

RESEARCH ON CONDENSATION OF DINITRILES, COORDINATION POLYMERS OF TRIAZINE, AND CONDENSATION POLYMERS OF TRIAZINE

I. B. Johns and H. R. DiPietro
Monsanto Research Corporation, Boston Laboratories

ABSTRACT

The research reported here arose from two discoveries. First, the nitriles of the lower dibasic acids condense at high pressure and elevated temperature to yield insoluble and fairly stable polymeric substances containing the $-C=N-C=N-$ chain. Second, the zinc and beryllium coordination compounds of tris(2-hydroxyphenyl)-s-triazine are polymeric and exhibit phenomenal thermal stability. This report summarizes the general structural principles of thermal stability and reviews the work on nitrile condensations and the synthesis of bifunctional aryl triazines which yield stable linear coordination polymers and stable condensation polymers.

INTRODUCTION

This research has employed the following five general principles of thermal stability: (1) only the strongest chemical bonds must be used, (2) the structure must allow no easy pathways for rearrangement, (3) there must be maximum use of resonance stabilization, (4) all ring structures must have normal bond angles, and (5) the polybonding principle must be utilized as much as possible.

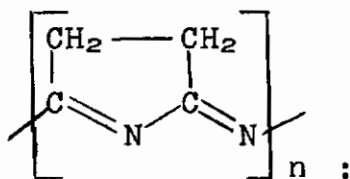
The polybonding principle requires that each skeletal atom be linked in the chain by more than one route. Polybonding is to be distinguished from multiple bonding as this latter term is defined in organic chemistry. Condensed rings are good examples of polybonded structures. Thus the "chains" in such extended compounds as anthracene, tetracene, pentacene, etc., cannot be broken by the rupture of only one carbon-carbon bond. Furthermore, if one bond is ruptured the natural bond angles of the structure hold the atoms near enough so that the bond can heal after the excess energy has dissipated by vibration through the molecule.

When the polybonding principle is applied to its fullest extent the products lack flexibility. They are the familiar "brick dust" and resist sintering into useful shapes even at very high pressure and temperatures. It is therefore necessary to build into the molecules some flexibility by means of single bonds. These flexible links should be made through inorganic units if great sacrifice of thermal stability is to be avoided.

It seems to be unimportant whether the building blocks are organic or inorganic since adequate stability can be realized by application of the principles mentioned above. In the present research several structures have been synthesized which are stable

to 500°C. It is in the flexible links that the strongest bonds are required, which probably can be realized only by employing elements other than carbon.

The work reported here falls into three general areas: First, the condensation of some dinitriles at very high pressure and temperature, which, in the case of succinonitrile, results in a poly ring system in which the repeating unit is



Second, the coordination polymerization of the bifunctional triazine, 2-(2-phenoxyphenyl)-4,6-bis(2-hydroxyphenyl)-s-triazine, resulting in a thoroughly polybonded structure;

Third, the condensation of the bifunctional triazine, 2-phenyl-4,6-bis(3-hydroxyphenyl)-s-triazine with diphenyldichlorosilane.

DISCUSSION

HIGH PRESSURE EQUIPMENT

For the high pressure work various modifications of the piston and cylinder apparatus and also the Bridgman anvil apparatus have been used. In some experiments internal thermocouples have been used for differential thermal analysis for observation of reaction rates. The piston and cylinder equipment has been used to 25,000-28,000 atmospheres and up to 450-500°C. The anvil apparatus has been used to 38,000 atmospheres and to 525°C.

