Letters

Intrinsic afterglow of crystalline melamine and a derivative resin and its role in a strong room temperature phosphorescent system

We have studied organic systems showing strong room temperature phosphorescence: for example, this was obtained when various dopants such as carbazole, dibenzothiophene, triphenylene, carbazole sulphonic acid, etc., were incorporated in a thermoset melamine–formaldehyde resin in bulk samples or as a spheroidal powder[1]. This intense phosphorescence showed negligible sensitivity to oxygen in contrast with other systems[2]. Certain chemical species, including water, affected the brightness. It was also found that an increase in the degree of cure beyond a certain level, typically at a temperature somewhat above the glass transition temperature, caused a decrease in the phosphorescence intensity. Optimally cured samples, from the heat treatment point of view, also gave diminished phosphorescence when exposed to u.v. irradiation. When more than one dopant was used, donor–acceptor type energy transfer resulted in increased intensity of the secondary dopant at the expense of the primary dopant. We have previously proposed that methylol free chain ends, which are found in large numbers even in the cured thermoset resin[3], may take part in energy transfer from the resin to dopant[4]. We now have noticed that melamine (2,4,6-triamino-*s*-triazine) and melamine–formaldehyde spray-dried resin exhibit a characteristic weak afterglow at room temperature. In our opinion, this is an intrinsic property which plays a significant role in the strong room temperature phosphorescence of doped melamine–formaldehyde resin samples. The spectra for melamine were the same for BDH Analar and OAS grades as well as recrystallized samples and there were only slight differences with the emission from the resin (BIP BL 34 resin).

We have undertaken quantitative measurements of the room temperature afterglow of melamine–formaldehyde resin using an emission spectrophotometer and a spectrophosphorimeter. *Figure 1a*, curve A, shows the emission spectrum corresponding to the afterglow of melamine (BDH OAS grade) and curve B shows that of commercial melamine–formaldehyde resin (BL 34 from BIP Chemicals Ltd). Both were recorded using the same setting of the spectrophosphorimeter. A recrystallized sample of Analar grade melamine gives emission indistinguishable from curve A. Curve C of *Figure 1a* shows the typical strong room temperature phosphorescence emission of carbazole doped melamine–formaldehyde resin. This curve was recorded on a much reduced gain (x1/20 factor) compared to curves A and B (*Figure 1a*). The peak wavelengths and lifetime of the various peaks of curve C (*Figure 1a*) are related to the triplet state of carbazole. The lifetimes and emission spectra of crystalline melamine (OAS) and BL 34 resin powder are quite different from those of the carbazole doped systems but show sufficient correlation to suggest that in the first two cases (curves A and B, *Figure 1a*) the origin and mechanism of the afterglow are the same.

Figure 1b shows the fluorescence emission spectrum of a dilute solid solution of melamine in poly(methyl methacrylate) as curve C′. Curves A′ and B′ (*Figure 1b*) show the emission spectra (mainly fluorescence) of melamine (OAS grade or recrystallized melamine) and of the commercial resin. Whereas curve C′ (*Figure 1b*) shows the emission spectrum which is typical of dispersed solid solutions of organic dopants, curves A′ and B′ (*Figure 1b*) show much broader emissions which, we believe, may be due to a mixture of some molecular melamine along with interacting melamine pairs (possibly dimers) present in the crystalline samples.

The effect of exposure to high humidity and subsequent drying over silica gel for melamine–formaldehyde resin BL 34 and carbazole doped BL 34 resin is shown in curves A and B of *Figure 2*. Curve B is of an intensity factor an order of magnitude up on curve A. These normalized intensity variations of curves A and B (*Figure 2*) after humidity exposure and drying show remarkable correlation. We believe that this sensitivity to water vapour is predominantly due to the presence of methylol-type chain ends in the resin, since further curing which reduces the chain end concentration also reduces the water vapour sensitivity to negligible levels, i.e. from the 40–50% changes shown in curves A and B (*Figure 2*) to negligible changes of about 3–5% which are comparable to experimental error. We also note that the melamine crystal phosphorescence (which was shown in curve A, *Figure 1a*) shows no sensitivity to water vapour exposure. This effect is illustrated by curve C in *Figure 2* where an OAS grade melamine crystalline sample has undergone the same humidity exposure and drying cycles as the samples in curves A and B (*Figure 2*) but shows negligible intensity changes.

