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Note

Isomeric polyaminobenzophenones. Syntheses and thermal degradation

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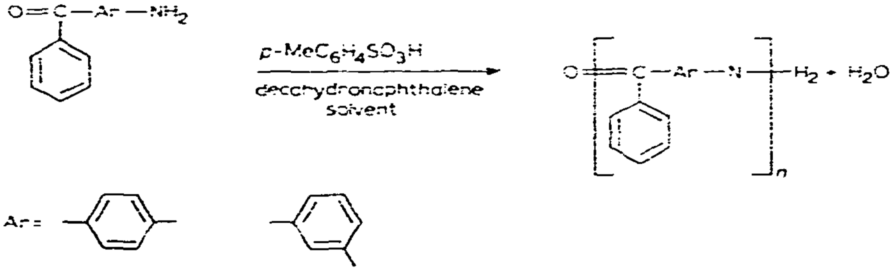
In the course of our investigations[2-4] of the molecular structure-thermal property relations of isomeric poly-Schiff bases, we have synthesized polymers from isomeric diketones and isomeric aryl diamines (AABB systems). However, in this work we are reporting the syntheses and thermal properties of two polymers which are the products of isomeric aminoketones (AB systems). These polymers were synthesized from 3-amino benzophenone and 4-aminobenzophenone by means of an acid-catalyzed, solution polycondensation. Our attempts to synthesize a polymer from 2-aminobenzophenone were unsuccessful.

Although 4-aminobenzophenone has been previously bulk polymerized, it has not been well-characterized[5]. In addition, our synthesis constitutes the first successful solution polymerization of the two isomeric aminoketones.

The general reaction and the specific conditions used for the polymerization of the aminobenzophenones were as follows:



Experimental

Comparative thermal stabilities of the polymer products were investigated in air and in a nitrogen atmosphere with a DuPont 950 thermogravimetric analyzer programed for a heating rate of 6°/min and with a gas flow rate of 40 ml/min. The initial sample weight in each case was 20 mg. Infrared spectra of Nujol suspensions of the products were obtained with a Perkin-Elmer Infracord. Mass spectral analysis was accomplished by means of a Hitachi Perkin-Elmer RMU-7 high-resolution mass spectrometer employing an electron energy of 70 eV and a resolution of 900. The polymer samples were vacuum volatilized by direct entry into the mass spectrometer and the inlet temperatures were 270° for the analysis of poly-3-aminobenzophenone and 345° for the analysis of poly-4-aminobenzophenone. Elemental analyses were performed by MHW Laboratories, Garden City, Michigan.

Preparation of poly-4-aminobenzophenone

A mixture of 0.98 g (0.005 mol) of 4-aminobenzophenone (Aldrich Chem. Co., Cedar Knolls, N. J.) and 0.05 g of *p*-toluenesulfonic acid monohydrate in 100 ml of dry decahydronaphthalene was refluxed, with stirring, under a nitrogen atmosphere for 24 h. The condenser was fitted with a Dean–Stark water trap. After the mixture was cooled, the precipitated polymer was collected by filtration and then Soxhlet extracted for several hours with a solution of equal volumes of ethanol and water. After drying for one hour at 100°, 0.30 g (34% yield) of a light tan powder was obtained. This material did not melt below 400°.

The infrared spectrum contained a C = N absorption at 6.2 μ which was consistent with that expected of the desired product[6]. In addition, the disappearance of the amino absorption peak at approximately 3.0 μ was noted. Direct inlet mass spectral analysis resulted in recovery of most of the starting sample, which did not volatilize. The small amount which did volatilize exhibited a molecular ion peak at *m/e* of 537 in its mass spectrum. This indicates the presence of cyclic trimer. Analysis: Calculated for $(C_{13}H_9N)_n$: C, 87.15%; H, 5.03%; N, 7.82%. Found: C, 87.04%; H, 4.95%; N, 7.67%.

Preparation of poly-3-aminobenzophenone

Synthesis of the monomer for this polymerization was accomplished by reducing 3-nitrobenzophenone with iron and hydrochloric acid[7]. The 3-nitrobenzophenone was synthesized by means of a typical Friedel–Crafts acylation of benzene with *m*-nitrobenzoyl chloride (Aldrich Chem. Co., Cedar Knolls, N. J.) using aluminum chloride as the catalyst. Molar ratio of catalyst to acid chloride was 2:1. The polymerization procedure was identical to the one used to prepare poly-4-aminobenzophenone. The polymer obtained in this instance was 0.26 g (29% yield) of a nearly colorless powder which melted at 275°.

The infrared spectrum of this material was also consistent with that expected of the desired product and the mass spectrum of the small amount which volatilized also contained a molecular ion peak at *m/e* of 537. Analysis: calculated for $(C_{13}H_9N)_n$: C, 87.15%; H, 5.03%; N, 7.82%. Found: C, 87.27%; H, 5.03%; N, 7.82%.

