

CHAPTER-I  
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Much of recent polymer research is concentrated in the development of thermally stable high-molecular-weight polymers. It has been found after investigation that addition polymers, in general, decompose thermally by low-energy routes, as their hydrogen content is relatively high and most of them consist of ethylenic linkages. Presence of aliphatic unsaturation and dissociable functional groups make them more vulnerable to oxidative attack and pyrolysis. Bulky substituents in the chain, which may provide additional rigidity, fail to produce the desired effect due to steric factors. Fused-ring polymer systems also are not very satisfactory. Even inorganic polymers lack in exceptional stability and possess the drawback of undergoing molecular rearrangement or cross-linkage, when heated and also hydrolysis. Replacement of some of the atoms or some units in the polymeric inorganic chain, however, may enhance the thermal stability as well as the tractability to some extent, whereas the low-molecular-weight semi-organic polymers containing electron-donating atoms like nitrogen, oxygen, etc., which are co-ordinated with metals, are not processable at all. On the contrary, aromatic-based linear condensation polymers with unsubstituted-ring-structured segments in the chain are usually thermo-resistant. Adequate degree of crystallinity, strong hydrogen-bonding accomplished through formation of polar bonds and close chain-packing due to vander Waals' forces confer greater thermal stability. Although the materials may thus acquire good thermal

stability and sustain extensive heating at high temperatures, they become practically insoluble and intractable. Lower degree of polymerization or introduction of hetero-atoms in the chain might avert these problems, but heating to below the decomposition-temperature causes the polymers to revert to the state of insolubility by cross-linking. Hence, in addition to the question of thermal stability, processing characteristics, such as solubility, flexibility, formability and mechanical strength, are also of important consideration, from the practical standpoint of view, for materials to be used as adhesives, molding powders, coatings and laminating matrices. The difficulties encountered in the synthesis of high-molecular-weight thermally stable polymers owing to poor solubility and abnormally high melting points, even at the intermediate or formative stage, and the inherent lack of purity of the species due to inseparability of the various products formed by side reactions, branching and cross-linking to different extents, have complicated the problem further. Suitable plasticizers, stabilizers, modifiers and curing agents are, therefore, yet to be sought for in order to convert the thermostable condensation polymers into their final completely insoluble and inert forms with minimum loss of volatile matter during their processing, because the usability of a material is always improved by the successful development of the process technology.

Lately, pyrolysis of aromatic polyimides has rendered

the path open towards high-temperature-resistant organic semi-conductors. Synthesis of a new class of linear polymers consisting of recurring conjugated azomethine (  $\overset{|}{-C=N-}$  ) bonds has also aroused considerable interest. The presence of nitrogen atoms with non-bonding electron pairs exerts a favourable influence, by interaction with the  $\pi$ -orbitals of the conjugated chain, on the conductivity of the polymers, because they serve as additional sources of delocalised electrons. The thermostable character coupled with different degrees of semi-conductiveness and insolubility in common organic solvents have made these materials offer immense possibilities and promise of wide scope. The methods used for the purpose of synthesizing them include the conventional hetero-polycondensation reaction using different types of catalysts, followed by chemical changes in the polymeric chain, such as, cyclisation, elimination of simple molecules, etc. Direct routes of the synthesis of the polymers, viz., homopolymerisation of aliphatic and aromatic nitriles at the  $-C\equiv N$  bonds and ring-opening polymerisation of s-triazine and its derivatives or other heterocyclics have also been reported. These polymerisations occur in presence of complexing agents like metallic halides and are initiated by proton-donors, the concentration of which determines the molecular weights of the polymers. The growth of the polymer chains is, however, subsequently autocatalytic. The nitrogen atoms in a hetero-polyconjugated chain are far more basic and complexable than those in a monomeric nitrile. Therefore, addition of a complexing agent in a

stoichiometric ratio may reduce the enthalpy of the system and favour polymerisation by evolution of heat. The entropy of polymerisation at the  $-C\equiv N$  groups is, however, negative and large. This causes the overall conversion to be accompanied by an increase of free energy of the system. Hence, at an early stage of propagation of the carbonium ion chains subsequent to initiation, there is a tendency for them to cyclise and regenerate the initiator. For these stable ring intermediates or any initial hetero-cyclic monomer to open up and polymerise, the floor-temperature of polymerisation must be high so that the reduction in the resonance energy of the rings due to complex formation<sup>or</sup> (even its loss due to opening up of the rings) are more than balanced by the positive entropy of the ring-opening reaction. The complexing agent also acts as a plasticizer for the polymer chains and increases the entropy of the final state. This heat of aggregation or the heat of interaction of the polyconjugated chains may ultimately play a decisive role in shifting the equilibrium towards polymer-formation. Hence, the conditions under which these polymerisations occur are generally not typical of the polymerisation of vinyl and acetylenic compounds.

