BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2622—2623 (1970)

The Reaction Route of 2,4,6-Triphenyl-*s*-triazine to the C=N Conjugated Polymer

Eizo OIKAWA and Atsushi OHKUMA

Faculty of Engineering, Niigata University, Nagaoka, Niigata

(Received January 13, 1970)

The heating of 2,4,6-triphenyl-*s*-triazine (cyaphenin) with a metal halide afforded a black polymer. A similar polymer was obtained from the benzonitrile complex with a metal halide. In this note, the reaction route of cyaphenin to the polymer was investigated in order to determine whether or not the polymerization proceeds by the usual ring-opening, since Kabanov *et al.*[1] have reported the conversion of cyaphenin to the polymer as a ring-opening. Their meaning was, however, ambiguous.

The reaction of cyaphenin[2] with zinc chloride[3] was carried out in an about-20-m*l*, vacuum-sealed ampule by heating a mixture in the molar ratio of 2 : 3 (2 : 1 based on the benzonitrile unit) at 350—430°C in both the presence and absence of metaphosphoric acid (MPA) for from 1 to 13 hr. The black solid formed was dissolved in sulfuric acid and precipitated by pouring the solution into water. The weight difference between the initial cyaphenin and the precipitates gave the weight of the benzonitrile, which remained unchanged. The unreacted cyaphenin was recovered by sublimation. The polybenzonitrile from the zinc chloride complex was prepared by heating a mixture of benzonitrile and zinc chloride in a 2 : 1 molar ratio. The black product was extracted with hot toluene. The toluene was removed by distillation, and the residue was sublimed at about 200°C to give cyaphenin.

The relation between the polymer yields and the reaction time at different reaction temperatures in the presence of MPA is shown in Fig. 1. Similar curves were obtained in the absence of MPA. The apparent activation energy was calculated to be 14 kcal/mol in the presence of MPA and 16 kcal/mol in the absence of MPA, on the basis of the maximum slope in the yield-time curves.[4] The heating of cyaphenin without zinc chloride in either the presence or absence of MPA in an ampule at 430°C for 4 hr gave no appreciable amounts of benzo-

---

[1] B. A. Kabanov, V. P. Zubov, V. P. Kobaleba and V. A. Kargin, *J. Polym. Sci.*, *Part C*, **No. 4**, 1009 (1963).

[2] A. H. Cook and D. G. Jones, *J. Chem. Soc.*, **1941**, 278.

[3] Guaranteed grade: commercially available.

[4] E. Oikawa and S. Kambara, *J. Polym. Sci.*, *Part B*, **2**, 649 (1964).

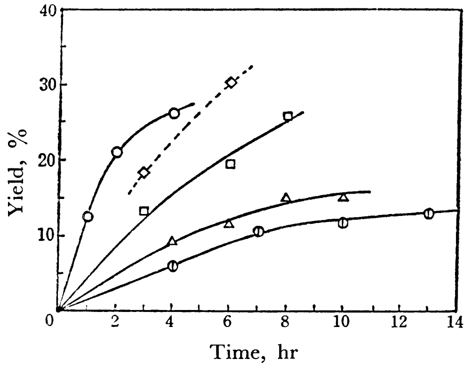


Fig. 1. Polymer yields in the presence of MPA.
○ 430°C, □ 400°C, △ 370°C, ⦶ 350°C,
◇ from $2C_6H_5CN : ZnCl_2$ at 400°C

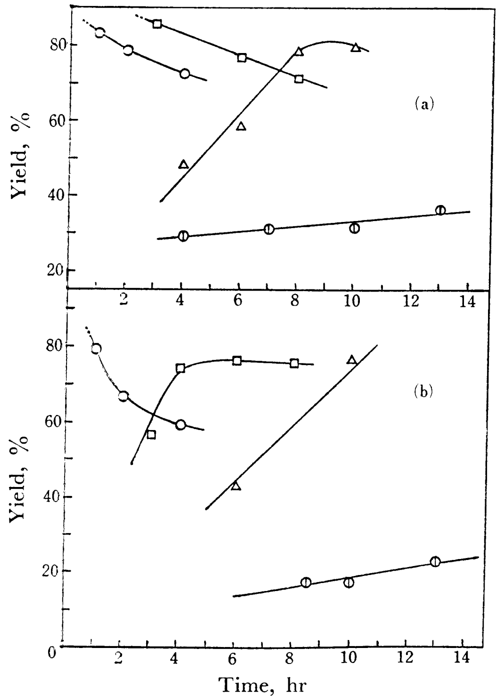
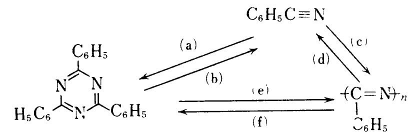


Fig. 2. Yields of unreacted benzonitrile in the presence (a) and absence (b) of MPA.
○ 430°C, □ 400°C, △ 370°C, ⦶ 350°C

nitrile, although in the presence of MPA a little stronger smell of benzonitrile was perceived. In order to examine the influence of MPA on the trimerization, benzonitrile was heated with 5% MPA in an autoclave at 300°C for 24 hr. This gave only a 0.3% yield of cyaphenin. These facts indicate that MPA neither initiates the trimerization nor decomposes the trimer by itself.

Unreacted benzonitrile, as is shown in Figs. 2 (a) and (b), was formed by the decomposition of cyaphenin and was not changed to either the polymer or cyaphenin. The yields of benzonitrile decreased at higher temperatures and increased at lower temperatures with the reaction time. The decrease in the yields of the unreacted nitrile reveals that the decomposition of cyaphenin took place in the initial reaction period and in the subsequent reaction period the benzonitrile thus formed was converted to the polymer. In other words, the rate of the decomposition of cyaphenin is very rapid compared with the rate of the polymer formation at higher temperatures. On the other hand, the increase in the yields of the unreacted nitrile at lower temperatures corresponds to the accumulation of benzonitrile due to the difference between the decomposition and the polymer-formation rate of cyaphenin, since the decomposition of cyaphenin to benzonitrile proceeds at a higher rate than the conversion of benzonitrile to the polymer. Therefore, the activation energies noted above indicate those of the polymerization reaction of benzonitrile. The variations in the yields of the unreacted benzonitrile indicate that MPA acts as a promoter in the decomposition of the trimer to the monomer in the presence of zinc chloride. These results can be summarized as in the following diagram:



The once-produced polymer is thermally stable and remains unchanged except for a slight decomposition, accompanied by NH_3 formation.5) The routes (d) and (f) can, therefore, be neglected compared with the other routes. The ring-opening path of cyaphenin *via* (b) to give benzonitrile is made possible by the preferential formation of benzonitrile in Figs. 2 (a) and (b). The route (c) from the benzonitrile complex with zinc chloride to the polymer is preferential to the route (a) back to cyaphenin, as is demonstrated by the higher yields of the polymer. Consequently, the route (e) should not be appreciable compared with (b) and (c). The presence of the equilibrium between (a) and (b) is demonstrated by the higher polymer yields from the complex than those from cyaphenin at 400°C, as is shown in Fig. 1, and by the simultaneous formation of cyaphenin from the complex.

---

5) E. Oikawa and S. Kambara, This Bulletin, **37**, 1849 (1964).