# Influence of thermal transformations on room-temperature phosphorescence of doped hexamethylol-melamine

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Room-temperature phosphorescence of a dopant in hexamethylolmelamine and in a related condensation resin is influenced by several physical and chemical changes involving water and condensation reactions. The latter affect the degree of cure and thus the influence of humidity on the methylol–methylol hydrogen bonding of the system. The transformations involved are investigated by thermal analysis and the results correlated with the specific effects of each transformation on phosphorescence intensity Initially, the transformations involve absorbed water and water of crystallinity. The subsequent condensation reactions producing water take place in two stages: the first reaction occurs in the molten phase, the second takes place at a higher temperature in the solid state. The two stages differ distinctly, showing endothermic and exothermic behaviour, respectively. Variations in phosphorescence intensity during high humidity exposure and drying cycles confirm the significance of absorbed water in the methylol–methylol hydrogen bonding of the system.

## INTRODUCTION

Our previous studies of room-temperature phosphorescence in an amorphous thermosetting resin, namely doped melamine–formaldehyde, have shown that condensation reactions have an important influence on triplet emission intensity[1,2]. We have reported the variation of phosphorescence intensity on exposure to high relative humidity (r.h.)[3]. it is influenced by the degree of crosslinking in the resin and by the number of methylol groups for various crystalline doped methylol-melamines. Spencer and O'Donnell[4] reported that hydrogen bonding between carbazole and benzophenone increases the intersystem crossing rate in the carbazole at the expense of its fluorescence. They observed triplet emission of the acceptor benzophenone and demonstrated that it originated from the carbazole. Furthermore, in the presence of a hydroxylic solvent, the excited carbazole singlet ($S_1$) to triplet ($T_1$) intersystem crossing ($S_1-T_1$) is diminished and the carbazole triplet to benzophenone triplet donor–acceptor ($T_1-T_1$) energy transfer does not take place. In our systems, the triplet emission of the dopant is sensitive to: (i) variation of r.h. and thus the amount of absorbed water[5]; (ii) the presence of other dopants capable of being acceptors; and (iii) the degree of cure[2]. In some experiments, after humidity treatment and subsequent drying, the phosphorescence intensities of samples were higher than the original value (unpublished results). The present studies also demonstrate the importance of the thermal history of the sample. It is important to note that phosphorescence intensity of all of these samples appeared to be unaffected by the presence of atmospheric oxygen, although sunlight, fluorescent room-lighting and u.v. irradiation reduced the intensity significantly[2]. This insensitivity to oxygen is of considerable value in the practical application of the present system, e.g. in postal coding with phosphor inks.

In this paper, we present some thermal balance results for the various transformations taking place in a doped melamine–formaldehyde resin particulate powder. These are correlated with the data from phosphorescence studies. We also present the results of derivative thermogravimetry (d.t.g.), differential scanning calorimetry (d.s.c.) studies and phosphorescence data on a related but chemically simpler system, doped hexamethylol-melamine, in order to elucidate the influence of individual thermal transformations upon the phosphorescence intensity of these systems. Our studies have defined the temperature regions for various water-associated transformations as well as for the final condensation process above the melting point of hexamethylol-melamine[6]. Three categories of water are identified by these studies: absorbed water, water of crystallinity[6] and water produced in the course of the condensation reaction[7]. Some of the latter may be retained as absorbed water. A large number of unreacted methylol groups remain in the condensed resin and hydrogen bonding therefore has an important influence on the properties of the system[8,9]. The three categories of water appear to have differing effects on the hydrogen bonding of the system and thus exert different influences on phosphorescence intensity.

## EXPERIMENTAL

Doped hexamethylol-melamine (HMM) was produced by dissolving 1 mol of melamine (Analar BDH, recrystallized twice from water) in 8 mol of neutral formaldehyde solution (37–41% solution, Analar BDH) at 80°C. Naphthalene-2-sulphonic acid (NSA) dopant was dissolved (1% by wt relative to melamine) and the solution allowed to cool. Doped crystals of HMM were filtered from the cool solution. More recently, but not in this study, we have found it easier to prepare similar samples at pH 9.5 and 60°C.

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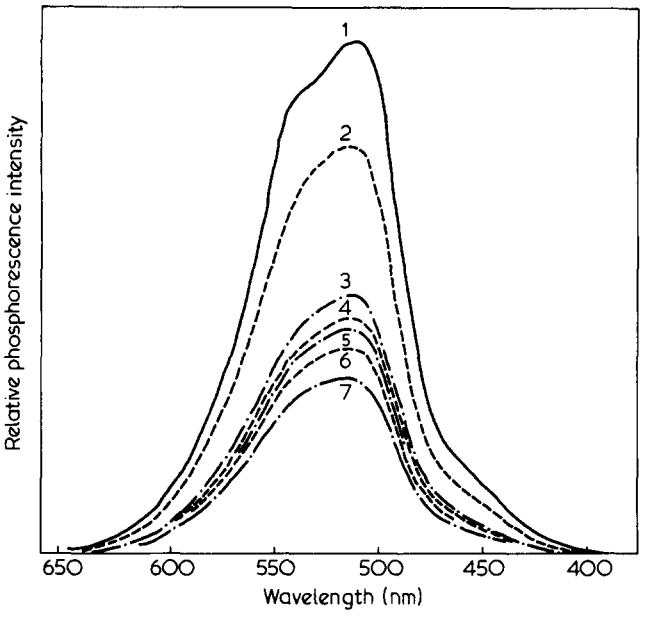