Review of Earlier Work on poly-  
heteroconjugated systems

Nitriles:

Kargin et al<sup>1</sup> were the first to report the polymerisation of aliphatic and aromatic nitriles in 1960. The reactions

were carried out at 150-300°C in presence of 30-50 percent by weight of halides of metals of Groups II, III, IV and VIII of the Periodic Table. The polymers obtained were reported to be soluble in strong acids only, stable to 500°C and semi-conducting. The low-molecular-weight fractions, on the contrary, possessed good moldability and had softening points around 180°C, whereas the very high-molecular-weight fractions were completely infusible. The effect of the metallic halides on the shift of the C=N stretching frequency in the polymerisation of saturated nitriles was studied by Oikawa and Kambara<sup>2</sup> and the magnitude of the shifts was in the order: Al > Ga > Zn > Fe > Sn > Ti > Zr and not coincident with the order of the respective activation energies. From infra-red (IR) and electron paramagnetic resonance (EPR) studies, Kargin<sup>3</sup> suggested the structure of the polymer as  $-C(R) = N - C(R) = N -$ . Some viscometric and electrophysical data on these polymers were also published.

#### Polycyanamides and Polycyanic acids:

In 1963, Paushkin and Lunin<sup>4</sup> reported for the first time high-molecular-weight compounds consisting of recurring  $-C(NH_2) = N -$  and  $-C(OH) = N -$  (polycyanamide or polyiminoamine and polycyanic acid respectively) from mixtures of ammonium chloride, sodium carbonate and sodium bicarbonate, mixtures of ammonium carbonate and ammonium bicarbonate and from urea, by heating in an inert atmosphere in presence of anhydrous zinc chloride. The mixtures of sodium carbonate, sodium bicarbonate

and ammonium chloride were required to be heated to 250-300°C under 20-25 atmospheric pressure for 25-30 hours<sup>5</sup>, whereas the mixtures of ammonium carbonate and ammonium bicarbonate required heating to 250-300°C under 20-45 atmosphere for 5-30 hours<sup>6</sup>. For urea<sup>7,8</sup>, the temperature range was 300-500°C and the duration of heating was 1-20 hours, but the pressure was not mentioned. The structures of the polymers were ascertained on the basis of infra-red spectra, elemental analysis and the determination of amine number by diazotization in 96% H<sub>2</sub>SO<sub>4</sub> followed by heating to collect and estimate the amount of nitrogen evolved. EPR-spectra confirmed the presence of polyconjugation in the systems. The values of intrinsic viscosities,  $[\eta]$ , in 96% H<sub>2</sub>SO<sub>4</sub> at 30°C varied from 0.020-0.077. All the polymers were crystalline, infusible and soluble in organic and inorganic acids. The polymer from mixtures of sodium carbonate, sodium bicarbonate and ammonium chloride was also soluble in formamide. The polymer from mixtures of ammonium carbonate and ammonium bicarbonate was claimed to decompose above 600°C and that from urea above 500°C. Potentiometric titration curves were found similar in shape to those of aniline.

#### Polyisonitriles:

High-molecular-weight and high-melting polymers were also claimed to be prepared from cyclohexyl isonitrile in solutions in diethyl ether at -10°C in nitrogen atmospheres by using BF<sub>3</sub> catalyst by Stackman and Evers<sup>9</sup>. Hagiwara<sup>10</sup>



also polymerised cyclohexyl isocyanide by heating its complex with cobalt carbonyl in dry benzene at  $110^{\circ}\text{C}$  in nitrogen atmosphere for 5 hours. Millich and Baker<sup>11</sup> obtained homopolymers of  $\alpha$ -phenylethyl isonitrile using a different type of catalyst system. The polyisonitriles are reported to be insoluble solids, the melts of which were stable above their flow points in nitrogen.

#### Polynitriles:

Polymerisation of hydrocyanic acid in presence of ammonia catalyst was investigated by König<sup>12</sup>. Different organic acids, formamide and ethylene glycol were excellent solvents for the polymer, but it was revealed that the dissolution of the polymer resulted in considerable hydrolysis and during acetylation lot of nitrogen was lost in the form of ammonia.

