PHOTODEGRADATION STUDY OF METHYLENE BLUE (MB) TRAPPED IN POLY (METHYL METHACRYLATE) (PMMA) MATRIX

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Abstract

Photochemical reactions of the methylene blue (MB) doped in PMMA matrix was studied using a UV-visible fibre optics spectrophotometer. The absorbance peak of each MB doped PMMA sample centered around 660 nm decayed significantly with the increasing of exposure time to UV-visible light. A decrease in absorbance with time indicated that the UV-visible irradiation caused photobleaching of MB in the polymer matrix. The main absorption peaks for each sample increased at higher concentration due to the increase in the number of dye molecules. The absorbance of the sample at lower concentration decreased with time much faster than that at higher concentration of MB. This indicated that a faster photobleaching process occurred at the lower dye concentration of MB compared with that at the higher concentration of MB.

Introduction

The last decades of the twentieth century can be characterized as a period in which the use of computers for information storage has impinged on all parts of society. The continuously increasing amount of data to be stored and manipulated has generated the need for high-speed computers and large storage capacities. Digital optical data storage is a promising method, where recording of information is carried out by using the light. The best known example of optical recording used in a practical device is the compact disk, designed for the distribution of pre-recorded information (Feringa *et al.*, 1993).

Although read-only and write-once-optical disks are available in the markets, there is a need for truly reversible optical recording media with the opportunity to read, write, erase and rewrite. The development of these technologies has become of prime importance in industry in recent years (Feringa *et al.*, 1993). Although some problems still remain to be solved, the investigated materials at present for these purposes are based on alloys of rare earth elements and transition metals as the recording substrate thereby combining the magnetic and optical recording techniques. Future development will focus at further increasing the rate of data storage and storage density, for example by applying all practical writing or reading systems

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and other materials. The role of organic materials in this field has become increasingly important with main emphasis on dyes and polymers as photoactive component. This development is further stimulated by the notion that a large increase in information storage, theoretically to the molecular level, might be obtained (Feringa *et al.,* 1993).

During the past few decades, several studies on photostability of organic dye molecules trapped in transparent polymer matrices were carried out and became the focus of research. Such studies have great importance due to the various applications of these materials, such as for active laser element, optical data storage, phase hologram, optical computing, signal processing, optical waveguides etc. Suitable materials for different applications can be prepared by properly selecting the type of polymeric matrix and the dye incorporated into it. For example, laser dyes doped in polymers can be used as matrices for fabrication of solid-state dye lasers and dye-sensitized gelatin or poly (vinyl alcohol) can be used as a holographic recording medium (Nibu *et al.,* 1999; Capolla and Lessard, 1988).

In this paper, we report for the first time the photostability studies on methylene blue (MB) embedded in poly (methyl methacrylate) (PMMA) matrix using a UV-visible fibre optics spectrophotometer (OCEAN Optics, S2000). Methylene blue (MB) is a blue thiazine dye with the chemical formula ($C_{16}H_{18}ClN_3S$) and has the molecular weight 319.9 g/mol. This type of dye (MB) has been used for formation of high spatial frequency amplitude and phase holograms with a conventional He-Ne laser as a light source. The principal mechanism of grating formation is photobleaching of MB (Stanislaw and Miniewicz, 1995). It is known that MB cannot be bleached in a pure form. In order to bleach the MB molecules, they must be put into a suitable polymer matrix. The most frequently used polymeric matrix for photosensitive material is poly (methyl methacrylate) (PMMA). This matrix shows the best optical transparency in the visible spectra range and with regard to its laser damage resistance, it rank first among the polymers that could be employed as host materials in high power lasers (Wadsworth *et al.,* 1995).

Experimental Procedure

PMMA and MB supplied by BDH Chemicals Ltd., England were used in our measurement. Chloroform (BDH Chemicals Ltd. England) was used as a solvent for both compounds. The required amount of PMMA was dissolved in chloroform and then mixed with a solution of 8% (w/v) of PMMA containing three different dye concentrations of 6.3×10^{-4} mol/l, 1.9×10^{-3} mol/l and 3.1×10^{-3} mol/l. The MB embedded PMMA samples was obtained by leaving the polymer solution in a flat bottom dish at room temperature in the dark for 24 h. The samples were then cut into pieces of a circular shape with 10 mm in diameter for the following investigation.

