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# THERMAL BEHAVIOUR OF MELAMINE

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Melamine undergoes condensation on heating with elimination of ammonia and formation of insoluble products. Thermogravimetry and infrared characterisation show that two products of successive condensation can be reproducibly obtained upon heating at $T < 500$ °C and then at 600 °C. Above 620 °C, the melamine condensate undergoes thermal degradation with quantitative formation of volatile products.

Melamine and its salts are widely used in the formulation of fire retardant additive systems for polymeric materials [1, 2]. However, little is known about its mechanism of action. In particular, discrepancies are found in the literature concerning the chemical structure of products formed by heating melamine at temperatures at which polymeric materials undergo fragmentation to volatile combustible products ($T > 300°$).

Melamine is known to undergo condensation reactions on heating with elimination of ammonia (deamination). Two schemes have however been proposed for the condensation process:

Route (a) leads to the fused-ring structure of cyameluric triamide which reacts then as a trifunctional monomer to give the final condensate [3, 4]. In route (b), melamine is the trifunctional monomer which progressively condenses to give a product in which triazine rings are linked by —NH— bridges [5]. It can be seen that major differences between routes (a) and (b) concern the formation of "melam" as an intermediate of condensation and the structure of "melem" and of "melon". As far as the chemical structure of the products of deamination of melamine is concerned, confusion arises in the literature from the fact that they have been given the conventional names: "melam", "melem", "melon" before reaching wide agreement on their structure. These names are indeed those used to indicate s-triazine derivatives previously prepared by other methods such as the pyrolysis of thiocyanates [6] in which case "melam" was shown to have structure (I) while

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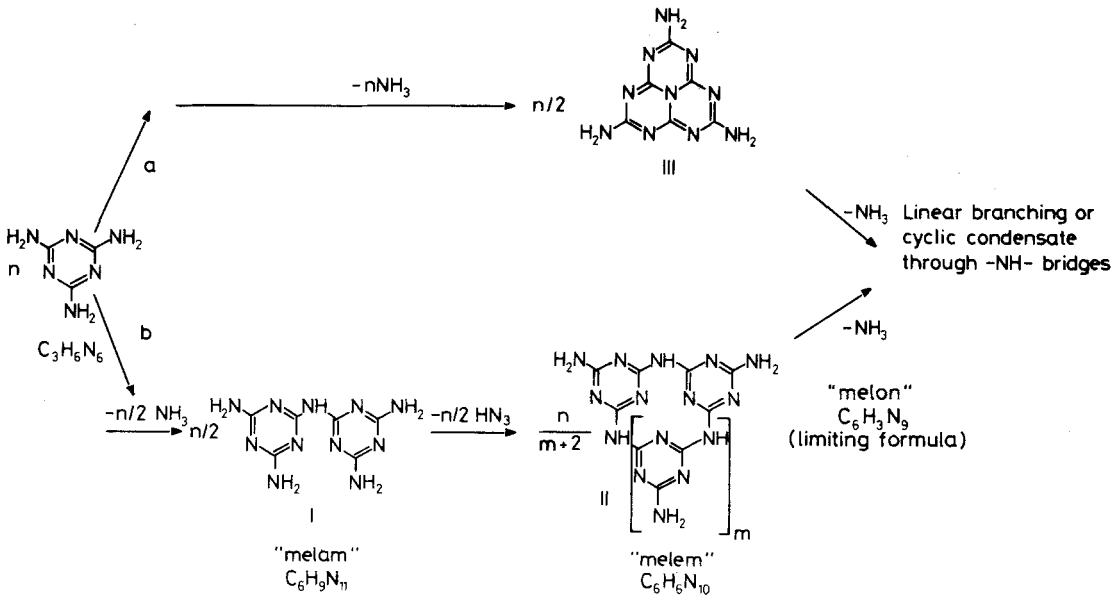


**Scheme** for the thermal condensation of melamine

"melem" and "malon" should contain cyameluric rings. The very small solubility of these products is a major drawback encountered in studies aimed at definition of their structure.

Since the products of condensation of melamine may play a role in the mechanism of fire retardance, we have undertaken a systematic study of the thermal degradation behaviour of melamine. The results obtained so far are reported and discussed here.

