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Effects of Crystallinity, Cross-linking and Hydrogen Bonding on the Strong Room Temperature Phosphorescence of Doped Methylolmelamines

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The strong room-temperature phosphorescence of doped hexamethylolmelamine is reported. The dopant triplet emission sensitivity to differing relative humidity and to heating at various temperatures is investigated. These luminescence results correlate well with results from other thermal techniques such as TGA, DTA and DSC. Weight loss changes on heating indicate three distinct regions which are ascribed respectively to losses of absorbed water, water of crystallisation and water produced by condensation reactions, the latter generally resulting in cross-linking. The three categories of water show a complex relationship to the phosphorescence intensity of the system. An explanation of such behaviour is based upon the influence of the absorbed water and the water of crystallisation upon the effective hydrogen-bonding of the methylol groups present in the system, such groups being reduced in number upon cross-linking.

INTRODUCTION

The triplet emission of doped organic systems at 77K has received extensive study.[1] Crystallinity and hydrogen bonding are known to be important;[2,3] moreover, substrates containing —OH groupings likely to participate in hydrogen bonding yield higher triplet emission as compared with hydrocarbon matrices. The low-temperature glass formation properties of the systems used are sometimes inadequate, when micro-crystallites are formed and dopants rejected. We have studied the strong phosphorescence which can be readily achieved at room temperature in polymer systems including glasses,[4] crystalline systems[5] as well as in an amorphous thermoset resin.[6,7] We considered a possible explanation of the high-intensity triplet emission based on efficient energy transfer to the dopant triplet levels arising from excitation migration both in high molecular weight systems (see, for example, Ref. 8) and in crystalline lattices of organic compounds (see, for example, Ref. 9). Our studies of the thermoset resin system indicate that the room-temperature triplet emission intensity is sensitive to: variations of relative humidity (RH); the presence of other dopants (capable of being acceptors); and the degree of cure. There were indications that the phosphorescence of fully-cured resin samples containing only a few unreacted methylol groups, or of doped melamine crystalline samples showed little or no sensitivity to high RH (relative humidity).[5] The studies on the thermoset resin have yielded information on the role of the parameters affecting the population of the dopant molecule triplet state. Energy transfers may be responsible for the strong room-temperature phosphorescence observed, in spite of thermal non-radiative deactivation of the triplet state. The elucidation of the parameters which are predominantly responsible for the triplet emission of these room-temperature phosphors is rendered difficult by the chemical complexity of the thermoset resin, although we know that crystallinity, cross-linking and degree of hydrogen bonding play important roles in governing the triplet emission.

The present paper presents the results of studies undertaken on related but much simpler systems. These include some of the intermediate species which may be formed during the production of the thermoset resin (melamine-formaldehyde) samples studied up to now, namely, doped hexamethylolmelamine as well as doped methylolmelamines with decreasing numbers of methylol groups. The luminescence results obtained with hexamethylolmelamine are supplemented by parallel experiments using thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). There is good correlation of results using these methods. TGA and DTA results have provided finer details of the processes occurring during the stages of weight loss and condensation. The present studies have highlighted the relative significance of each parameter affecting the energy transfer processes in these systems.

EXPERIMENTAL

The doped methylol derivatives of melamine were produced by reacting the appropriate molar proportions of melamine (BDH) and neutralised 37–41 % formaldehyde solution (BDH) at 80°C, i.e., 1 : 6 for hexamethylolmelamine, adding 1 % by weight relative to melamine of naphthalene sulphonic acid as the dopant and cooling to crystallise the products. In this way, doped derivatives with up to a maximum of six methylol groups were obtained.

The resulting methylolmelamine was subjected to heating in an oven at various temperatures below and above the melting point of the sample.