*Figure 1* Phosphorescence spectra of CSA/PABN doped melamine–formaldehyde resin at different stages of cure. Curve 1, as prepared without heating; Curves 2 to 7, with increasing periods of heating at 210°C of 2.5, 19, 23, 43, 50 and 115 h

The melamine–formaldehyde resin was produced by a similar procedure to that for HMM, replacing the dopant NSA with 4% carbazole sulphonic acid (CSA) and 1% of the sodium salt of *p*-aminobenzoyl naphthalene sulphonic acid (PABN) (Derby Luminescents). The solution was continuously heated until one drop of the syrupy solution placed in a large volume of ice-cold water produced faint opalescence, indicating onset of a hydrophobic condition. Heating was then stopped.

The resin was then prepared in a particulate form by a proprietary process[10] at 170°C and allowed to cool. The result of this process is extensive condensation and low water sensitivity. The luminescent properties of the particulate resin were generally similar to those of the resin prepared in bulk form.

Thermogravimetric analyses of the two materials were performed on a Mettler Mk 2 Thermal Balance. Differential scanning calorimetry (d.s.c.) studies were carried out with a Perkin–Elmer DSC 2.

Measurements of the variation of phosphorescence intensity were performed for each sample after exposure to high humidity and subsequent drying using a laboratory-made spectrophosphorimeter. This apparatus employed a Thorn ME/D 250 W high-pressure mercury lamp as the source of excitation light, focussed through quartz lenses and filtered with $NiSO_4$ solution and an OX7 filter. Samples were compressed into a shallow circular cavity (10 mm diameter, 1.5 mm depth) in a brass sample holder, and placed in a light-proof chamber with a rotating can as a light-chopper. The samples were excited normal to the front face and analysed at 45°. The mechanical arrangement of the sample holder ensured a high degree of reproducibility of position with less than 2% variation of sample phosphorescence intensity upon removal and subsequent re-examination. Compressed samples in the above arrangement gave consistent intensities compared with solid samples contained in cylindrical quartz tubes. The latter method was only suitable for the luminescence of homogeneous solutions. The phosphorescence emission was analysed using a high-resolution (Hilger and Watts 330/1 Mark II) grating monochromator. The spectrum was plotted by means of a motor drive scan of 100 nm $min^{-1}$. The detection system for the emission was a photomultiplier (EMI 6256B) in a standard e.h.t. circuit and the output connected to an XYT chart recorder (Servoscribe XY).

## RESULTS AND DISCUSSION

### *Thermal and phosphorescence data for the resin*

We have reported that the phosphorescence intensity varies with the degree of cure in the doped melamine–formaldehyde resin[2]. This effect is illustrated in *Figure 1* in which the phosphorescence spectra of CSA/PABN-doped samples at differing degrees of cure are shown. The resin samples were prepared at 170°C. Tubes containing portions of the powder were placed in an oven at 210°C for periods up to 115 h. The spectrum for an unheated sample is shown in Curve 1. It may be seen that a large (50%) decrease in intensity occurs after 19 h heating (Curve 3). Further heating reduces the intensity to 28.5% of the original value after 115 h (Curves 4–7 of *Figure 1*), whereas the spectral distribution of emission remains essentially unchanged.

In order to elucidate the processes taking place on heating the resin, thermal balance investigations including d.t.g. studies were undertaken. Samples of resin (10 mg) of known phosphorescent intensities (*Figure 1*) were weighed and placed in the sample chamber of the thermal balance. The resulting d.t.g. curves (*Figure 2*) show significant differences. Curve 1 identifies the various regions of weight loss which correspond to the peak positions; these are associated with the various solid state transformations of this sample. The first (semi) peak (20–30°C, region A) may be associated with traces of formaldehyde. Such traces are also indicated by a faint formaldehyde smell from most of the unheated samples. The second peak B, between 30–97°C (60°C maximum), can be attributed to absorbed 'free' water in the sample. The third peak C, between 100–208°C (170°C maximum), may be related to 'complexed' water of partially-cured regions of the samples. We have also found that this type of water is expelled by prolonged heating of an HMM sample below curing temperatures.

The fourth peak D, between 208°–326°C (246°C maxi-

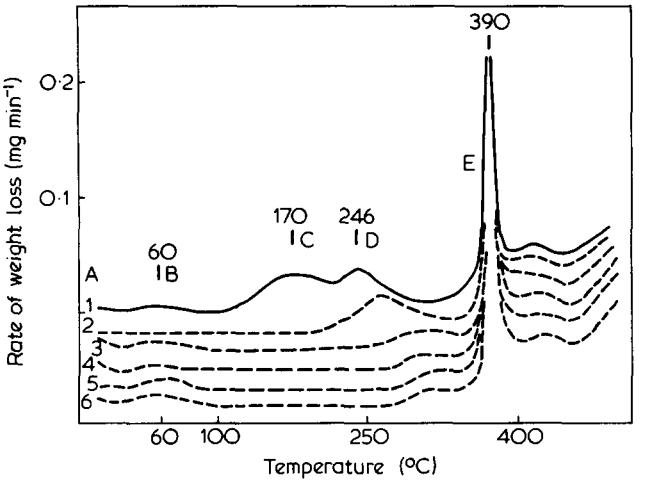


*Figure 2* The d.t.g. results of samples corresponding to different degrees of condensation and matching to samples of *Figure 1*. Curve 1, as prepared, no heating; Curves 2 to 6, with increasing periods of heating at 210°C of 2.5, 19, 23, 43 and 50 h. Each successive curve has been displaced by 2 mm for clarity

