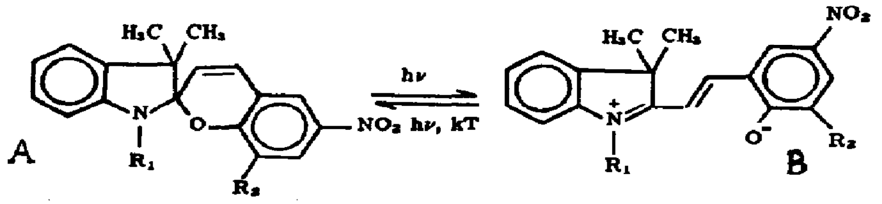
DIPOLAR CRYSTALS PRODUCED PHOTOCHEMICALLY AND THEIR BEHAVIOR IN LYOPHILIC COLLOIDAL SOLUTIONS

V.A. Krongauz, E.S. Goldburt and S.N. Fishmann

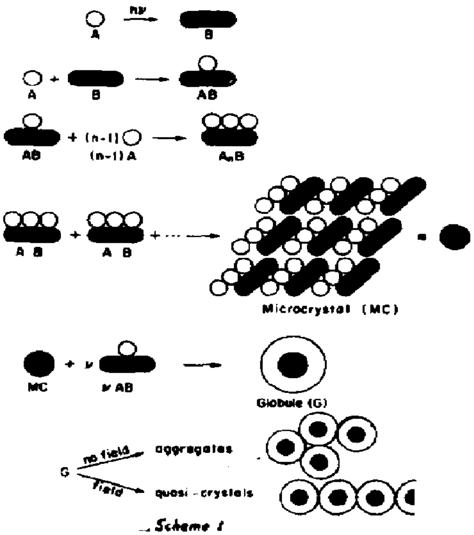
Depatrment of Structural Chemistry, The Weizmann Institute of Science, Rehovot (Israel)

Colloidal suspensions are formed during the photochemical transformation of solutions of photochromic spiropyrans



in saturated non-polar solvents. The suspensions consist of globules ~0.1-0.4 μm in diameter. The globules are composed of crystalline nuclei enclosed in amorphous envelopes, and the nuclei in turn consist of complexes A_nB (with n=2-3), while the envelopes consist of dimers AB (A is the colorless form of a spiropyran and B is photocolored merocyanine form). The crystalline nucleiexhibit spectral red shift of about 100 nm as compared to the amorphous envelopes.

During irradiation of spiropyran solutions in a constant electric field (5-25 kV/cm) a linear quasi-crystalline material (threads) is formed composed of globules joined together like straight strings of beads aligned along the electric lines force. Linear dichroism measurements showed that the complexes A_nB of which the crystalline nuclei are made are oriented along the thread axes. Orientation of single A_nB complexes in weak electric fields for any reasonable molecular dipole is very unlikely in view of the thermal motion. For a field of 5 kV/cm the orientation can take place only if the dipole moment is greater than 10^3D. We therefore conclude (see Scheme 1) that A_nB complexes form one dimensional dipolar molecular stacks (similar to J-or Scheibe-stacks inherent in many cyanine dyes). A number of such stacks are combined in three dimensional dipolar microcrystals. The globules are formed when the microcrystals become coated with an amorphous phase composed of dimers AB. In an electric field the transition from the state in which the dipolar globules are oriented in a colloidal solution along the field but spaced at random to the ordered thread structure occurs, according to a theoretical estimation, if the dipole moment is greater than 10^4D.



Scheme 1

An alternating electric field has no effect on the systems, indicating that induced dipoles do not play a prominant role in the phenomenon under consideration.

It was experimentally demonstrated that the nuclei of globules obtained in the absence of an electric field are also dipolar. This suggeststhat the formation of these huge crystalline dipoles(probably pyroelectrics)is a spontaneous process proceeding without an electric field.

All stages of quasi-crystal growth were observed in the electron microscope: formation of microcrystals, their consolidation into globular nuclei,coating of the nuclei by amorphous material and finally formation of quasi-crystal threads.

There are two remarkable regularities concerning the quasi-crystal growth:(a)Every quasi-crystalline thread consists of globules of equal size.(b)The globule radii increase step-wise during irradiation, resulting in the appearance of several generations of threads. In our experiments the radii of globules of which threads of the first, second,third and forth generations are composed are in the ratio ~4:7:10:18. These characteristic features of quasi-crystal growth were explained by considerations of the thermodynamics and kinetics of this process.

References

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