We also have obtained the carbazole dopant phosphorescence when molecular carbazole was incorporated into the melamine crystalline lattice. This was achieved firstly by heating melamine with 1% of its weight in carbazole just about the melamine melting point and cooling until resolidification took place. Some carbazole is lost through sublimation resulting in a dopant level of ~ 0.1%. Secondly, carbazole doped melamine crystals were grown from saturated boiling water solution. The

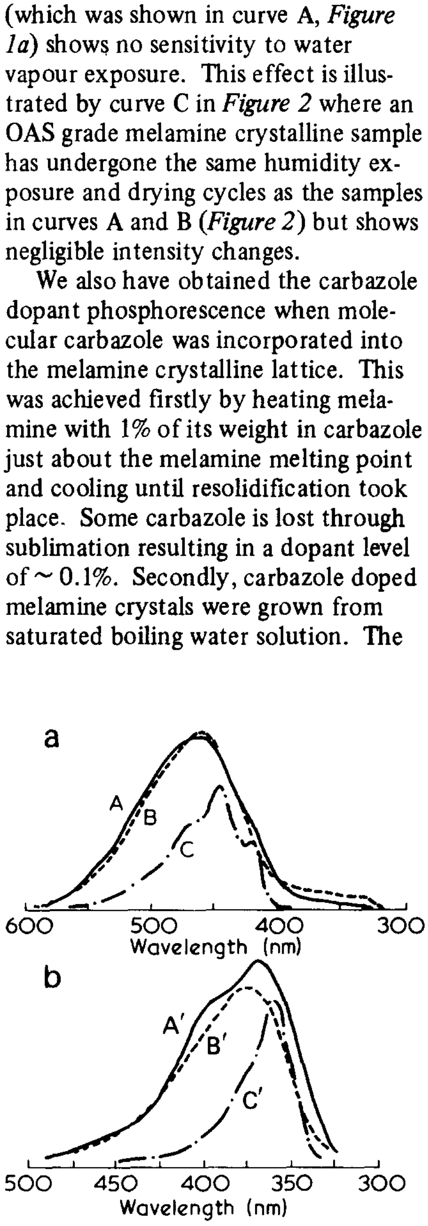

Figure 1 (a) Phosphorescence mode emission spectra of crystalline melamine (A) and melamine–formaldehyde resin (B). C, shows strong room temperature phosphorescence emission from carbazole doped melamine–formaldehyde resin on a much reduced gain factor (x 1/20). (b) Fluorescence spectra corresponding to crystalline melamine (A′) and melamine–formaldehyde resin, (B′). C′ shows the fluorescence emission spectrum of monodispersed melamine in poly(methyl methacrylate) matrix

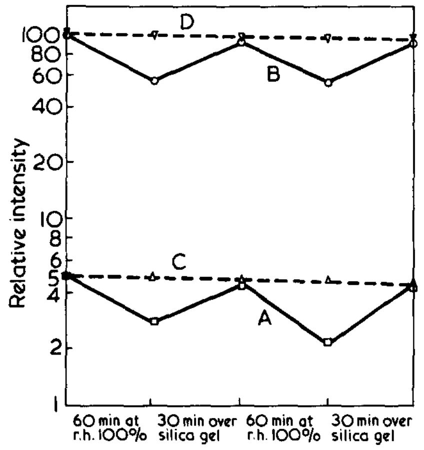

Figure 2 Variation of afterglow and phosphorescence emission intensity with exposure to high relative humidity and subsequent drying over silica gel for materials: A, undoped BL 34 Resin; B, carbazole doped BL 34 Resin; C, undoped crystalline melamine; D, carbazole doped melamine crystals. Relative intensity is indicated on a logarithmic scale