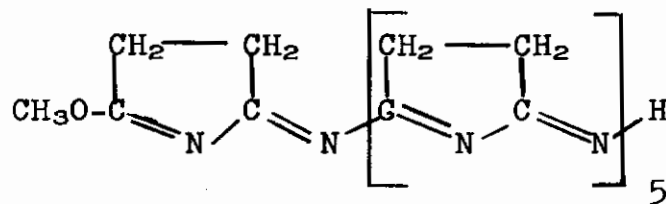
CONDENSATION OF NITRILES

The work of Cairns, et al., and of Bengelsdorf has shown that mononitriles condense under high pressure to yield sym-triazines. The condensation proceeds with moderate speed, as compared with the chemical trimerization at one atmosphere. In the case of the nitriles of the lower dibasic acids a more complicated reaction occurs which can proceed with explosive violence unless moderated by dilution with an inert solvent. Such compounds as malononitrile, fumaronitrile, and succinonitrile must be handled with great care under high pressure. Anionic catalysts such as sodium methoxide and sodium 2,4-dichlorophenate markedly lower the temperature and pressure required for initiation of condensation.

The effect of pressure on the condensation is exactly as expected for a bimolecular addition reaction. The rate is increased at any given temperature by increasing the pressure, while the temperature at which reaction is initiated is lowered by increasing the pressure.

Contrails

Analysis and end-group determinations show that the product from succinonitrile, initiated by sodium methoxide in methanol, has the structure:



The infrared spectrum shows the complete absence of $-C\equiv N$ groups and the presence of $-C=N-$ groups. When sodium dichlorophenate in methanol was used as catalyst, the product has a degree of polymerization of 66 and the chain is initiated by a dichlorophenoxy group.

The measured thermal stability of these products was somewhat disappointing. Gases were slowly evolved at 300°C . Ammonia was the principal gaseous product. The limited thermal stability is obviously due to the large number of single bonds per molecule.

Other nitriles were studied at high temperature and pressure. Terephthalonitrile mixed with benzonitrile yielded the three expected products; namely, triphenyltriazine, the double triazine of terephthalonitrile with four benzonitrile molecules, and the polymeric triazine of terephthalonitrile alone. This latter compound is an infusible, insoluble, tan powder. The condensation of 2,6-dicyanopyridine yielded a very hard black solid. Infrared spectra show that the nitrile groups had condensed to triazine rings to form a network polymer. The diimide of pyromellitic acid and p-aminobenzonitrile condensed via the terminal nitrile groups only partially at 20,000 atmospheres and 500°C . About 80% of the nitrile groups remained after 20 minutes at these severe conditions.

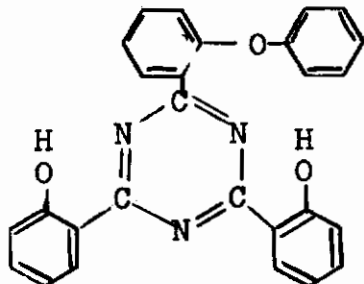
Not all nitriles will condense under these conditions. Anthranilonitrile refused to condense; salicylonitrile, however, easily yields the corresponding triazine. The phenyl ether of salicylonitrile, o-cyanodiphenyl ether, has resisted all our efforts to trimerize it.

COORDINATION POLYMERS

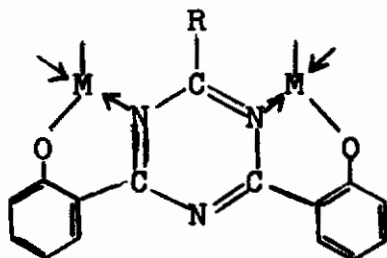
The structure of the trimer of salicylonitrile, 2,4,6-tris(2-hydroxyphenyl)-s-triazine, suggests that it should coordinate with divalent tetracoordinate metal ions to form polymeric products. Since there are three sites for coordination in this triazine the products are likely to be somewhat crosslinked even when only enough metal ion is used to satisfy two sites. An extensive study of this ligand and its metal chelates was made, which is presented in a paper in the Journal of Organic Chemistry, vol. 27, p.592. The zinc and the beryllium compounds are completely stable at 500°C .

