INTRODUCTION TO SYNTHESIS OF ELASTOMERS*

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ABSTRACT
Polymerization and crosslinking reactions used for the synthesis of elastomers are reviewed. Step and chain polymerizations are characterized in terms of the reaction variables which must be controlled to obtain an elastomer. Radical and ionic chain polymerizations are discussed as well as the structural variations possible through copolymerization and stereoregularity.

INTRODUCTION
Elastomers or rubbers are polymers which can undergo very large, reversible deformations at relatively low stresses. Only a polymer molecule can undergo large deformations since it can respond to stress without bond rupture by extension from a random coil to an extended chain molecule through bond rotation. Only an amorphous polymer with low glass transition temperature and low secondary forces has the required chain flexibility to meet these requirements. Crystalline polymers (e.g., polyethylene or isotactic polypropylene) or highly polar polymers (e.g., polyamides) do not have the necessary chain flexibility. Amorphous polymers with large bulky substituents (e.g., poly(methyl methacrylate) and polystyrene) are also too rigid to be elastomers. Elastomeric behavior is limited to those non-polar amorphous polymers with irregular structures (e.g., ethylene-propylene copolymers) and/or flexible chain units (e.g., polyisobutylene, polysiloxane, polysulfide, polystyrene).

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1,4-polyisoprene). Crosslinking of a polymer to form a network structure is an essential part of synthesizing an elastomeric product. The presence of a crosslinked network prevents polymer chains from irreversibly slipping past one another upon deformation. Either chemical or physical crosslinking can be used to produce the network structure. The various reactions for synthesizing polymers from monomers are discussed below together with a consideration of the processes used to achieve crosslinking.

POLYMERIZATION

The prime consideration in any polymerization reaction is the control of polymer molecular weight (MW). A polymer requires a minimum molecular weight in order to possess sufficient physical strength to be useful. This minimum MW may be as low as a few thousand but is generally considerably higher. In any specific application, the desired MW is some compromise high MW which yields sufficient strength for the end-use application while retaining ease of processing the polymer into its final product shape. The need to control molecular weight places significant restrictions on any reaction used for polymer synthesis.

Step Polymerization

Polymerizations are classified as either chain or step polymerizations. The two processes differ in the time required for the growth of large-sized (i.e., polymer) molecules compared to the time for achieving high conversions. Step polymerizations typically involve two different bifunctional reactants (referred to as monomers), each containing a different functional group X or Y. Polymer growth occurs through the formation of xy functional units by reaction of X and Y groups

\[ nX-X + nY-Y \rightarrow (X-xy-Y)_n \]  

(1)

The synthesis of polysulfides (Eq. 2) and polyurethanes (Eq. 3) are examples of step polymerizations which yield elastomeric materials.

\[ nCl-R-Cl + nNa_2S_m \rightarrow NaCl \rightarrow (R-S_m)_n \]  

(2)

\[ nHO-R-OH + nOCN-R'-NCO \rightarrow (O-R-OCO-NH-R'-NH-CO)_n \]  

(3)

The structural entity which repeats over and over again in the polymer, i.e., the structure within the parenthesis in Eq. 1 or 2 or 3, is referred to as the polymer repeat unit.

Step polymerization proceeds by the stepwise reaction between X and Y groups to form dimer, trimer, tetramer, pentamer, and so on until eventually polymer molecules are formed. As each larger-sized species is formed, it competes with the smaller-sized species for further reaction. Any two molecular species containing X and Y groups can react