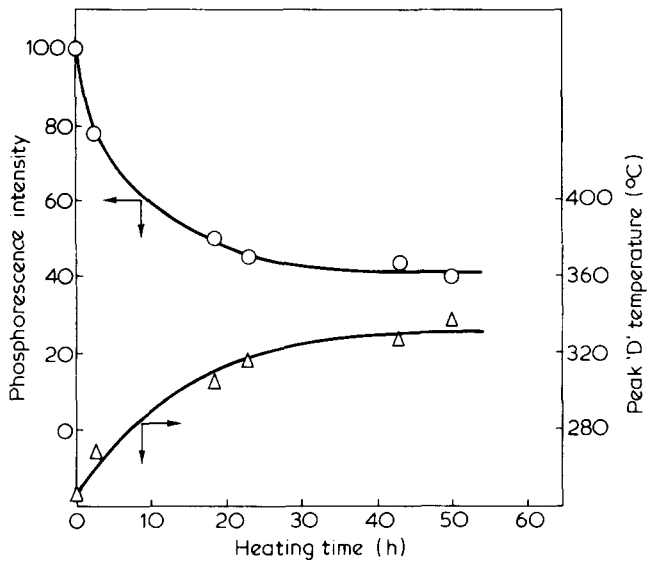


*Figure 3* Plots of phosphorescent intensity and temperature of the maximum of 'curing peak' D during different stages of cure obtained with increasing heating periods at 210°C

mum), seems to be associated with further condensation of the partially cured regions which result in production and release of water. All the sample peaks (A, B, C and D) corresponding to Curve 1 are broad, suggesting ranges of degree of condensation due to the variation of particulate sizes as well as differences in curing time. The fifth peak E, between 326°–417°C (390°C maximum) is thought to be associated with reactions of the melamine ring structure and amino groups. These deammonation reactions take place around 350°C in the case of pure melamine[6]. Further peaks between 417°–464°C (433°C maximum), 464°–589°C (526°C maximum) and 589°–629°C (598°C maximum) are associated with resin degradation and pyrolysis. However, we have excluded consideration of processes occurring beyond peak D, 270°C, i.e. when condensation is practically complete and where degradation products other than water would be evolved.

In Curve 2, peaks A and C are virtually non-existent and peak B (30°–104°C) is very small in magnitude, which suggests that 150 min heating (210°C) has drastically reduced the parameters responsible for these peaks in Curve 1. Furthermore, peak D which was prevously at 246°C in Curve 1 has its maximum shifted towards higher temperatures (170°–348°C, 303°C maximum) thus confirming a greater degree of condensation over 150 min heating. Curves 3, 4, 5 and 6 show both partial recovery of the absorbed 'free' water peak lying below 100°C and progressive reduction in the magnitude of peak D, indications of increased condensation.

It is clear from *Figure 1* that as the period of storage at 210°C increases, the intensity of phosphorescence emission falls considerably (by up to 71.5%) while spectral characteristics are essentially unaltered. The d.t.g. results for the particulate resin (*Figure 2*) identify five temperature regions A, B, C, D and E. D is particularly significant. This temperature region, which exhibits a peak at 246°C, is found to move towards higher temperatures for resin samples which have been heated for longer periods. These changes would be expected as a result of increased condensation. The temperature of maximum loss rate for D is plotted against the duration of cure time and compared with the change in relative phosphorescence occurring in the same samples (*Figure 3*). Both curves undergo rapid initial changes, becoming asymptotic during the final periods of heating (upwards of 40 h at 210°C).

The comparison in *Figure 3* illustrates that phosphorescence intensity, related to the temperature of onset of further curing, has within certain limits an inverse linear relationship to the degree of cure of the system. One limit for this linear relationship is the point at which the matrix rigidity becomes sufficiently high to minimize collisional quenching of the dopant triplet emission; the other limit is governed by a minimum critical concentration of OH groups at which energy transfer fails to be effective. Both of these limits are functions of the degree of cure.

*Thermal studies of HMM*

*Figure 4* gives the results of thermal balance experiments on various samples of crystalline HMM doped with NSA after differing heat treatments. Curve 1 shows the d.t.g. result for a standard unheated sample and identifies five main regions of weight loss existing below 300°C. These are caused by loss of formaldehyde (peak A, up to 30°C), absorbed water (peak B, maximum 93°C), complexed water (peak $B_1$, maximum 128°C) and water formed by condensation reactions in the resin (peaks C and D, maxima 154 and 264°C). Heating within each of the weight loss regions (below 100°C, between 100–154°C and above 170°C) has a characteristic effect on phosphorescence intensity[3], observed by heating the samples at 90°, 125° and 170°C. The lower (90°) temperature cannot give the effect achieved by higher temperature