#### Hetero-polycondensates:

Apart from the homo-polycondensation reactions, mentioned above, Paushkin et al<sup>13</sup> also carried out hetero-polycondensation reactions of ammonium bicarbonate with acetaldehyde in absence of oxygen at  $300-400^{\circ}\text{C}$  with zinc chloride as the catalyst. The dark-brown, powdery, polyconjugated copolymer is soluble in nitrobenzene and has an irregular micro-structure, which is responsible for some of its properties really better than those of polycyanic acid or that of acetaldehyde, but unfortunately it melts at  $200-230^{\circ}\text{C}$  only.



Polymers from acid amides and ammonium salts of organic acids:

Synthesis of polymers with conjugated azomethine bonds by splitting off water from organic acid amides or ammonium salts of organic acids by means of dehydrating agents, was also reported by Paushkin et al<sup>14</sup>. Chemical composition and IR-spectra of these polymers were found to be identical with those of the polymers prepared by the direct route synthetic methods from the corresponding nitriles. It was further shown that 2-chain ladder systems of polymers could also be formed by using derivatives of dibasic acids. This is suggestive of a probability that the polymerisation reactions proceeds linearly through  $\overset{|}{\text{C}} = \text{N} -$  bonds. The polymers, however, are coloured, insoluble, infusible, crystalline and highly thermostable. Specific electrical conductivity, activation energy for conduction, number of unpaired electrons per gram of the samples were also determined by them and they measured the e.m.f. produced from the thermally treated samples.

Ring-opening polymerisations:

Paushkin and Lunin<sup>15</sup> also reported cationic polymerisation of melamine and cyanuric acid at 500°C, giving  $[\text{C}(\text{NH}_2) = \text{N} - \text{C}(\text{NH}_2) = \text{N}]_x$  and  $[\text{CONHC}(\text{O})\text{NH}]_x$ , with keto-enolic tautomerism possible for the latter, as reddish products, which are infusible and partially soluble in acids. The soluble fraction was stable only to 200°C. The temperature-

dependence of the specific conductivity of the polymers is exponential.

Reactions of cyanuric chloride with amines or alcohols gave 2,4,6 - alkylamino or arylamino/2,4,6 - alkyloxy or aryloxy 1,3,5 - s - triazines, which, when heated to 350-500°C without any catalyst formed deep-coloured polymers of the formula:  $\left[ \text{C}(\text{NHR})=\text{N} \right]_x$  or  $\left[ \text{C}(\text{OR}) = \text{N} \right]_x$ <sup>16</sup>. These polymerisations of s-triazine derivatives yield polymers in larger-amount compared to those from melamine or cyanuric acid due to facilitation of the opening up of the rings caused by the substituents.

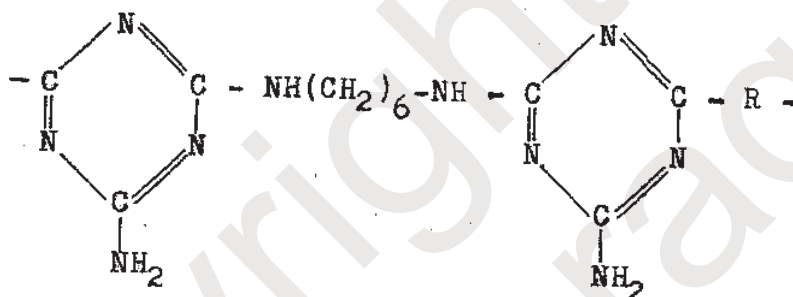
#### Triazine polymers:

In an attempt to prepare polymers containing conjugated triple bonds and triazine-rings by condensing cyanuric chloride with sodium acetylide at 230°C in an inert atmosphere, Paushkin et al<sup>17</sup> obtained an oligomer of the formula,  $\text{C}_{43}\text{N}_{24}\text{NaCl}$ , as a brown-powder, insoluble in organic solvents. It was found that the thermal stability of the oligomer depended markedly on the electronegativity of the substituents in the triazine rings.

Cyanuric chloride or alkylamino-substituted cyanuric chloride and bis-4-hydroxyphenyl methane, when condensed in ditolylmethane at 180-240°C, gave polyphenylene-s-triazinyl ethers or polymers containing triazine ring in the chain<sup>18</sup>.

They are powdery substances and on heating become cross-linked, brittle and insoluble.

A new class of linear polymers, containing s-triazine rings in the main chain<sup>19</sup>, has been synthesized from a mixture of an alkaline solution of hexamethylene di-biguanide hydrochloride and a solution of any phthalic acid in isobutyl methyl ketone at 0-2°C and the formula assigned to them is



where R is the phenylene group.

