Effects of Wavelength and Matrix on Four-Center Type Photopolymerization of 2,5-Distyrylpyrazine and Its Photodepolymerization

Masaki HASEGAWA, Yasuzo SUZUKI and Takashi TAMAKI

Research Institute for Polymers and Textiles, Sawatari, Kanagawa-ku, Yokohama, Japan

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In previous papers,1–5) preparative, kinetical and crystallographic studies on four-center type photopolymerization in the solid state have been reported for a series of several diolefine compounds.

As a result, a number of new types of highly crystalline linear polymers with cyclobutane in the main chain has been prepared mostly in quantitative yield.

Recently the polymerization was found to be lattice-controlled, that is, the chain growth is strictly governed by three axes of the monomer crystal and proceeds through a direct rearrangement from monomer crystal to polymer crystal.

For example, crystals of 2,5-distyrylpyrazine (DSP) and poly-2,5-distyrylpyrazine (poly-DSP), belong to the same space group (Pbca).6)

We have investigated the effects of wavelength and matrix on four-center type photopolymerization of 2,5-distryrylpyrazine and its photodepolymerization.

First, DSP oligomer (average molecular weight ≃900, mp 285—290°C) was obtained from DSP crystals in water-methanol (4 : 6) nearly quantitatively by irradiation of the light with a wavelength longer than 400 mμ for about one hour at room temperature while DSP crystals were converted into a high molecular weight of the polymer (mol wt >100000) in a quantitative yield by xenon or high pressure mercury lamp under a similar condition.

DSP oligomer crystals (*as*-polymerized) were converted quantitatively into a high polymer by the irradiation of monochromatic light of 340 mμ from a Shimadzu Bausch & Lomb monochrometer.

DSP crystals show an absorption occurring at 440 mμ with a maximum peak at 380 mμ while DSP oligomer has no absorption of a wavelength longer than 380 mμ. It is presumed that a longer wavelength (>400 mμ) can excite only the monomer, and a shorter wavelength (<380 mμ) is required for further growth of terminal groups in the oligomer.

On the other hand, DSP oligomer crystals (recrystallized) which differ from the crystals (*as*-polymerized) from X-ray patterns, does not polymerize by the same light (340 mμ).

Moreover, a solution of the DSP oligomer in chloroform promptly returns to the monomer by the same light (340 mμ).

It is noteworthy that the DSP oligomer (*as*-polymerized) consists of thermally irreversible crystals as well as the resulting poly-DSP crystals7): DSP oligomer crystal (*as*-polymerized) can never be reproduced after the oligomer becomes amorphous and the oligomer with a different crystal form is reprecipitated from a solution of above oligomer crystal (*as*-polymerized).

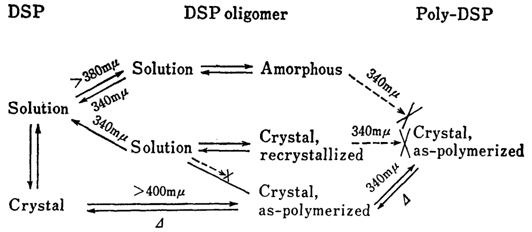
DSP oligomer does not grow further into high polymer by the irradiation of 340 mμ without an effective "topotactic assistance", as is the case in the crystalline oligomer (as-polymerized).

It is interesting that chemically the same substance behaves in three different ways according to physical states.

This is a clear-cut example of matrix effect originating in the topochemical procedure.

Amorphous DSP oligomer results from the solution of DSP in chloroform by the prolonged irradiation of light with a wavelength longer than 380 mμ in nitrogen atmosphere. As expected, amorphous oligomer does not polymerize in the solid state and depolymerizes in the solution in the same way as the oligomers from DSP crystals.

A schematical diagram of photochemical interrelationship in DSP, DSP oligomers and poly-DSP is shown below:



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