Thermal stability

When heated in nitrogen and in air at a rate of 6°/min, poly-3-aminobenzophenone was thermally stable up to 300° (Fig. 1) and poly-4-aminobenzophenone was stable up to 400° (Fig. 2). Thermogravimetric analysis pointed out two unusual thermal properties of these polymeric systems: (1) they exhibit essentially the same resistance to initial thermal decomposition in an oxidative as well as in an inert atmosphere and (2) even in an inert atmosphere, both polymers are nearly completely volatilized. In the case of poly-3-aminobenzophenone essentially complete thermal

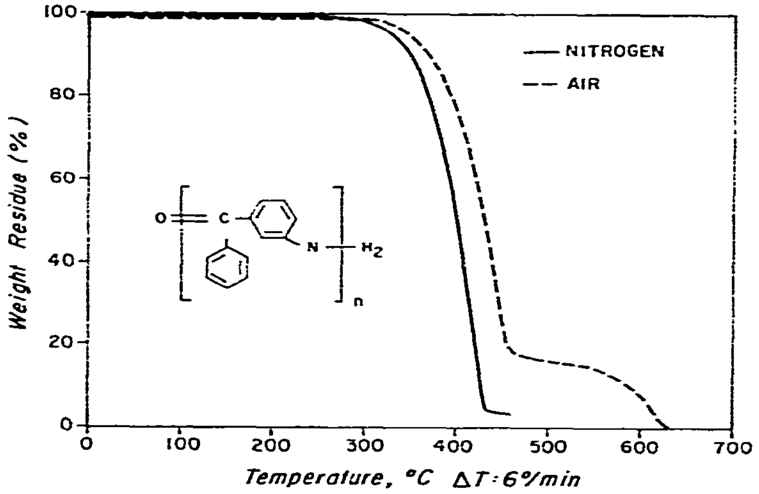


Fig. 1. TGA of poly-3-aminobenzophenone.

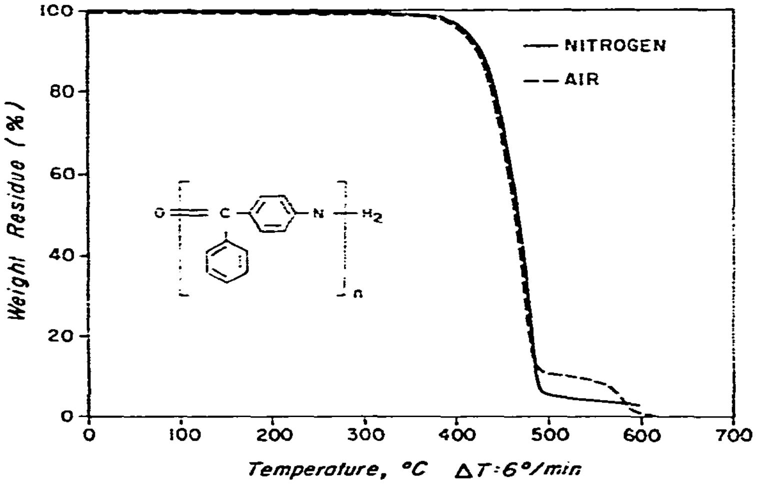


Fig. 2. TGA of poly-4-aminobenzophenone.

volatilization occurred below 500° whereas poly-4-aminobenzophenone underwent essentially complete volatilization at approximately 550°.

Having the same resistance to initial thermal decomposition in an oxidative and in an inert atmosphere seems to be a general characteristic of poly-Schiff bases. In our previous investigations of AABB polymers, this property was exhibited without exception[2-4]. The reasons for this behavior, however, are not presently known. The factors involved in the complete volatilization of the AB systems in an inert atmosphere are also not known. This behavior, unlike resistance to initial thermal decomposition, is in marked contrast to the behavior of the AABB systems which have shown as little as 25% weight loss in nitrogen at 800°.

There are several factors, however, which, individually or in combination, may explain the high degree of volatility of the two polymers in nitrogen. One is that the presence of cyclic trimers, which were detected by direct inlet mass spectroscopy, may increase volatility. Secondly, the linear polymer formed may not be of very high molecular weight. A degree of polymerization of only nine or ten would be required to render the end-groups negligible and yield the excellent elemental analysis which we have obtained. A polymer of this low a molecular weight (less than 2000) could conceivably be volatile. Finally, volatility may be an inherent property of the AB systems up to a fairly high molecular weight.

The higher degree of thermal stability of poly-4-aminobenzophenone over that of poly-3-aminobenzophenone is predictable from their respective molecular structures. One would expect the polymer molecules of the *para* isomer to be more symmetrical and more highly oriented and therefore, more resistant to thermal stress. In addition the cyclic trimer of 4-aminobenzophenone would be expected to be more thermally stable than the trimer of 3-aminobenzophenone on the basis of molecular structure. Molecular models of the trimers indicate that the eighteen-membered ring from 4-aminobenzophenone is much more strain-free than the fifteen-membered ring from 3-aminobenzophenone.

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