CHEMISTRY LETTERS, pp. 497-498, 1975. Published by the Chemical Society of Japan

A NOVEL TYPE OF POLYMER-EFFECT DUE TO A RIGID ROD-SHAPED CHAIN. THERMAL DEPOLYMERIZATION BEHAVIOR OF POLY-2,5-DISTYRYLPYRAZINE

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A novel type of polymer-effect due to a rigid rod-shaped chain, was observed. On the thermal depolymerization of poly-2,5-distyryl-pyrazine at 290°C, a high molecular weight polymer crystal is much less stable than the same of low molecular weight. This is the first example of chemical reaction that the breakage of chemical bond is dependent on the molecular length.

A rigid rod-shaped configuration of poly-2,5-distyrylpyrazine (poly-DSP) was confirmed from the crystallographic study on DSP and poly-DSP[1] as shown in Figure 1.

In a recent paper,[2] it was suggested that the thermal chain scission of as-polymerized poly-DSP crystal proceeded in the crystalline state not at random on the position of cyclobutane ring in the molecular chain but somewhat favorably on the position of cyclobutane ring in the middle of the chain.

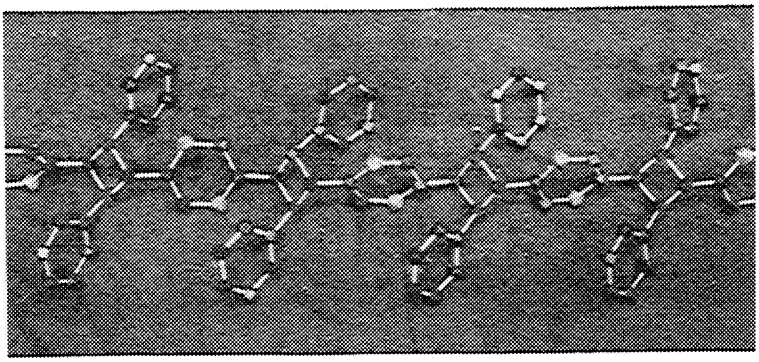

Fig. 1. Molecular structure of poly-DSP

In the present paper, thermal stabilities of high and low molecular weight of as-polymerized poly-DSP crystals were

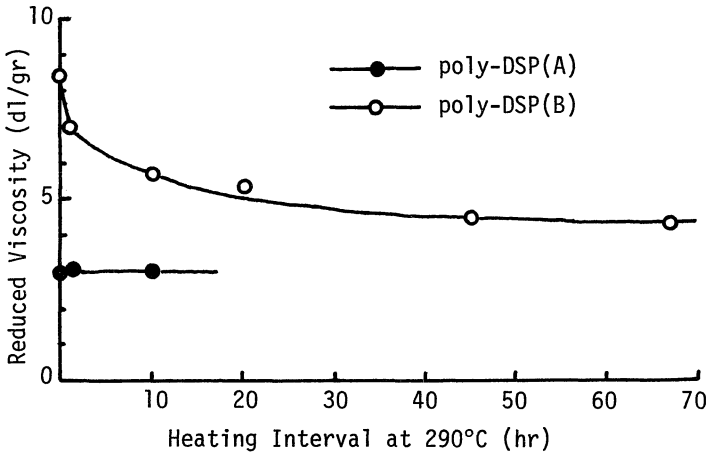

Fig. 2. Change of reduced viscosity of poly-DSP crystal by the heat-treatment at 290°C (the original molecular weight; poly-DSP(A) = 10,000, poly-DSP(B) = 63,000)

compared in oredr to make clear the position of thermal scission of the rigid polymer chain.

As shown in Figure 2, when the as-polymerized poly-DSP of which reduced viscosities are 3.0 (poly-DSP(A), Mol. Wt. = 10,000 and Mol. Length = 265 Å) and 8.4 (poly-DSP(B), 63,000 and 1670 Å) were kept at 290°C in long periods, the longer polymer chain of 8.4 was broken down to 4.0 (14,000 and 370 Å), while the shorter one of 3.0 stayed at the original length even after 10 hours.

As a result, it was confirmed that the longer rigid chain of poly-DSP crystal is strikingly less stable than the shorter. In other words, there is a limit of chain length where the rod shaped molecule can exist stably in a given condition, such as 370 Å of molecular length at 290°C for poly-DSP.

The result can be understood by considering such a popular phenomenon that the long but slender stick is easily broken around at the center part whereas the same but shorter one is not broken by the same force.

This is a novel type of polymer-effect due to a rigid rod-shaped chain, indicating that the breakage of chemical bond depends on the molecular length, although an analogous effect has been reported on sonic treatment of Tabacco Mosaic Virus[3] where the polymer aggregates are dissociated.

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(Received March 24, 1975)