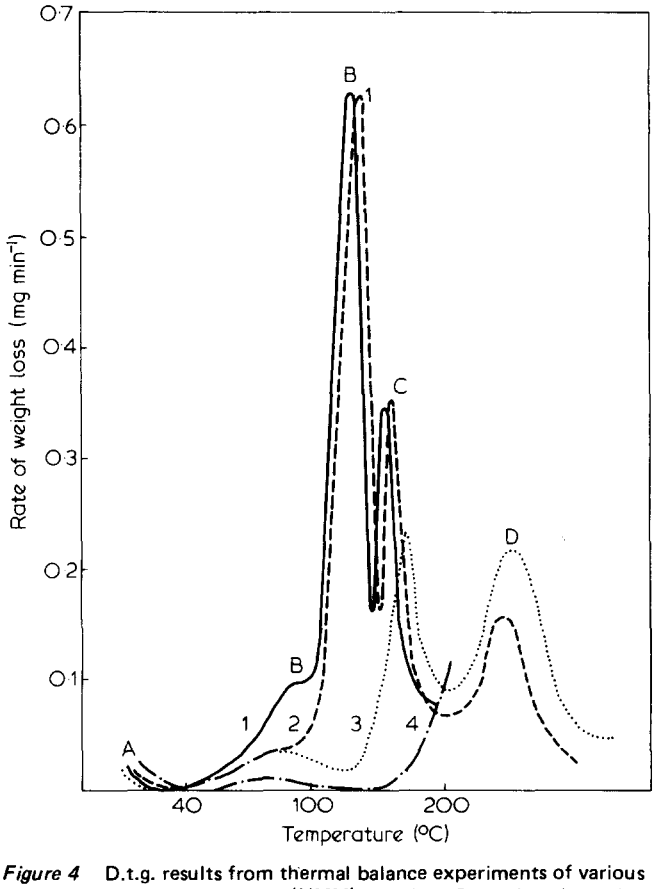


*Figure 4* D.t.g. results from thermal balance experiments of various doped hexamethylolmelamine (HMM) samples. Curve 1, unheated sample; Curve 2, doped HMM sample after 60 min heating at 90°C; Curve 3, doped HMM sample after 60 min heating at 125°C; and Curve 4, doped HMM sample after 30 min heating at 172°C

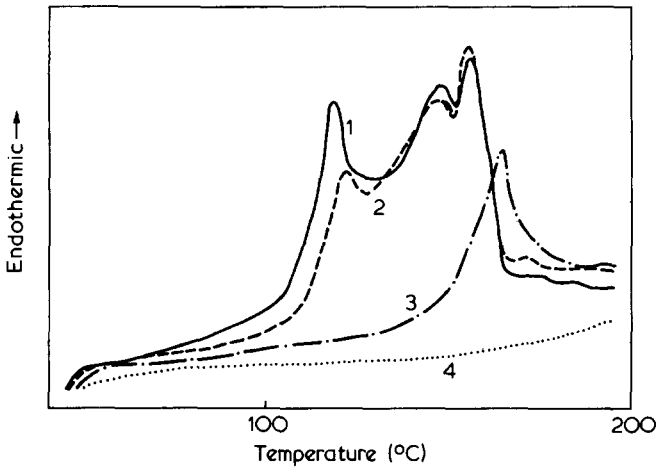


*Figure 5* D.s.c. results of various samples of doped HMM after different treatments. Curve 1, sample as prepared, no heating; Curve 2, sample heated for 60 min at 90°C; Curve 3, heated for 60 min at 125°C; and Curve 4, sample heated for 30 min at 172°C

heatings. Each temperature region corresponds to a specific transformation in the sample. This is confirmed by heating various samples at a temperature near each of the maxima of the particular peaks under study e.g. for peak B the maximum is obtained at 93°C for an unheated sample. A fresh sample was heated at 90°C for 60 min and yielded the d.t.g. result shown (Curve 2, *Figure 4*). Peak B is greatly reduced while the three other peaks now at 132, 157 and 264°C ($B_1$, C and D) remain substantially unaffected compared with Curve 1.

A fresh doped hexamethylol-melamine sample was later heated at 125°C for 60 min. It was examined by d.t.g. (Curve 3, *Figure 4*) and peak B was found to be greatly diminished as before. Peak $B_1$ previously observed in Curves 1 and 2 has completely disappeared, indicating the absence of transformations responsible for this peak. Peak C, which occurred at 154°C in the unheated sample, is diminished considerably and shifted to a higher temperature (170°C). Recalling that the temperature of the 'secondary' curing peak D (*Figure 2*) of the resin shifted to higher temperatures, the HMM shift for peak C may be explained by partial condensation of the HMM. Peak D, however, is shifted by only two degrees to 266°C during the heating at 125°C, this temperature being too low to affect significantly the secondary curing which occurs at D.

Curve 4, *Figure 4* shows a similar thermal balance result for a doped HMM sample heated for 30 min at 172°C. It shows only a residual low peak B at about 90°C corresponding to absorbed 'free' water, and no further peaks up to 170°C suggesting that the factors responsible for the peaks $B_1$ and C in Curve 1 are absent in this particular sample. Thus, these results illustrate that controlled heating at differing temperatures leads to progressive abolition of the transformations responsible for the various peaks. Differential thermal analysis (d.t.a.) curves were also obtained during the thermal balance experiments. These gave the results in *Figure 4* which were consistent with the interpretation of the weight loss curves.