Also 2-anilino-, 2-diphenylamino- or 4,6-dichloro-s-triazine has been condensed with either hexamethylene diamine or m- or p-phenylene diamine or benzidine to similar triazine polymers.<sup>20</sup> Linear polycondensates of triazine<sup>21</sup> obtained from bisphenols or diamines and dichloro triazine monomers have been reported. 2-amino; 2,4-diamino<sup>or</sup> 2-amino-4-o-toluidine; 6-vinyl-s-triazine has been homopolymerized and also co-polymerised with styrene, methyl methacrylate, acrylonitrile or vinyl acetate in dioxane solutions at 50-80°C with azo-bis-isobutyronitrile as the initiator.

The polymers, prepared by the condensation of terephthalaldehyde or other aromatic aldehydes with trimethyl-s-triazine, triphenyl-s-triazine, 2,4,6-tristyryl-s-triazine or 2-methoxy 4,6-dimethyl-s-triazine in concentrated sulphuric acid at 100°C, were insoluble due to cross-linking and a highest inherent viscosity of 130 ml/g at 25°C in H<sub>2</sub>SO<sub>4</sub>, indicating an average degree of polymerization of 11. UV-spectra of these compounds showed that there was main chain unsaturation, but they were not completely conjugated<sup>22</sup>.

Cyanuryl chloride and tetramethylene diamine gave reactive linear chlorinated polymers<sup>23</sup>, which can form derivatives with piperidine or other compounds containing mobile hydrogen atoms, but their thermoresistant character is not satisfactory.

#### Other Polyconjugated systems:

Reaction of poly- $\alpha$ -chloroacrylonitrile with triethylamine in  $\beta$ -methoxy propionitrile solvent at 80°C gave a brilliant black-powder having conjugated double bonds and softening at 195°C<sup>24</sup>. A polymer with semi-conducting properties has been prepared by the homopolycondensation of 2-methyl-6-pyridine aldehyde under pressure in presence of acetic anhydride or zinc chloride at 200°C<sup>25</sup>.

The IR-spectra of the products of polymerisation

of pyridine<sup>26</sup> and quinoline<sup>27</sup> in melted stoichiometric complexes with zinc chloride, titanium tetrachloride, etc. indicate that the reaction consists in opening up of rings and formation of chains having the structure:  $\left[ \text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{N} \right]_n$ . Copolymers of pyridine and quinoline<sup>28</sup> with some of the pyridine and quinoline rings kept intact have also been produced from their complexes with zinc chloride heated to 350°C with metaphosphoric acid as the initiator. The number of pyridine rings in the copolymer increases with increase of reaction time; the number of quinoline rings, on the other hand, increases the degree of conversion, i.e., polymerisation.

New polybenzimidazoles<sup>29</sup> stable to < 450°C in air were also obtained by condensation of 3,3'-diaminobenzidine, o-phenylenediamine, 3,3',4,4'-tetraaminodiphenyl methane, 3,3',4,4'-tetraaminodiphenyl oxide, etc. with pyromellitic anhydride at 150-200°C.

Lastly, the list remains incomplete, if mention is not made of the poly-(oxyquinolines)<sup>30</sup>, which are stable to 550°C in argon and the polyquinazolones<sup>31</sup>, which are tough, wear-resistant, resilient and stable to 425°C in nitrogen, although they do not strictly belong to the class of linear hetero-polyconjugated systems. The polyazopolyarenes<sup>32</sup> are very highly unsaturated polymers, which also contain heteroconjugation along the main chain and their magnetic, dielectric, catalytic and other properties including solubility can be varied and modified by varying the structure.

Action of heat on Dicyanodiamide and Melamine

Studies on the effect of heat on dicyanodiamide and melamine under atmospheric and super-atmospheric pressures, by differential thermal analyses, paper-and ion-exchange chromatography and ultra-violet absorption spectrophotometry, reveal that melam, melem and melon are together produced from dicyanodiamide at temperatures above  $350^{\circ}\text{C}$ <sup>33</sup>. Below  $250^{\circ}\text{C}$ , melamine is formed as an intermediate and its deammoniating condensation gives rise to melam, melem and melon. Nitrogen atmospheres decrease their yields, while presence of ammonia accelerates the formation of melamine and suppresses the formation of melam, melem and melon.