Phosphorescence intensity and weight loss, each measured at room temperature, were recorded at intervals during heating using a laboratory-made spectrophosphorimeter and a Mettler H 80 balance. The spectrophosphorimeter employed a Thorn ME/D 250 W high-pressure mercury lamp as the excitation source, the light of which was filtered ($NiSO_4$ solution and 0X7 filter) and focused with quartz lenses. Samples were placed in a chamber with a rotating can as a light-chopper. The phosphorescence emission was analysed using a Hilger and Watts 330/1 Mark II high resolution grating monochromator. A photomultiplier (EMI 6256) detection system was used, feeding directly to a Servoscribe XYT recorder, model RE 551.20. Thermogravimetric studies were performed on a Mettler Mk. 2 thermal balance. Differential scanning calorimetry studies were carried out using a Perkin-Elmer DSC 2.

RESULTS AND DISCUSSION

Figure 1 shows the effect of exposure to high humidity (cycle X) and subsequent drying (cycle Y) over silica gel. The phosphorescence intensity of doped crystalline melamine (Curve A) along with similar results for doped

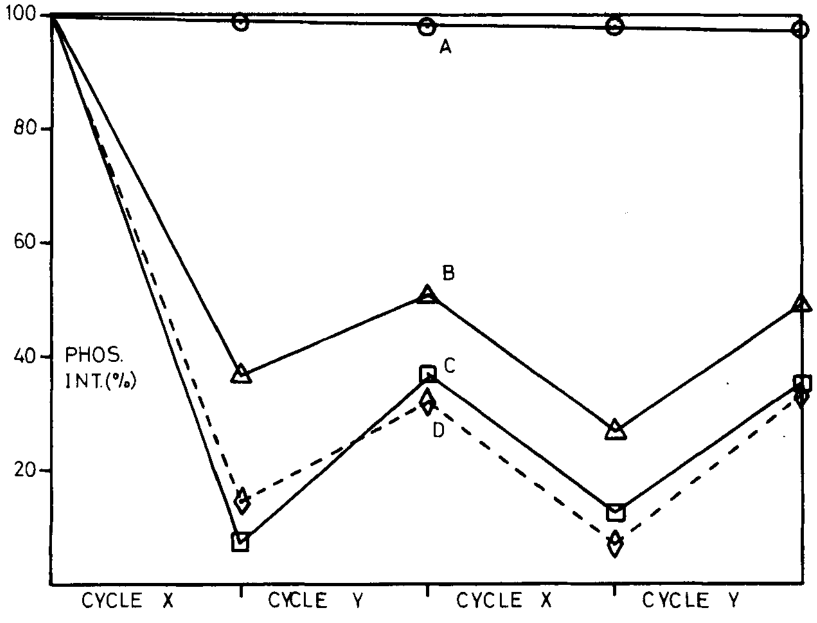

FIGURE 1 Effect of humidity and drying on the phosphorescence intensity of doped melamine (Curve A) and dimethylolmelamine (Curve B) tetramethylolmelamine (curve C) and hexamethylolmelamine (curve D). Cycle X represents 60 minutes at 100% RH and Cycle Y is 30 minutes at 0% RH.

crystalline samples of dimethylolmelamine, tetramethylolmelamine and hexamethylolmelamine (Curves B, C, and D) respectively are shown in Figure 1. The crystalline melamine sample shows no sensitivity to high humidity and, furthermore, seems to be unaffected when left in water for a number of days. The dimethylolmelamine sample shows phosphorescence intensity variations of about 60 % and, subsequently, 25 % and tetramethylolmelamine and hexamethylolmelamine samples show initial decreases of about 90% and recovery between 20% to 30%. There are significant differences between Curves A, B, and C with respect to each other whereas Curves C and D do not show such marked differences. The water sensitivities of the methylolmelamines become progressively larger, reaching saturation for tetra and hexamethylolmelamine.

