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The Mechanism of Solid-state Polymerizations

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The Mechanism of Solid-State Polymerizations

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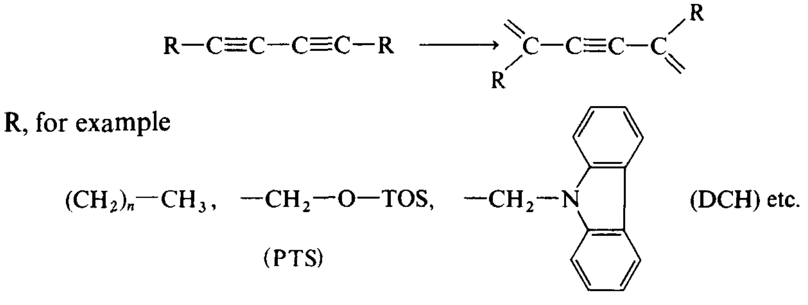
A solid-state polymerization can be treated as a special case of a phase change which may proceed homogeneously or heterogeneously. If solid-state chemistry is understood in its broadest sense, also such reactions may be considered which occur at the interphase between a gaseous educt and the crystalline product where e.g. each step of crystal growth occurs with formation of a chemical bond. In polymer science such reactions are called simultaneous polymerization and crystallization.

Recent results on the mechanism of such reactions will be discussed, using the following reactions as actual examples: The topochemical polymerization of diacetylenes, the four-center-polymerization of diolefines and the formation of polyoxymethylene under conditions of simultaneous polymerization and crystallization.

1 THE TOPOCHEMICAL POLYMERIZATION OF DIACETYLENES

The topochemical polymerization of diacetylenes allows synthesis of macroscopic nearly defect free polymer single crystals starting from the single crystals of the corresponding monomer



(1)

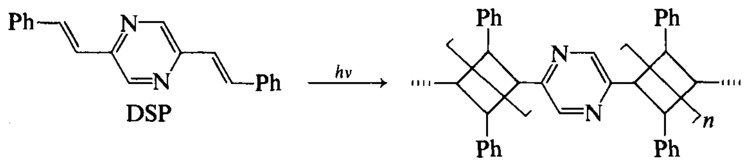
Polymer chains grow individually along a unique crystallographic direction starting from points which are randomly distributed throughout the lattice. A polymerizing crystal is thus classified as a solid solution of extended macromolecules in the lattice of residual monomer. This is directly proven by observation of the Brillouin scattering of polymerizing single crystals which also allows to determine the variation of the elastic constants and of the average molecular weight of the polymer chains as a function of conversion.

Sometimes phase changes occur during polymerization due to the strain which is exerted onto the monomer lattice by the growing polymer chains. Such a phase change is described for the case of DCH which, nevertheless, does not destroy the single crystal character of the final polymer crystal because coherence of the lattice is guaranteed by the chains already formed when the phase change occurs.

Another interesting aspect is the photophysics and photochemistry of such systems. More insight was gained recently by investigation of multilayer assemblies of appropriate diacetylenes. Thus, the quantum yield and its dependence on conversion could be determined. The initial quantum yield $\Phi_{254} \geq 14$ decreases exponentially with increasing conversion.

2 FOUR-CENTER POLYMERIZATION OF DIOLEFINES

The four-center photopolymerization gives rise to crystalline polymers with a cyclobutane ring as constitutive element of the backbone. DSP was used as model for the whole class of compounds undergoing this reaction which is merely a translation of cinnamic acid dimerization into polymer chemistry.



Single crystals of DSP disintegrate into polycrystalline polymer during photoirradiation. The space group changes from Pbca (monomer) to $P2_1ca$ (polymer). Nucleation and growth of the polymer can be observed by light and electron microscopy. Nucleation occurs at defect sites. The polymer grows with different rates into different crystallographic directions. Polymerization thus occurs at the transition region between monomer crystal and polymer product phase and not in the bulk of the undisturbed lattice, as was previously assumed.

Similar observations were made in photodimerization of cinnamide. Thus, the question is raised, how the concept of topochemistry which considers the packing within the unperturbed lattice as the reaction determining factor can be brought into agreement with the present results.

3 SIMULTANEOUS POLYMERIZATION AND CRYSTALLIZATION

The cationic polymerization of trioxane provides an interesting case not only of crystal growth of a polymer under polymerization conditions but also of crystal growth controlled by a catalyst. The growth features such as nucleation, growth spirals etc. were observed by electron microscopic techniques. The polymer crystals grow both in width and in thickness indicating that there are at least two different chemical reactions involved in crystal growth. With $HClO_4$ as the catalyst the basic growth features are

a) Formation of a hexagonal base lamella during the nucleation step in which all polymer chains are aligned with their axes perpendicular to the lamella surface; the chains are most probably folded in the lamella surfaces.

b) Spiral growth in thickness in direction of the chain axes by insertion of monomer into the chain folds. The step width of the growth spiral is a well defined function of the catalyst concentration.

c) Growth in lateral direction most probably via addition of oligomer chains to the side-surfaces of the hexagonal crystals. It thus turns out, that the kinetics of this (technical relevant) polymerization is completely controlled by crystal growth.

In conclusion it will be emphasized that the observation of the morphology and texture of the reaction products of solid-state reactions is absolutely necessary in order to obtain insights into the mechanisms and the kinetics of such reactions.