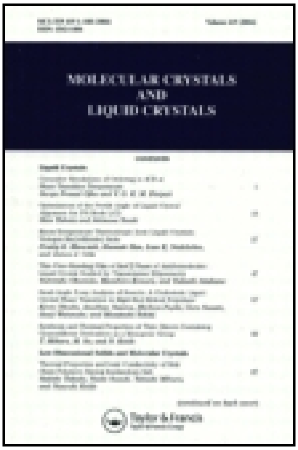

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Tasnim Husain [a], Geoffrey. R. Mitchell [a] & Andrew Gilbert [a]

[a] The Polymer Science Centre, University of Reading, Whiteknights, Reading, RG6 2AF, UK

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THE INFLUENCE OF SOLVENTS AND POLYMER MATRICES ON THE PHOTOINDUCED ISOMERIZATION OF AN AZOBENZENE CHROMOPHORE

TASNIM HUSAIN, GEOFFREY.R.MITCHELL, ANDREW GILBERT
The Polymer Science Centre, University of Reading, Whiteknights, Reading, RG6 2AF, UK.

Abstract The thermal cis to trans (Z to E) isomerization process following the photoisomerization of *N,N*- dimethylaminoazobenzene (methyl yellow) in a number of different solvent matrices; solutions, polymers and a liquid crystal are compared. In the solvents, dichloromethane, methanol, and polyacrylonitrile, a photoinduced stable cis isomer population could only be observed at $^{-}90°C$. In other solvents such as toluene and polycarbonate, at room temperature, the half-life of the cis form was about thirty minutes. The trans to cis conversion of the methyl yellow was exploited in a low molar mass liquid crystal matrix. Photoinduced shifts of up to 17°C were observed in the nematic to isotropic phase transition temperature .

INTRODUCTION

One important class of photoactive compounds are the aromatic azo compounds such as azobenzene. Photoisomerization about the N=N double bond gives rise to photochromism. The E to Z conversion process can be stimulated photochemically; the reverse reaction proceeds either photochemically or thermally.[1] In this work the thermal cis to trans reaction of methyl yellow, is investigated in three different environments. Firstly in a selection of organic non-polymer solvents; secondly dispersed in a range of polymers in the form of solid films and in the final section methyl yellow is incorporated into a low molar mass liquid crystal system. On selective irradiation the increased population of the cis isomer resulted in the destabilisation of the liquid crystal phase. A marked photoinduced depression of the nematic to isotropic (T_{NI}) transition temperature of the liquid crystal component was observed.

EXPERIMENTAL

In the first set of experiments solutions of 3 to 4 x 10^{-6} M concentrations of dye were prepared in acetonitrile, dichloromethane, methanol, and toluene. Irradiation of the solutions was carried out using a 150W Xenon Mercury arc lamp coupled to a monochromator system. The wavelength of irradiation was chosen as the value at the peak of the $\pi \rightarrow \pi^*$absorption band which was 400nm. The solutions were irradiated for 30 minutes until a photostationary state had been reached. The population of trans and cis isomers were monitored periodically using uv spectroscopy.

In the second set of experiments, films, 100μm thickness, of various polymers and methyl yellow were prepared by dipping clean glass slides into a solution of 2% dye to polymer. The solvent, either dichloromethane or trihydrofuoran was allowed to evaporate while the film annealed at 80°C for several hours. The polymers used were polyacrylonitrile (PAN), polycarbonate (PC), Polymethylmethacrylate (PMMA), polystyrene (PS), polyvinylchloride (PVC).

These polymer films were irradiated in the same manner as the solutions. Once irradiated the film and solutions were kept in the dark. The extent of the thermal back reaction was monitored for each sample by uv spectroscopy.

In the final set of experiments mixtures of methyl yellow and K15 were prepared with concentrations in the range of 2% to 20% w/w methyl yellow. The films were prepared by allowing the solvent, dichloromethane, to evaporate. Each film was irradiated at 400nm at a temperature of 30°C. The phase behaviour and the transition temperature (T_{NI}) were measured using a polarising microscope equipped with a hot stage and a photodiode system connected to a microcomputer.

RESULTS AND DISCUSSION

Figure 1 shows the set of uv spectra obtained at various stages during the thermal back reaction of the polycarbonate and methyl yellow system. Two isosbestic points can be clearly seen, indicating that the reaction is reversible. Similar plots were obtained for the other systems studied. It is clear from Figure 2a that there is no response to irradiation in the polyacryonitrile and dye system at room temperature. However when the system was cooled to $^{-}90$°C, a change in the uv spectrum was seen corresponding to a photostationary state. Similar observations were made for the methanol and dichloromethane systems.