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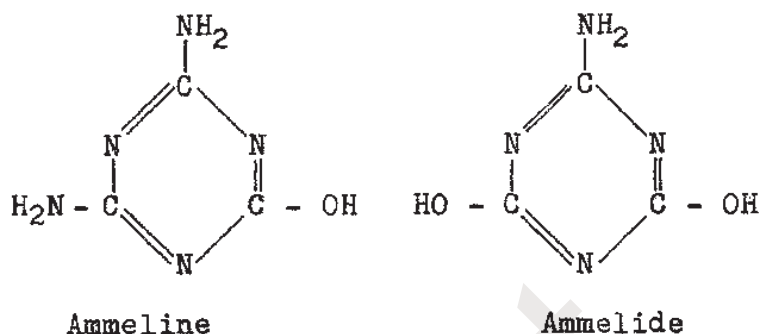
In order to understand the nature of these thermo-reaction products, brief descriptions of their properties and methods of preparations are given below. The structural relationship of these various compounds is also shown graphically. Although a simple amino-structure has been given here for melamine, no single structural formula is able to clearly portray all of its physical and chemical properties. It may have an amino-, imino- or a mixed structure.

Melam may be prepared by fusion of dicyanodiamide at  $350^{\circ}\text{C}$  and recrystallization from aqueous alkali. It is an insoluble white powder, evolves ammonia when heated, and passes first into melem and then into melon with loss of ammonia. Boiled with acids and alkalies, it yields ammonia,





melamine and ammeline.



Melam may be obtained by fusion of melamine at  $500^\circ\text{C}$  under pressure with evolution of ammonia. It is a white insoluble powder. When boiled with concentrated caustic potash solution, it is converted to ammeline (or cyanmeluric acid) and ammonia.

Melon may be obtained as the final product by strongly heating melamine, melam, pseudosulfocyanogen, mercuric thiocyanate, ammeline or ammeline. It is a light-yellow powder, insoluble in water, dilute acids or alkalies. When heated with caustic potash, it gives ammonia and potassium melam and with nitric acid, it gives cyanuric acid and ammonia.

Ammeline is obtained by boiling melamine for some time with dilute acids or alkalies. It is also formed together with melamine, when dicyanodiamide is heated with concentrated aqueous ammonia in a sealed tube for three hours at  $120^\circ\text{C}$ . It forms flocculent microscopic needles almost insoluble in water,

completely insoluble in alcohol and ether, soluble in mineral acids and warm alkalies, but insoluble in acetic acid.

McClellan<sup>34</sup> observed that when dicyanodiamide begins to melt at 209°C, a vigorous reaction occurs and copious fumes are evolved which contains ammonia and sublimed melamine, temperature rising to as high as 350°C.

Stollé and Krauch<sup>35</sup> obtained melamine by heating dicyanodiamide for 3 hours at 120°C. Davis<sup>36</sup> corroborated this fact offering evidences of the formation of guanylurea, followed by guanidine and cyanamide. Heating dicyanodiamide with liquor ammonia in sealed tubes at 80-140°C gives higher yields of melamine along with cyanomelamine, cyanamide, guanidine, guanylmelamine, biguanide and guanidino-cyanomelamine.

Kurabayashi and Yanagiya<sup>37</sup>, while studying the thermal conversion of dicyanodiamide into melamine, observed that when dicyanodiamide is fused in a thin layer on the bottom of a flask, immersed in an oil bath at 213°C, cyanamide, guanylmelamine, cyano-melamine, biguanidine and a deammoniated polymer, were detected in the fusion products. They further confirmed that a part of this deammoniated polymer was derived from dicyanodiamide by way of degradation and recombination through melamine, cyanamide or guanylmelamine in presence of molten dicyanodiamide.

### Object and Scope of the present work

Though Paushkin and his co-workers had synthesised simple linear polycyanamide from urea as early as 1963 under much lower pressure and had ascertained its structure as poly-aminonitrile or poly-imino-nitrile, a systematic study of its physico-chemical and electro-physical properties has seldom been attempted so far. Effect of use of higher pressures at the time of its formation on the yield and structure of the polymer and also the influence of co-polymerisation with small quantities of substituted ureas on its thermo-stability and solubility characteristics have not been investigated at all. Further, the deammoniated polymer, reported to be obtained by Kurabayashi and Yanagiya, while attempting to devise a method of preparation of melamine from dicyanodiamide by thermal reactions under atmospheric pressures, was neither identified nor characterised.

The primary aim of the present series of investigations as embodied in the thesis is to synthesise related polymers from both urea as well as dicyanodiamide under more severe conditions, specially using high pressure technique and to determine their chemical structures and finally characterise them by a systematic and comprehensive study of their different properties. Establishment of the optimum conditions of temperature, pressure, monomer-catalyst ratio and duration of heating for maximum yield of the polymers is also another end in view.

The work thus accomplished may, therefore, be split up into two broad divisions, namely (i) synthesis, elucidation of structures and thermogravimetric analyses of the different polymers belonging to the same class of poly-heteroconjugated systems and (ii) study of their viscometric, osmometric and dielectric properties.