Figure 2 shows the dopant phosphorescence intensity behaviour for hexamethylolmelamine during heating at 110° and 154°C and at 172°C. In Curves I and II the phosphorescence intensity goes up by a factor of about 5 compared with the starting intensity and subsequently shows a small decrease (5 % to 8 % of the maximum intensity). Curve III shows the phosphorescence behaviour for a sample which, additionally, has previously undergone the heating treatment shown in Curve II, and has been subsequently raised to and maintained at a temperature of 172°C (i.e., above the

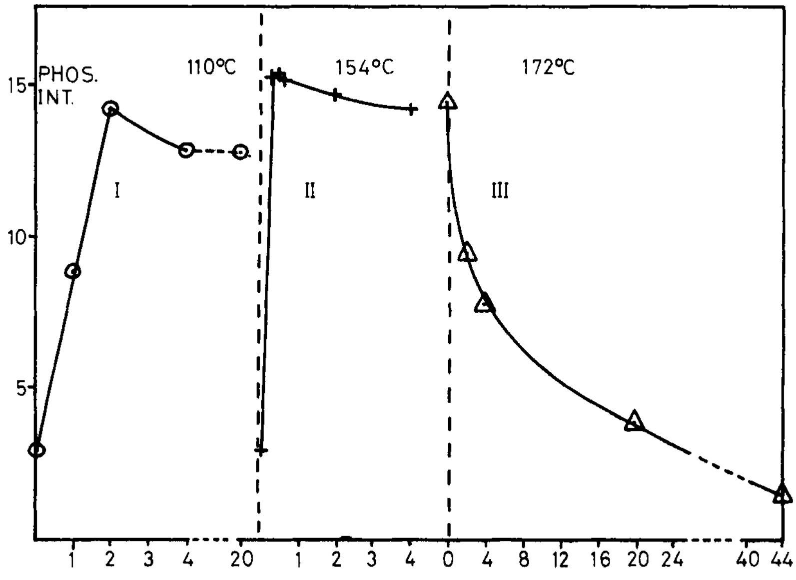

FIGURE 2 Effect of heating at 110°C, 154°C and 172°C on the phosphorescence intensity of hexamethylolmelamine.

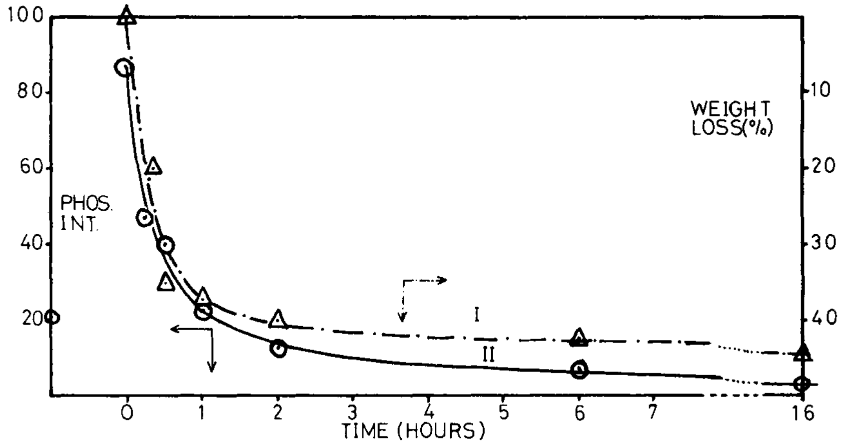

FIGURE 3 Comparison of weight loss (Curve I) and phosphorescence intensity (Curve II) of hexamethylolmelamine during heating at 178°C.

melting point). The drastic reduction of the phosphorescence of this sample after heating at this higher temperature appears to be due to the condensation which has taken place. It seems likely that the phenomenon is associated with the melting point of hexamethylolmelamine. The literature gives this as 150°C, but our results indicate that the m.p. is above 154°C for our particular sample (perhaps slightly cross-linked). The large scale condensation of crystalline hexamethylolmelamine is unlikely, due to the lack to translational and rotational freedom in the solid phase, but at temperatures above the melting point the freedom of movement is expected to result in a higher condensation rate (for those regions which are not already reacted).