The results of d.s.c. experiments on crystalline hexamethylol-melamine sample doped with NSA, again subjected to similar heat treatments as above, are shown in Curves 1 to 4 in *Figure 5*. Curve 1 shows three endothermic peaks starting or emerging at 98°, 136° and 161°C. These are consistent with the three d.t.g. peaks at 93°, 128° and 154°C in the curves obtained in the thermal balance experiments. We attribute the first two endothermic changes to the loss of 'free' water at 98°C and the loss of 'complexed' water associated with crystals at 136°C.

The final sharp peak emerging at 161°C is maximized at 164°C and represents both the melting transition (m.p. 154°C) and the loss of condensation water. Curve 2 shows the d.s.c. result for a sample previously kept at 90°C for 60 min. The magnitude of the peak starting at 98°C is significantly smaller compared with Curve 1, but the other peaks remain virtually unaltered in position and magnitude. Curve 3 of *Figure 5* shows the d.s.c. curve of a fresh sample previously heated at 125°C for 60 min. This curve does not show any of the endothermic peaks starting at 98° and 136°C, but exhibits only one peak: this has a maximum at 172°C and we attribute it to the combination of melting and condensation processes. We note that this peak maximum has shifted by 8°C compared with Curve 1. Curve 4 of *Figure 5* gives the d.s.c. result for the corresponding sample heated at 172°C for 30 min. It does not show any of the peaks observed in Curves 1, 2 and 3. A high degree of cure and the absence of any significant removable water is therefore indicated.

*Correlation of thermogravimetric results and phosphorescence of HMM*

In *Figure 6* we present the changes in weight (Curves 1 and 3) and in phosphorescence intensity (Curves 2 and 4) when a doped HMM sample was heated to the indicated temperatures (90°, 125° and 170°C) for various periods (and then cooled to room-temperature for measurements). Curves 1 and 2 illustrate these variations during the heating cycles described. Initial sample weight and phosphorescence intensity were recorded. The sample was then heated at 90°C for 60 min and subsequently for four further 15 min periods at 125°C: phosphorescence intensity and weight was recorded at room-temperature after each interval. Finally, the sample was heated at 170°C for a series of 30 min intervals (30, 60 and 90 min) and measurements were also made after 16 h. During heating at 90°C, there is a small weight loss (5%) and a slight increase in phosphorescence intensity. In separate experiments using a fresh sample, heating at 90°C overnight gave only a slight further weight loss (3%) and the increase in intensity was negligible. In the second stage of heating at 125°C (Curves 1 and 2), the sample weight decreases significantly. During this heating, the phosphorescence intensity increases four-fold to a maximum after the first 30 min, then slightly decreases. We believe that the water of crystallinity is lost during this stage of heating. The final heating of the sample took place at 170°C, i.e. above the melting point of pure hexamethylol-melamine crystalline samples. Further water was lost, produced during the condensation reactions. Associated with this change is the major reduction in phosphorescence intensity of the sample.

Later, in a similar heating experiment, a doped HMM sample was used which had been stored in the dark for *3 months* at room-temperature. Different but similar variations were recorded both for weight loss and changes in phosphorescence. The respective curves are shown as broken lines in *Figure 6* (Curves 3 and 4). These curves confirm the three trends seen in Curves 1 and 2, but they differ in two particular respects. First, the sample used for Curves 3 and 4 loses slightly less weight during heating at 125°C and the phosphorescence intensity maximum was not achieved after 30 m heating. Then after the third stage of heating at 170°C, the sample exhibited extensive bubbling and became a much ex-

