TOPOCHEMICAL EFFECTS IN CHEMICAL REACTIONS OF CRYSTALLINE ORGANIC COMPounds

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INTRODUCTION

A topochemical effect in a solid state reaction is any effect on the structure and properties of the product or the kinetics of the reaction that can be directly attributed to the geometric arrangement of the reacting groups or the distance between those groups. Such effects can conveniently be classified in three categories: (a) Reactions in which the reactant and product form solid solutions over the entire range of compositions. (b) Reactions in which the product phase is nucleated but a crystallographic relationship between the reactant and product phases is maintained. (c) Reactions which result in an amorphous product or crystalline product having no crystallographic correlation with the reactant.

The following presentation is not intended to be a review of this field in the usual sense. Rather, an example of each class of reactions will be discussed: (a) The polymerization of o,o-diacytelyenediphenyl glutarate and 5,7-dodecadiinediol-1,12-bis-phenylurethane. (b) The cyclization reaction of N-(para-chlorophenyl) phthalanilic acid to N-(para-chlorophenyl) phthalimidine with the elimination of water. (c) The polymerization of crystalline methacrylic acid. Finally a discussion will be undertaken of the polymerization of molecular multilayers of a number of monomers, such as vinyl stearates and α-octadecylacrylic acid, which may not fit conveniently into any of the above categories.
A central theme will be an examination of the molecular mechanism of these reactions and how the structure and properties of the product is related to reactant structure and morphology.

**DIACETYLENE POLYMERIZATION**

Many substituted diacetylenes have been found to be highly reactive in the solid state (1). By exposure to uv, x-ray or gamma radiation or by annealing topochemical polymerization is initiated. Each monomer molecule joins with two neighboring molecules in a 1,4-addition reaction at the conjugated triple bonds to form a linear fully conjugated polymer chain. In this way large, nearly defect-free polymer single crystals can be obtained (1). During such a reaction unit cell dimensions show only slight changes, the space group is retained and a solid solution exists at all conversions (1). From x-ray diffraction (2,3) and Raman spectral studies (4) the polymer backbone is best represented by the mesomeric structure I (acetylenic)

\[
\begin{align*}
\text{I} & : \quad R - \overline{\text{C}} \equiv \text{C} \equiv \text{C} - R \\
\text{II} & : \quad R - \overline{\text{C}} \equiv \text{C} \equiv \text{C} - R
\end{align*}
\]

\[
\begin{align*}
\text{I} & : \quad R = \text{H}_2\text{C} - \text{O} - \text{C} - \text{NH} - \text{O}, (2); \\
\text{II} & : \quad R = \text{H}_2\text{C} - \text{O} - \text{S} - \text{CH}_3, (3).
\end{align*}
\]

However, there is in some polymer spectroscopic evidence for significant resonance contribution from structure II (butatriene) corresponding to considerable \(\pi\)-electron delocalization (4).

In contrast to the crystal structures (2,3), in which