Figure 3 shows a general correlation of the weight loss of a hexamethylolmelamine sample at 178°C (Curve I) with change in phosphorescence (Curve II). The weight loss of ~50% observed in Curve I seems to be too high to be explained in terms of condensation reactions alone. We believe this indicates the presence of absorbed water or water incorporated in a crystalline hydrate present in the hexamethylolmelamine samples. The initial five-fold increases in the phosphorescence intensities of Curve I (110°C) and Curve II (154°C) of Figure 2 appear to be associated with the removal of such water present in the sample.

Figure 4 Curve I shows the rate of weight loss of crystalline hexamethylolmelamine against temperature, up to 200°C in air. It shows three regions of weight loss for this sample. The first region between 50–100°C gives a shoulder at 93°C. The corresponding weight loss is only 6%. The second region between 100–146°C, peaking at 127°C, corresponds to the largest weight loss for this sample, at 22% of the original weight. The third region

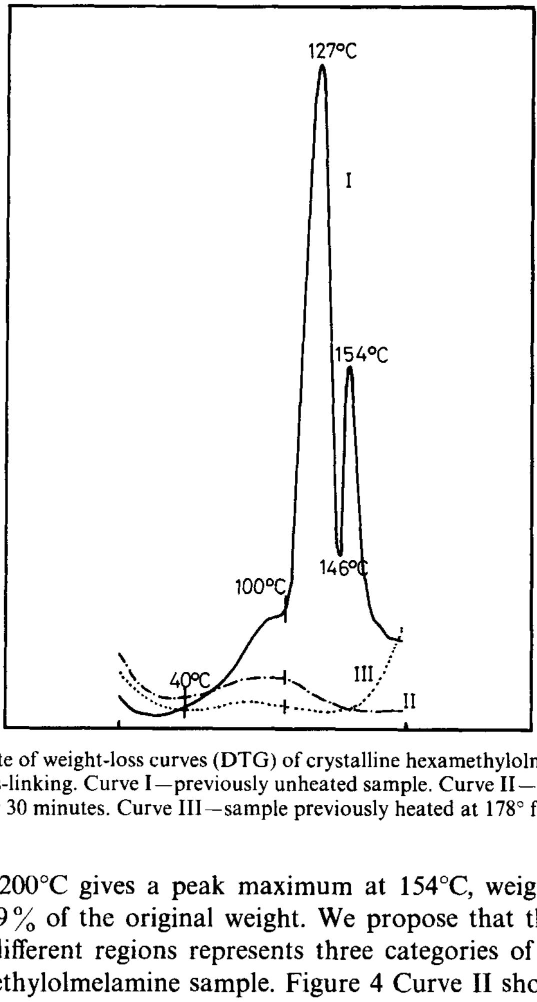

FIGURE 4 Rate of weight-loss curves (DTG) of crystalline hexamethylolmelamine at differing stages of cross-linking. Curve I—previously unheated sample. Curve II—sample previously heated at 178° for 30 minutes. Curve III—sample previously heated at 178° for 6 hours.

between 146–200°C gives a peak maximum at 154°C, weight loss in this region being 9 % of the original weight. We propose that the weight loss in the three different regions represents three categories of water present in the hexamethylolmelamine sample. Figure 4 Curve II shows the rate of weight loss of a fresh sample of hexamethylolmelamine previously heated at 178°C for 30 minutes. As expected, the rate of weight loss is considerably less than that of the previous sample, and there are no distinct weight losses at 127°C and 154°C. However, between 38°C and 150°C there is an 8.2 % weight loss with a broad maximum rate at 75°C to 100°C which would appear to be mainly due to only one type of water being present in the system, i.e., absorbed water.

Curve III shows the rate of weight loss of a further sample which has been heated at 178°C for 6 hours. The rate of weight loss is diminished compared to the sample which has been heated for only 30 minutes. Between 44°C and 120°C there is a weight loss of only 4.8 % with a maximum rate occurring around 85°C. The last result suggests that the greater cross-linking expected for the extensively heated sample permits less absorption of water compared with the crystalline sample (Curve I) or with the less cross-linked sample (Curve II).