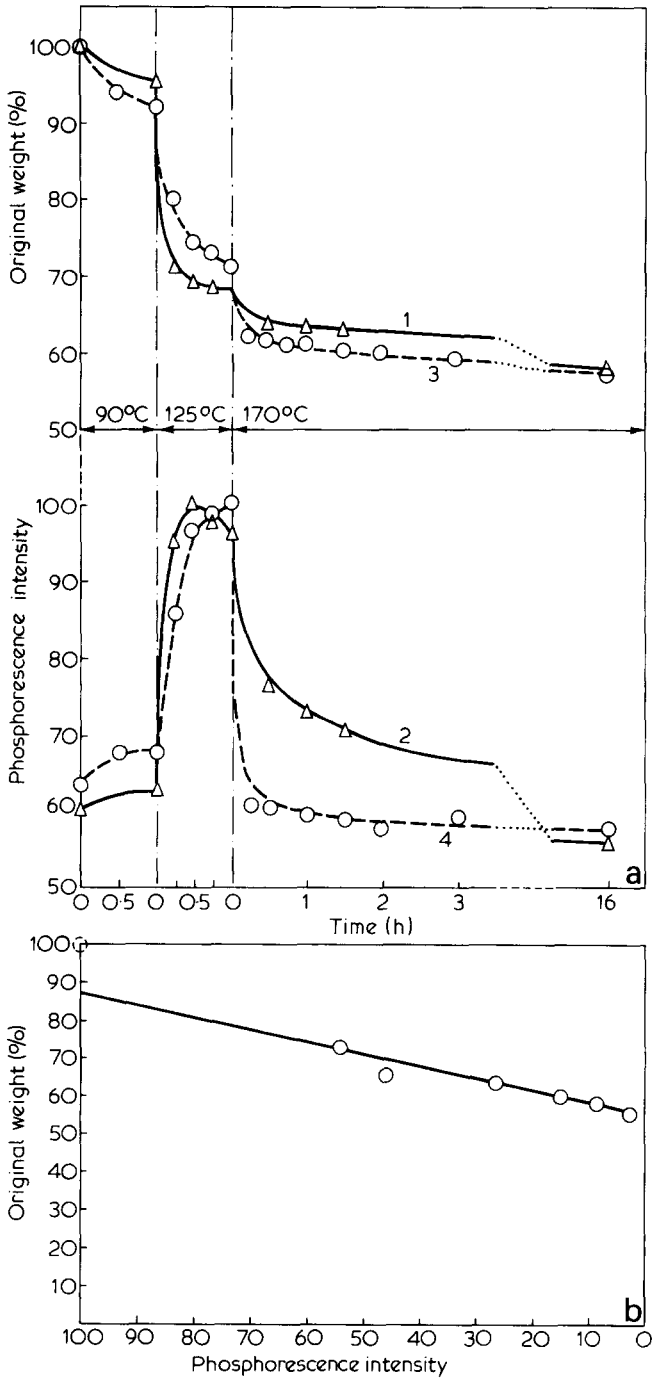


*Figure 6* (a) Comparison of phosphorescence intensity (Curve 2) and weight variation (Curve 1) of an HMM sample during heating at 90, 125 and 170°C. Curves 3 and 4 show similar variations for a sample stored in the dark under ambient conditions for *3 months*. (b) Plot of weight against phosphorescence intensity of an HMM sample during heating at 170°C

panded glassy mass. This aged sample, in contrast to all fresh samples, was the only one which displayed melting, bubbling and expansion: the previous sample, for Curves 1 and 2, and all other heated samples, sintered and contracted slightly. The initial sections of the third stage of Curves 3 and 4 are consistent with reactions in the molten state showing faster weight loss and a corresponding drastic reduction of the phosphorescence intensity during the first 15 min.

*Figure 6a* clearly identifies the category of water having the most interesting effect on phosphorescence emission, i.e. water which is expelled on heating at 125°C. This is probably water of crystallization, as HMM is known to be crystalline and to form hydrates. The four-fold increase in phosphorescence intensity observed upon removal of this water suggests that there is now reduced interference between the hydrogen-bonding groups within the HMM crystals and water of crystallization. Hydrogen-bonding groups will also be affected by water contained within the cured resin. We consider that energy transfer occurs between the hexamethylolmelamine, the resin and the dopant. We believe that this is facilitated by the presence of methylol groups associated with the melamine moiety, but provided that they are free from interference by absorbed or complexed water molecules. Furthermore, condensation of the methylol groups to give methylene or other types of linkage reduces the phosphorescence intensity drastically (shown in the last part of the intensity curve of *Figure 6*).

Another fresh doped HMM sample was heated at 170°C for periods of 15, 30, 60, 120 and 360 min and 16 h. Any effects due to absorbed water and water of crystallization will be expected to occur within the first few min at this elevated temperature. The weight loss and dopant phosphorescence intensity variation of these samples were recorded during this treatment. *Figure 6b* shows the relative phosphorescence intensity plotted against sample weight.

The intensity was optimized near its maximum by heating a fresh sample at 125°C for 30 min and this intensity was taken as 100%. The 100% weight point was taken from the original fresh sample but this has a contribution from absorbed water and water of crystallinity and thus lies above the straight line. The other points lie quite close to a straight line and, for doped crystalline hexamethylol-melamine, the phosphorescence intensity is linearly related to the degree of condensation. The change in weight is due to water loss during the condensation reaction and represents a loss of methylol groups. In the absence of water interference, a linear relationship may be inferred between phosphorescence intensity and the concentration of unreacted methylol groups.

### *Role of hydrogen bonding*

*Figure 7* shows the phosphorescence intensity behaviour of various samples with different thermal histories (heated at differing temperatures) when subjected to high humidity followed by drying: 60 min at 100% r.h. (Period X), then 30 min at 0% r.h. (Period Y). Curve A shows these variations for unheated NSA doped HMM. The initial drop of 90% is followed by a recovery of 30% and a drop of 30%. Curve B shows the corresponding variation for a sample heated at 90°C for 60 min and Curve Bb shows the changes using this sample again after it was kept at 78°C in a vacuum oven overnight (16 h). Curve B shows intensity variations of 92–95% and Curve Bb shows an initial variation of 84%, followed by recovery and changes of 55–60%. This indicates that some condensation has taken place during this prolonged heating. There are marked differences in Curve B as compared with Curve A: Curve B demonstrates throughout an almost complete reversibility of the humidity effect on the heat treated system (90°C) during exposure to high and low humidities. This may be accounted for by the removal of most of the absorbed water from within the sample during heating at 90°C. In this case (Curve B) water absorbed by samples during a 100% r.h. exposure is almost completely removed during the 0% r.h. drying period. The water vapour which is absorbed by the sample during exposure to humidity would be expected to affect the methylol–methylol hydrogen bonding in the system and thus the triplet emission.