Contrails

Truly linear coordination polymers can be prepared from bifunctional triazines such as the monophenyl ether of the above compound. To investigate this possibility 2-(2-phenoxyphenyl)-4,6-bis(2-hydroxyphenyl)-s-triazine was prepared. It can coordinate with metal ions at only two sites and should yield a linear polymer that is thoroughly polybonded. The ligand has the structure shown here, where R is the phenoxyphenyl group:



The coordination compounds with bivalent tetracoordinate metal ions have the structure:



The infinite linear polymer contains one metal ion per triazine unit. This composition is never obtained exactly because the polymer chains are rather short, containing 6 to 8 triazine units. The chains are terminated by metal ions carrying small groups such as acetate, acetylacetonate, or hydroxyl, from the solution. For this reason the metal content is always slightly higher than that calculated for the infinite polymer. No method is yet available for determination of molecular weight except the metal or end-group analyses, which are uncertain because thorough purification of the polymer has not been possible.

The phenoxyphenyl group, at R, greatly improves the sinterability of the polymer, as was expected. Although the zinc compound is infusible at 500°C it sinters at only 240°C under a pressure of 12,000 atmospheres to yield a strong, hard, translucent yellow solid.

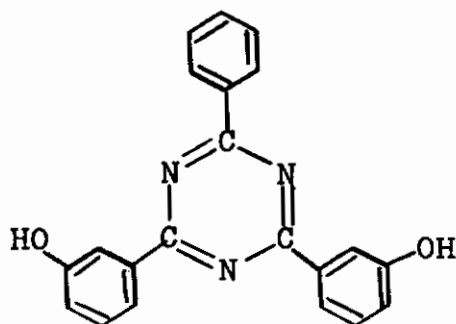
The thermal stability of these coordination polymers is due to the fact that they comply well with the principles mentioned in the introduction. The polybonding principle is particularly well illustrated. The main chain of the polymer cannot be broken by the rupture of any one bond. Resonance extends throughout the whole molecule. Only strong chemical bonds are employed and bond

Contrails

angles are normal. Models of the compound show that the structure is tightly packed but not strained. Beyond doubt strong Van der Waals forces give high crystal lattice energy, which contributes to the thermal stability as well as to the high melting point. A careful study of these principles in relation to structure will lead to even more substantial polymers.

CONDENSATION POLYMERS

The lack of flexibility of the above coordination polymers suggested that this physical property might be improved by coupling stable triazine molecules by single bonds. It is obvious that the coupling must be done through very strong chemical bonds if great sacrifice of thermal stability is to be avoided. Even so, the loss of polybonding will be detrimental. The -O-Si-O-linkage was the obvious choice. It was also clear that coupling could be done more easily at the meta- or para- positions on the benzene rings than at the ortho-position. To investigate this system the synthesis of 2-phenyl-4,6-bis(3-hydroxyphenyl)-s-triazine was undertaken. The structure of the triazine is:



The synthesis involved the preparation of the dinitro derivative, 2-phenyl-4,6-bis(3-nitrophenyl)-s-triazine by the Eitner and Krafft synthesis, using 3-nitrobenzotrile and benzoylchloride with aluminum chloride and ammonium chloride. After careful purification this product was hydrogenated with platinum oxide and 50 psi hydrogen to yield 2-phenyl-4,6-bis(3-aminophenyl)-s-triazine, which was then diazotized to yield the desired compound. Purification of the product was accomplished by preparation of the dibenzoate and subsequent hydrolysis.

The condensation polymer was prepared by heating the pure dihydroxy compound with diphenyl dichlorosilane in diglyme under dry nitrogen, while titrating the slowly evolved gaseous HCl with standard sodium hydroxide solution. The product is a brown solid that softens at 175°C. It is completely stable at 360°C and can be sintered under high pressure to yield a coherent, but somewhat brittle solid. Analysis indicates that the polymer molecule contains seven triazine units and six silicon atoms.

CONCLUSIONS

1. The high pressure condensation of dinitriles yields reasonably stable solid, black polymers. The products are very insoluble, brittle, and unsinterable. A more thorough study of the structure of these products and the mechanism of the reaction must be made before useful materials can be prepared.
2. Coordination polymers whose structures agree with the principles for thermal stability offer great promise.
3. Methods are needed for control of chain length in the coordination reaction, as are also methods for determination of chain length.
4. Polymers produced by linking thermally stable bifunctional units by means of single bonds will require the strongest inorganic links if maximum thermal stability is to be realized.