## Experimental

*Heat treatments.* Melamine (Montedison) was heated for 1 h at 360, 400 and 480° respectively in glass tubes sealed under vacuum.

*Thermogravimetry (TG).* Thermogravimetry at a heating rate of 10 deg/min was carried out under nitrogen flow, 60 $cm^3$/min on 10 mg samples using a DuPont 951 thermobalance—1090 thermal analyser system.

*Analysis of degradation products.* Gaseous products of degradation were condensed out of the gas sweeping the thermobalance by cooling at liquid nitrogen temperature in a U glass trap connected to the thermobalance and provided with up-stream and down-stream stopcocks. The trap was then closed by the stopcocks,

removed from the thermobalance and connected to a vacuum line for transfer of the products to a gas cell for infrared analysis (IR) which was performed using a Perkin–Elmer 1710 FTIR instrument.

High boiling products of degradation condensing in the cold section of the quartz tube enveloping the thermobalance which emerges from the furnace and the residues were collected and their IR spectra taken in KBr pellets.

## Results and discussion

*Product of deamination of melamine.* Melamine heated at 10 deg/min under nitrogen flow, mostly evaporates unaltered as shown in Figure 1, solid line: 5% weight loss at 315°, maximum rate of weight loss at 380°. Upon heating in the closed system, melamine undergoes elimination of ammonia which could be detected after breaking the sealed tubes. The TG curve of the product recovered at the end of the heat treatment shows two main steps of volatilisation (Figure 1, interrupted line). The first occurs in the same range of temperature (350–400°) in which melamine heated alone volatilises, the second being at 450–500°. The presence of unreacted melamine in the mixture is also shown by absorptions at 3470, 3420, 815 $cm^{-1}$ in its IR spectrum (IR b, Figure 2) which are most typical of melamine IR a, Figure 2; Table 1). Furthermore, these absorptions disappear upon extraction of the mixture with boiling water in which melamine is soluble (IR c, Figure 2). The extracted residue which is a white product, is stable up to 450° in TG (Figure 3). The yield of

**Table 1** Infrared absorptions of melamine

| Wavenumbers, $cm^{-1}$ | Assignement | Reference |
|---|---|---|
| 3470, 3420 | $NH_2$ stretching, typical of melamine, absent in salts of strong acids | [7] p. 395 |
| 3335 | asymmetric $NH_2$ stretching | [7, 8] |
| 3125 | symmetric $NH_2$ stretching | [7, 8] |
| 1653, 1630 | $NH_2$ deformation | [7] p. 235 |
| 1580, 1555 | 1,3,5-*s*-triazine ring "quadrant stretching" | [7] p. 234 |
| 1470, 1440 | 1,3,5-*s*-triazine ring "semicircle stretching" | [7] p. 234 |
| 1030 | C—N stretching, primary amines, tertiary C | [8] p. 288 |
| 815 | 1,3,5-*s*-triazine ring, out of plane ring bending by "sextants" | [7] p. 234 |