In these two latter systems the absence of any increase in the isomer content could possibly be because the trans form of the dye is heavily solvated due to the existence of hydrogen bonding. This allows a stable association complex to form between the solvent and the methyl yellow, which will lower the energy of the stable trans isomer, hence resulting in a more rapid cycling from the cis to the trans form.

For the polyacrylonitrile the unchanging isomer population at room temperature may arise due to the surrounding polar groups, however this is unlikely, due to the appreciable lifetime of the cis isomer in other polar polymers such as PMMA and PC as can be seen in Figure 2b. This therefore suggests that there are specific structural interactions between the dye and the PAN. These results show that the solvent environment is an important factor in determining the stability and lifetime of the photoinduced cis isomer.

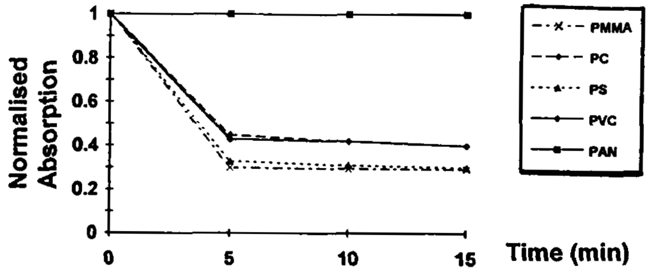

FIGURE 2a The change in the maximum absorption at 410 nm with time of irradiation for various polymer hosts containing 2% methyl yellow dopant.

FIGURE 2b The changes in absorption at 410nm after increasing periods of time in the dark for each sample.

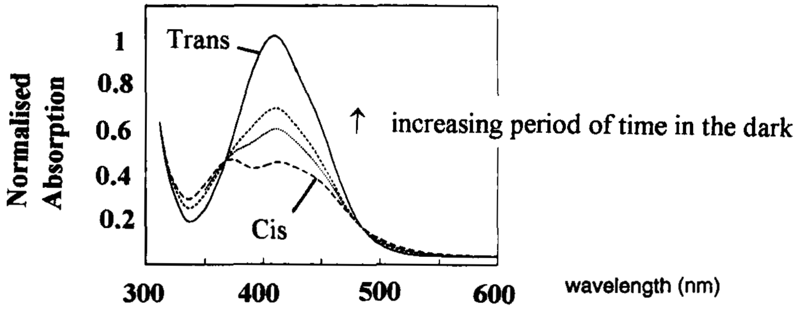

FIGURE 1 UV absorption spectra of methyl yellow in polycarbonate

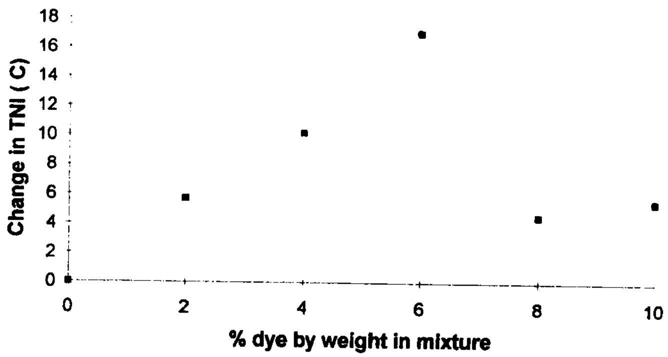

FIGURE 3 Plot of the depression in T_{NI} against increasing percentages of cis methyl yellow.

The mixtures of methyl yellow and liquid crystal present another polar solvent in which it is possible to promote a shift in the cis isomer content upon selective irradiation.[2] Such mixtures form an orientationally ordered nematic liquid crystal phase. In this system the induced isomerization of the dye disrupts the ordering of the liquid crystal system and hence produces a structural change in which the liquid crystal acts to amplify the photoinduced geometric isomerization. Figure 3 is a plot of the change in the T_{NI} upon irradiation against fraction of dye in the mixture. The change measured is the difference in the phase transition temperature for a dye containing trans isomers and an equivalent system containing cis isomers. At dye concentrations of 8% and over phase separation occurred in the system. The maximum photoinduced change observed was 17°C. It is shown that the structure of liquid crystal and azo dye systems can be easily manipulated to produce large photoinduced structural changes that can be utilised in applications such as optical image and data storage.

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