Curve C shows the variations after the sample of Bb above

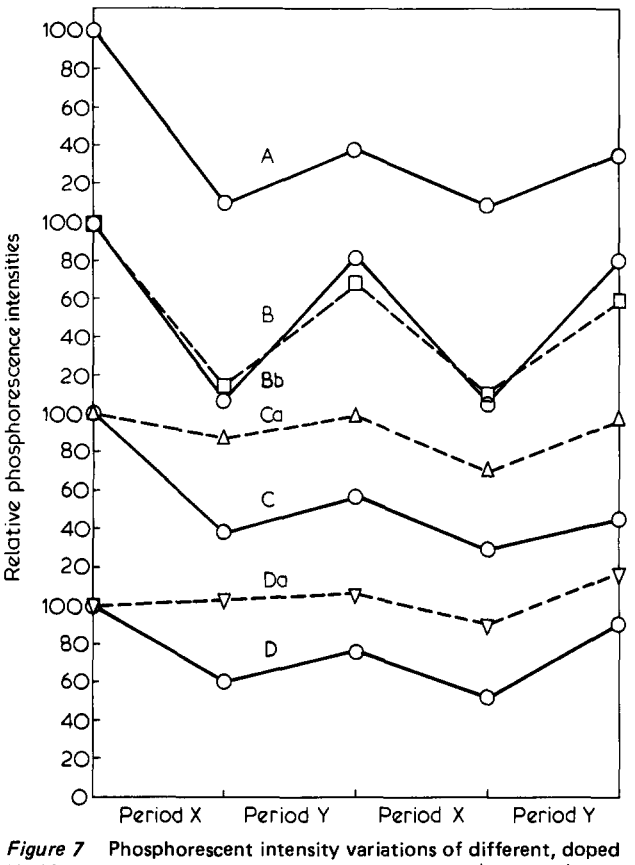


*Figure 7* Phosphorescent intensity variations of different, doped HMM samples during cycles of humidity exposure (Period X) and subsequent drying (Period Y). Curve A, sample as prepared, no heating; Curve B, sample heated at 90°C for 60 min; Curve Bb, sample as used for Curve B, heated overnight (16 h) in a vacuum oven at 78°C; Curve C, sample used for Curve Bb, further heated at 125°C for 30 min; Curve Ca, fresh sample of HMM heated at 125°C for 30 min; Curve D, HMM sample used for Curve C, further heated at 170°C for 30 min; and Curve Da, fresh HMM sample heated at 170°C for 30 min

is heated further at 125°C for 30 min. We know from *Figure 6* (Curve 2) that phosphorescent intensity increases by a factor of about 4 during this treatment. The sample, which had a high intensity, shows an initial drop of only 60% and subsequent variations of 10–15%. Curve Ca shows the corresponding variation for a fresh HMM sample heated at 125°C for 30 min. There are considerable differences between Curves C and Ca, in that the fresh sample heated for 30 min at 125°C shows 100% recovery after drying and variations of 15–30% during the humidity cycles. Furthermore, it shows a higher decrease within the second cycle (14% in the first cycle to 30% in the second cycle) compared to Curve C (60% in the first cycle to 26% in the second cycle).

The differences between Curves C and Ca are consistent with the fresh sample reaching a higher degree of cure than the sample in Curve C, i.e. the more highly cured sample suffers less variation in phosphorescent intensity. Similarly, Curve D shows the r.h. sensitivity result after subsequent heating of the sample of Curve C at 170°C for 30 min; and Curve Da represents the corresponding result for a doped *fresh* HMM sample heated for 30 min at 170°C only. Again the sample of Da is clearly more cured compared with the sample of Curve D. Thus the curing effect and resultant r.h. sensitivity of heating of HMM samples at 125° and 170°C is dependent upon details of the previous thermal history. This conclusion is reinforced by the observation that a fresh HMM sample placed directly on a hot-stage at 155°C melts immediately at this temperature and undergoes extensive cross-linking, whereas a sample slowly heated on a hot-stage from room temperature does not melt even at 200°C. The importance of water loss during the heating at 125°C (or in any preheating process) in affecting the melting behaviour must not be underestimated. It is evident from *Figure 6*, that the condensation reaction in the final section of Curve 3 is much faster (in the molten phase) when compared with the solid-state reaction illustrated by the final part of the weight loss curve (Curve 1). The phosphorescence curves, 2 and 4, reflect this even more dramatically.

A comparison of d.t.g., d.t.a. and d.s.c. curves of the samples heated at 90° and 125°C is shown in *Figure 8*. The d.s.c. results for the samples heated at 90° and 125°C for 60 min are shown as Curves 1 and 2, the d.t.g. results as Curves 3 and 4, the d.t.a. results as Curves 5 and 6. For the sample heated at 90°C, Curve 3 exhibits distinct rate of weight loss peaks at 125°, 154° and 264°C. The corresponding d.s.c. and d.t.a. curves (1 and 5) each exhibit endothermic peaks at 130 and 160°C. Similarly, the d.s.c. and d.t.a. curves for the sample heated at 125°C (2 and 6) each give an endothermic peak at 172°C corresponding to the rate of weight loss peak at 170°C. The d.t.a. curves for both samples, however, show no *endothermic* peaks at 266°C corresponding to the rate of weight loss (d.t.g.) peak at 266°C. On the