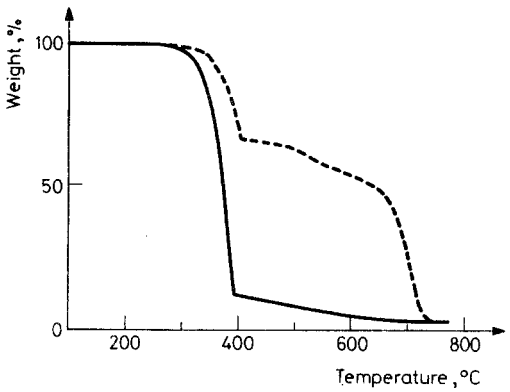


**Fig. 1** TG curves of melamine (———) and of the product of reaction at 400° (— — —)

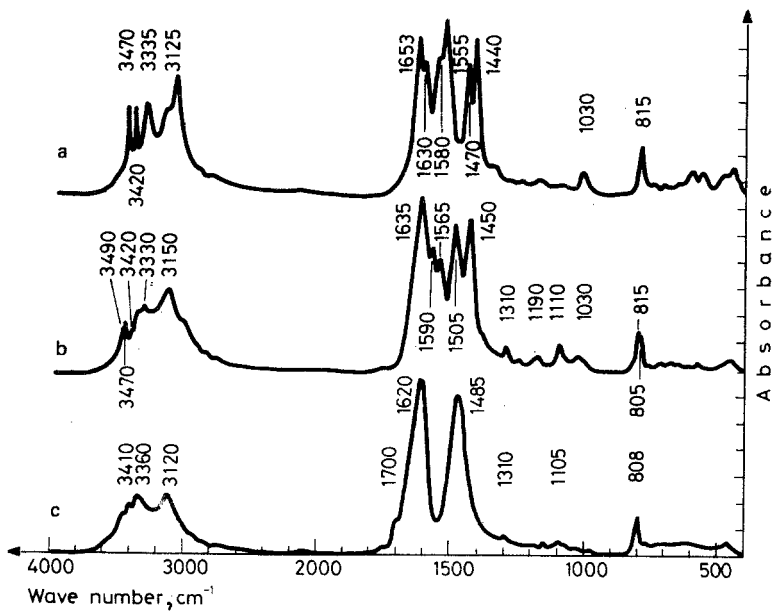


**Fig. 2** Infrared spectra of: melamine (a); product of reaction at 360°, crude (b) and after extraction with boiling water (c)

water-insoluble product of condensation of melamine varies with the temperature of reaction, increasing from 50% at 360° to 80% at 480°. These results are in agreement with those of Finkel'shtein [4] and van der Plaats et al. [9], in contrast to those of May [5] who claims almost quantitative condensation of melamine in the same conditions. Van der Plaats et al. [9] suggested that at 320–400°, melamine forms mixed crystals with the condensation product.

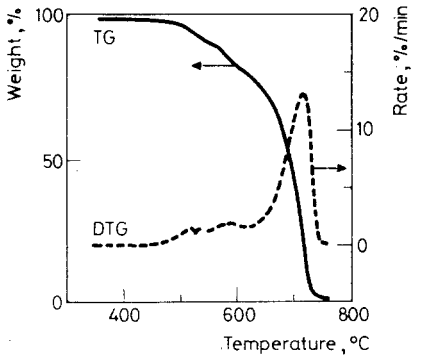


**Fig. 3** TG and differential TG (DTG) of water insoluble fraction of melamine heated at 400°

The IR spectra of the water-insoluble condensation product of melamine obtained at 360, 400 and 480° are closely similar. Differences concern minor changes of the relative intensity of some absorption bands and the noticeable progressive shift of the triazine ring absorption from 808 to 795 $cm^{-1}$ as the temperature of heating increases from 360 to 480°. On the basis of the published IR spectrum of "melam" [10], it seems that it should not be produced in detectable amount under the above conditions since, for example, two of its strong absorptions at 1355 and 1252 $cm^{-1}$ are absent in the IR spectra of either the crude mixture of products of condensation of melamine or in those of the water-extracted residues (e.g. IR b, and c, Figure 2). Similar results were published by Finkel'shtein [4] and by van der Plaats et al. [9], whereas May [5] suggested that "melam" is the product formed on heating melamine at 360° on the basis of the stoichiometry of ammonia evolved and of its products of hydrolysis.

The water-insoluble product we obtained from melamine deamination at 360–480° shows an IR spectrum (IR c, Figure 2) comparable to that of the product obtained in similar conditions by Finkel'shtein [4] and van der Plaats et al. [9] which they called "melem". In particular, Finkel'shtein [4] attributed to this product a structure based on cyameluric rings on the basis of comparison with IR spectra of derivatives of cyameluric acid prepared from thiocyanates [6]. He has shown that the cyameluric rings should be characterised by the presence of typical absorptions at 1600, 1435 and 798 $cm^{-1}$ and the absence of absorption at 1560 $cm^{-1}$ which is typical of the s-triazine ring. Apart from a shift of the bands at 1600 and 1435 $cm^{-1}$ to 1620 and 1485 $cm^{-1}$ respectively, possibly due to differences in wavelength calibration which is more accurate in FTIR instruments than in the one previously used, similar considerations could apply to the water-insoluble condensate we obtained at 360–480° (e.g. IR c, Figure 2).

