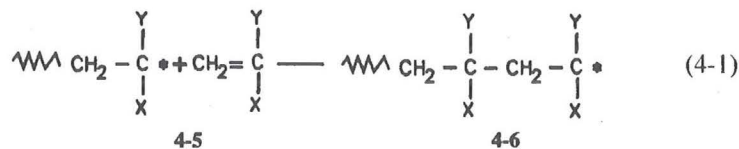
4-3

In principle, the monomer can be enchainment by head-to-tail linkages or head-to-head, tail-to-tail enchainments (4-4). Poly(vinyl fluoride) actually has about 15% of its monomers in the head-to-head, tail-to-tail mode. This is exceptional, however. Head-to-tail enchainment appears to be the predominant or exclusive constitution of most vinyl polymers because of the influence of resonance and steric effects.

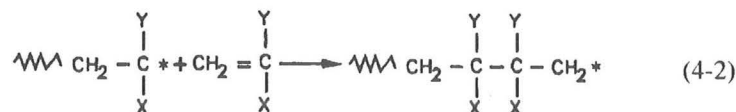


4-4

Vinyl monomers polymerize by attack of an active center (4-5) on the double bond. Equation (4-1) represents head-to-tail enchainment:



while Eq. (4-2) shows the sequence of events in head-to-head, tail-to-tail polymerization:



4-7

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