The variation of weight loss was recorded on heating a crystalline sample of hexamethylolmelamine at 90°C for 1 hour, followed by 1 hour at 125°C and finally for 16 hours at 170°C. The resulting weight loss is shown as a function of time in Curve I of Figure 5. At 90°C only a slight weight loss is evident; an extended period of heating at 90°C (16 hours) gave only a slight further weight loss of less than 3 %. The second part of the Curve shows the weight loss behaviour during heating at 125°C, when the largest weight loss is observed. We believe that this is due to the removal of water of crystallisation preceded by the removal of the remaining absorbed water and probably followed by some cross-linking of the sample. Finally, the last portion of Curve I shows a further weight loss resulting from the condensation reaction

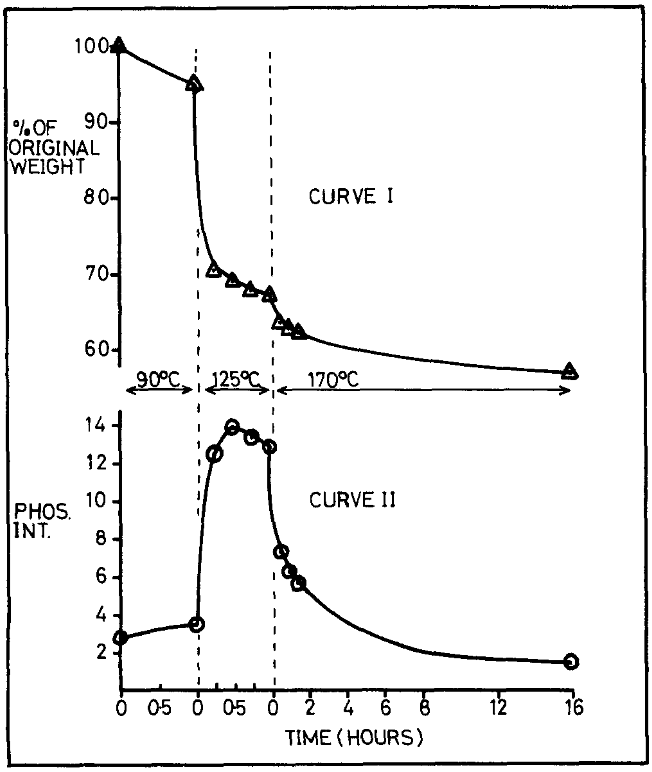

FIGURE 5 Isothermal weight-loss curves for hexamethylolmelamine heated at 90°C, 125°C and 170°C (Curve I) and the related phosphorescence intensity variations (Curve II).

taking place at 170°C. We also recorded the phosphorescence intensity variation of this sample, shown in Curve II of Figure 5, during the above treatment. It may be seen that during the initial heating period at 90°C, a slight intensity increase occurs corresponding to the slight weight loss. During the heating at 125°C there is a four-fold increase in phosphorescence intensity corresponding to a maximum weight loss of 15%. The intensity then begins to show a slight decrease during the final stages of heating at this temperature. Finally, as a result of further heating of this sample at 170°C, the phosphorescence shows a drastic reduction over the final section of Curve II. This appears to be due to increasing cross-linking which takes place with a small weight loss. Over the various periods of heating, there was no noticeable alteration in the spectral characteristics of the phosphorescence emission of the sample.

From simple chemical considerations, it is expected that the dominant product evolved during various stages of heating is water. Thus, a weighed amount of hexamethylolmelamine was heated at 125°C for 20 minutes in a narrow glass tube (the lower half only) with a wad of cotton wool placed in the opening to prevent the escape of condensable vapour, where products such as formaldehyde would be lost. Although a considerable quantity of liquid condensed on the cooler unheated section of the tube, on reweighing it was found that only 1% weight loss had occurred. The liquid was found to hydrate anhydrous copper sulphate to the characteristic blue colour, verifying that the weight loss of hexamethylolmelamine during heating is essentially due to the loss of water.