relative concentrations of carbazole and melamine are of critical importance in the solution case. In our qualitative work, only 10% of the samples produced melamine crystals having incorporated molecular carbazole. Luminescence characteristics established that the carbazole was monodispersed. Crystals obtained by both methods show phosphorescence intensities about 10 times stronger than that for the weak afterglow of the pure melamine crystals. The exposure of these crystals to high humidity and drying over silica gel did not affect the phosphorescence intensity. The normalized curve for undoped melamine crystals, see curve C of *Figure 2*, may be compared with that for the carbazole doped melamine crystals, see curve D *Figure 2*. The similarities of curves A and B along with those of curves C and D point out quite clearly that the weak and strong carbazole dopant phosphorescence intensities are only affected by water vapour in the low cured resin system. The crystalline melamine, the melamine crystallites incorporating carbazole molecules and the fully cured resin system, each are not affected by water vapour as far as the phosphorescence intensity is concerned.

The melamine phosphorescence, observed for pure crystalline melamine and for the melamine–formaldehyde resin, is not characteristic of that derived from a monodispersed system, the latter being expected to show some vibrational structure. We have, however, shown a fluorescence which we can attribute to monodispersed melamine, using PMMA as a host, and which is characteristically different from the broad, almost featureless, fluorescence of the melamine or of the commercial melamine resin. The phosphorescence observed, we believe, is due to interaction between melamine molecules, possibly of a dimeric nature (see for example ref 5). In the case of carbazole in the melamine crystalline host, the phosphorescence is suggestive of a monodispersed system, however, the strong intensity indicates that an energy transfer mechanism is available, e.g., triplet–triplet transfer from the host to the carbazole.

Considering the typical intense room temperature phosphorescence of doped thermoset melamine–formaldehyde, this is perhaps due to methylol-type free chain ends present in the low cured resin. At this stage it is not clear whether these chain ends increase the triplet–triplet energy transfer by means of the large volume of hydrogen bonded systems surrounding each carbazole dopant molecule or whether hydrogen bonding of the matrix affects the internal S_1 to T_1 transfer efficiency of the carbazole molecule. We recall, for example, that hydrogen bonding, between benzophenone and carbazole in an EPA glass at 77K, was proven to be responsible for a significant increase in benzophenone phosphorescence at the expense of carbazole phosphorescence[6].

Furthermore, phosphorescence of this system was also sensitive to the presence of hydrogen bonding matrices. This much is also clear from our results in *Figure 2* (curves A and B) which show that the presence of water vapour appears to alter the degree of hydrogen bonding, implicating the methylol chain ends and/or the similar bonding between methylolated melamine and the carbazole dopant. Our earlier studies have also indicated increased S_1 to T_1 transfer of carbazole in the thermoset resin resulting in increased phosphorescence at the expense of fluorescence, in a manner similar to the findings of Spencer and O'Donnell[6]. The matrix is not fully understood, having complex fluorescence and phosphorescence properties of its own. Nevertheless, we believe that its role as a donor species is proven beyond doubt.

We are in the process of making melamine–formaldehyde resins with differing numbers of methylol groupings (lowest 1 to highest 6) in order to elucidate the role of the methylol groupings in the strong room temperature phosphorescence of this system and possibly clarify the mechanism by which water vapour affects the phosphorescence reversibly.

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D. J. Morantz, C. S. Bilen and
N. Harrison
London College of Printing,
Elephant and Castle, London SE1, UK
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On the possibility of crankshaft motion in polymers in dilute solution

Introduction

The local mode explanation of the molecular weight independent high frequency relaxation process in dilute polymer solutions requires the concept of a localized segmental motion which leaves the bulk of the molecule completely undisturbed. The most likely mechanism for this process is the crankshaft model proposed by Schatzki[1], in which five carbon–carbon bonds (numbered 2 to 6 in *Figure 1*) consti-