This point requires, however, further studies since formation of cyameluric rings

from melamine requires breaking and rearrangement of several bonds of the s-triazine structure which is known to be thermally stable whilst condensation already occurs at the relatively low temperature of 360°. In this respect, progressive deamination leading to polymerisation of melamine (route (b), above scheme) seems more likely but, at this stage, it lacks convincing proofs.

*Thermal degradation of melamine condensate.* Figure 3 shows that the product of deamination of melamine undergoes thermal degradation in three successive steps, partially overlapping, with maximum rate of weight loss at 520, 590 and 720° respectively (DTG curve). Ammonia is the main volatile product evolved in the first step (weight loss 10%) which is also evolved together with some HCN and a high boiling fraction in the second step (weight loss 10%). The colour of the residue gradually changes from white to yellow and brown in these two steps. Its IR spectrum (Figure 4) shows strong modifications in the region 1200–1700 $cm^{-1}$. The original absorptions at 1620 and 1485 $cm^{-1}$ (IR c, Figure 2) progressively decrease while strong bands appear at 1640, 1560, 1420, 1330 and 1250 $cm^{-1}$ on heating at 10 deg/min to 620°, that is to the end of the second step of degradation. At the same time, the band at 795 $cm^{-1}$ is progressively replaced by a band at 815 $cm^{-1}$ (Figure 4).

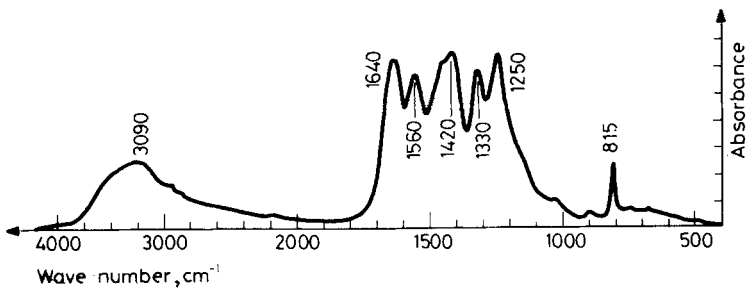


**Fig. 4** Infrared spectrum of the water insoluble product of reaction at 400°, heated to 620°

Evolution of ammonia between 450–620° should indicate that further condensation occurs although accompanied by some degradation of the structure, shown by formation of HCN and high boiling products, which is however likely to be limited to the upper temperatures in the range considered. Thus, the product obtained at 620° could be the final condensate of melamine called "melon" in the above scheme. According to Finkel'shtein's IR data [4], the IR of Figure 4 shows typical absorptions of the s-triazine ring, with particular reference to the band at 1560 $cm^{-1}$. On the basis of IR literature data, our results should be interpreted assuming that melamine progressively deaminates forming cyameluric structures at

first, returning then to *s*-triazine rings, which, however, seems unlikely. It is evident that further detailed study of the structures of products of melamine condensation is required.

Above 620° the melamine condensate undergoes extensive degradation with quantitative formation of volatile products among which HCN and high boiling fragments of the condensate have been identified at this stage.

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**Zusammenfassung** — Melanin geht beim Erhitzen eine Kondensation unter Abgabe von Ammoniak und Bildung unlöslicher Produkte ein. Durch Thermogravimetrie und Infrarotspektroskopie wird gezeigt, daß beim Erhitzen zwei Produkte von aufeinanderfolgenden Kondensationsreaktionen bei $T < 500$ °C und $T = 600$ °C reproduzierbar erhalten werden. Oberhalb 620 °C wird das Melaminkondensat vollständig unter Bildung flüchtiger Produkte thermisch zersetzt.

**Резюме** — Меламин при нагревании подвергается конденсации с выделением аммиака и образованием нерастворимых продуктов. Термогравиметрический и ИК спектроскопический анализы показали, что в результате последовательной конденсации всегда получаются два продукта, один из которых при нагревании до температуры ниже 500°, а второй — при температуре 600°. Выше 620° конденсат подвергается термическому распаду с количественным образованием летучих продуктов.