We recall that Curve I Figure 4 clearly distinguishes three stages of weight loss for hexamethylolmelamine. The first lies between 50°C to 100°C; the second between 100°C to 146°C, shows the largest weight loss as well as the largest rate of weight loss; and finally, there is a third stage between 146°C to 200°C. We have tentatively suggested that the weight loss occurring during the first stage is due to the loss of absorbed water. This view is reinforced by our finding that the phosphorescence intensity shows a slight increase during this weight loss. We have observed that a sample heated at 90°C for 1 hour retains a phosphorescence intensity variation, during humidity cycling, similar to that of a unheated hexamethylolmelamine sample as shown in Curve D of Figure 1. However, the magnitude of the reversible change in intensity during the high RH exposure and drying cycle is further increased from the 30% variation for the unheated crystalline hexamethylolmelamine, to a larger reversible variation of 80%. The magnitude of the reversible effect of water vapour on both the unheated hexamethylolmelamine and the sample heated for 1 hour at 90°C would appear to be due to the influence of absorbed water, affecting the hydrogen bonding of the doped hexamethylolmelamine.

The effect of water loss between 100°C to 146°C peaking at 125°C (Curve I Figure 4) is illustrated in the middle part of Curves I and II of Figure 5, when the sample was heated at 125°C. During this water loss, the intensity of the phosphorescence emission shows a four-fold increase, followed by a slight decrease. Furthermore the reversible intensity changes, during the high RH exposure and drying cycles, alter significantly and the variation is reduced to less than 10%, a range of 2–10% being recorded. The intensity, in general, remains high, i.e., 80–90% of the maximum intensity.

The weight loss during heating at 125°C is significant and appears to be mainly due to the loss of water of crystallisation. The corresponding and substantial changes in phosphorescence intensity may be attributed to changes in hydrogen bonding. Thus, it would follow that the extent of hydrogen bonding in hexamethylolmelamine is intimately connected with the presence or absence of the water of crystallisation. Furthermore, when the water of crystallisation is essentially driven off the variation in the phosphorescence intensity becomes less marked, although the overall magnitude is 4 times as high as in the untreated sample. This reflects a major change in the hydrogen bonding condition of the sample.

The drastic reduction of phosphorescence, measured at room temperature, during the heating exposure to 170°C is shown in the last part of Curve II Figure 5; this appears to be associated with the condensation reaction resulting in cross-linking. During this reaction there is considerable reduction in the concentration of methylol groups in the sample and some water is evolved (see the final section of Curve I Figure 5). A lower water vapour sensitivity is expected due to the lower number of —OH groups present in the system, as compared to the same sample in the middle section of Curve II, Figure 5. This sample would also be more resistant to water vapour penetration during high RH exposure. Thus, the samples at this stage of cross-linking show a very low sensitivity of the phosphorescence towards water vapour even after immersion in water for several days, as is the case for doped melamine crystals.

CONCLUSION

The weight losses of hexamethylolmelamine up to 200°C are due to the loss of three differing categories of water. The roles of absorbed water, water of crystallisation and water produced during the condensation reaction have been clarified to some extent. The first two categories of water compete, in effect, for the hydrogen bonding groups in the substrate, rendering these less effective in enhancing the dopant phosphorescence. The water lost in the condensation reaction, however, derives from these hydrogen bonding groups. Thus, the maximum phosphorescence intensity would occur when absorbed water and water of crystallisation are driven off, but before the condensation reactions set in. This conclusion, based on the condensation of the methylolmelamines bears out our previous suggestion[6] that "free chain ends" play a role in enhancing room temperature phosphorescence. The free chain ends would appear to be effective through hydrogen bonding by the methylol groups. The extreme sensitivity of the phosphorescence emission to the degree of cross-linking, state of crystallinity and the hydrogen bonding of this system has been demonstrated.

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