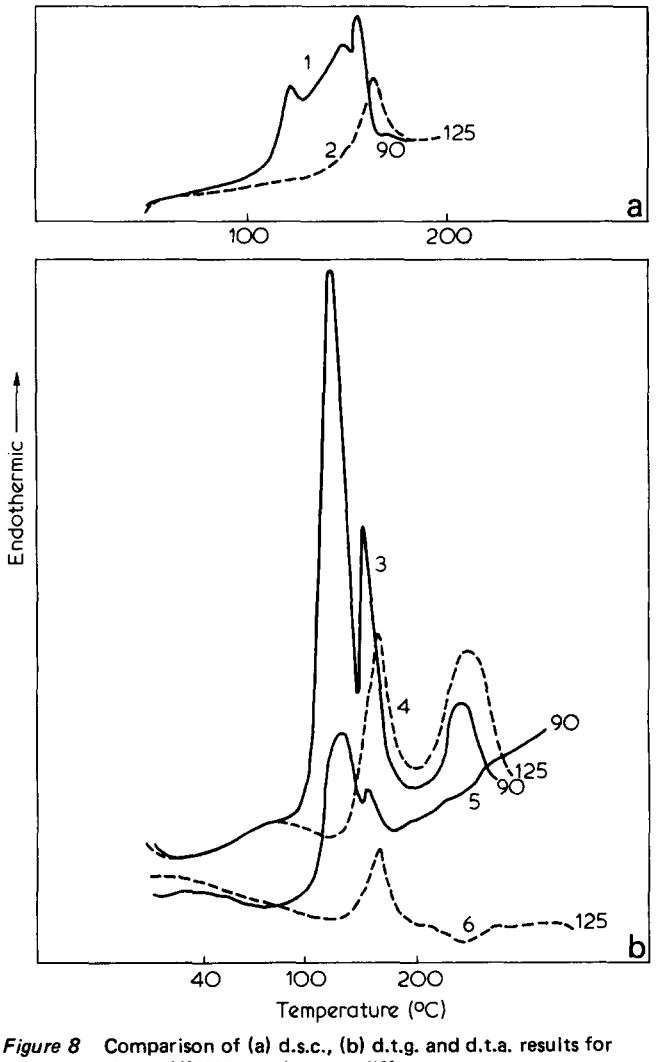


*Figure 8* Comparison of (a) d.s.c., (b) d.t.g. and d.t.a. results for samples of doped HMM heated at two different temperatures. Curves 1, 3 and 5 are for an HMM sample heated at 90°C for 60 min and Curves 2, 4 and 6 for an HMM sample heated at 125°C for 60 min. ——, Heated at 90°C; – – – –, heated at 125°C

contrary, low *exothermic* peaks are clearly indentifiable at that temperature. Thus it may be inferred that the low temperature transformations below, say, 200°C are accompanied by endothermic reactions, whereas the transformations responsible for the peaks at 264° and 266°C are exothermic.

The above qualitative difference between the low temperature transformations occurring at 125 and 154°C and the higher temperature transformations for the peak at 264°/266°C, as seen by the d.t.a. curves, is explained by the net heat changes taking place in each transition. The transformation (d.t.g.) at 125°C (for the sample heated at 90°C), results from the removal of water of crystallization from the system, an endothermic reaction. The peak at 154°C, Curve 5, results from a series of almost simultaneous processes which involve a liquid phase. First the HMM crystals melt; then resinification takes place, producing water; and this water is evolved. The melting of the crystals and evolution of water are both endothermic processes, whereas resinification is an exothermic change. Although the rate of weight loss is substantial, the corresponding resultant endothermic peak at 160°C has been extensively lowered by the concurrent exothermic processes. Similarly, for the sample heated at 125°C, Curve 6, displays an endothermic peak, in a slightly higher region, at 170°C; this again involves a liquid phase. Moreover, the large 125°C peak of Curve 5 is absent in Curve 6.

The further d.t.g. peak (at 264° and 266°C) represents distinct solid-state condensation reactions, in contrast with the reactions in the liquid at 154°/170°C, and shows up on the d.t.a. curves as an exothermic peak as expected. Again the peak magnitude is reduced to some extent by the accompanying endothermic evolution of water. Evidently the system had not been fully condensed in the more mobile liquid phase within the 150°/170°C temperature range, and further reaction is initiated in the resulting solid phase at the higher temperature.

The thermal balance result and weight loss curves (1 and 3) in *Figure 6* show more than 20% reduction in the sample weight during the transformation at 125°C. From this weight loss it can be estimated that between four and five molecules of water are associated with each molecule of HMM. However, we note that reference has been made to the formation, only, of an HMM crystalline monohydrate[11]. We are not aware of any definitive work on HMM hydrates and so hydration appears to warrant further investigation.

## CONCLUSION

Thermal analysis of the resin and HMM has enabled firm conclusions to be drawn about the nature of the transformations in the matrices which influence the phosphorescence of the doped system. The main transformations in the resin system are: removal of absorbed water below 100°C and of complexed water up to 200°C, followed by further condensation reactions between 200°C–300°C. The transformations in HMM represent: loss of absorbed water; loss of water of crystallization; and melting followed by some condensation reactions in the solidifying system with the accompanying loss of water and final condensation reactions in the solid state resin. The overlap of melting, water expulsion and crosslinking processes, as influenced by the thermal history, determines the extent and nature of further crosslinking and thus the complex influence of r.h. changes. This influence of thermal history is observed in the phosphorescence behaviour of samples. The importance of the extent of methylol–methylol hydrogen bonding in these systems to the dopant triplet emission has been established.

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