In the present study, a single beam UV-visible fibre optics spectrophotometer (OCEAN Optics, S2000) was used to measure the optical absorption spectra of the samples. All the measurements of the optical absorption spectra of the MB doped in the PMMA samples were recorded at room temperature. The photochemical reaction of the sample occurred while continuous UV-visible irradiation was monitored by recording the data for 600 s with the intervals of 60 s. The same procedure was applied for the samples with different dye concentrations.

Results and Discussion

The measured absorbance spectra of the MB-PMMA samples at different dye concentrations are shown in Figure 1. It could be observed that the characteristic absorption peaks occurred at 658 nm and these peaks increase with the increasing of the dye concentration. It is known that the observed absorption peak at 658 nm corresponds to the transitions between the ground state (S_o) and the first excited singlet state (S_1) of the dye molecules when irradiated with light energy (Sergey *et al.,* 1998). The main absorption peak increases at higher concentration due to the increase in the number of dye molecules.

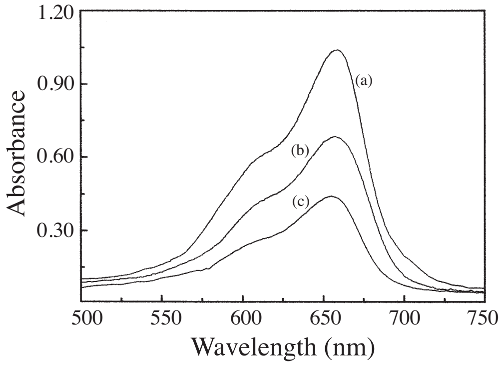

Figure 1. The UV-visivble absorption spectra of MB-PMMA samples at three different dye concentrations; $3.1x10^{-3}$ M (a); $1.9x10^{-3}$ M (b) and $6.3x10^{-4}$ M (c).

In Figure 2, we show a typical example of the variation of absorbance spectra during the continuous UV-visible irradiation on the MB-PMMA samples at dye concentration $3.1x10^{-3}$ mol/l. This figure indicates that the UV-visible irradiation decreases the overall absorption peak of the sample with the increasing of the exposure time. There is no significant shift of the absorption peak to higher wavelength. Each curve shows the same absorption peak located at 658 nm, as we observed in Figure 1.

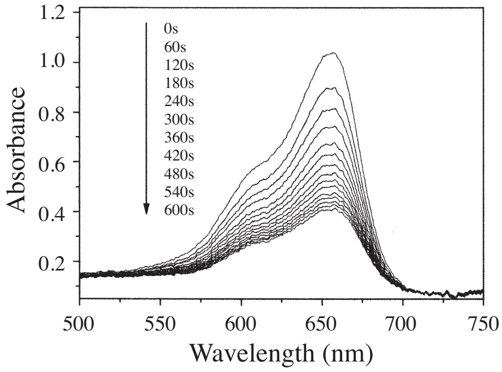

Figure 2. Variation in the optical absorption spectra with wavelength during uv-visible irradiation for MB-PMMA samples at dye concentration of $3.1x10^{-3}$ M.

A photochemical reaction which occurs during the photobleaching process of MB in polymer can be summarized as follows (Solano *et al.,* 1987; Mills and Wang, 1999; Carretero *et al.,* 1998; Capolla and Lessard, 1991):

$$MB \xrightarrow{h\upsilon} {}^1MB^* \longrightarrow {}^3MB^* \xrightarrow{+e^-} MB^{\bullet -} \xrightarrow{+H^+} LeucoMB \qquad (1)$$

When a dye (MB) molecule is irradiated with incident light hν, it passes to the first excited state (^{1}MB*), where it can make a transition to the triplet excited state with a longer lifetime (^{3}MB*). An electron is first transferred from the surrounding medium (polymer host) to the dye molecule producing the semireduced dye radical ($MB^{\bullet -}$). The MB dye molecule is then photoreduced by extract of an anion hydrogen from the polymer, to produce the leuco form of the dye molecules (colorless MB). Talhavani and Atvars (1998) reported that in the dye-polymer system, the polymer host itself is acting as an electron donor system and the production of the leuco form of the dye is a consequence of the electron-transfer process from the own polymer matrix, since no other electron donor additives were incorporated into the system. Therefore, this should be the most important contribution to the photodegradation process of MB in polymer. The chemical structure of methylene blue (MB), semireduced dye radical ($MB^{\bullet -}$) and Leuco MB (LMB) are shown in Figure 3 (Mills and Wang, 1999).

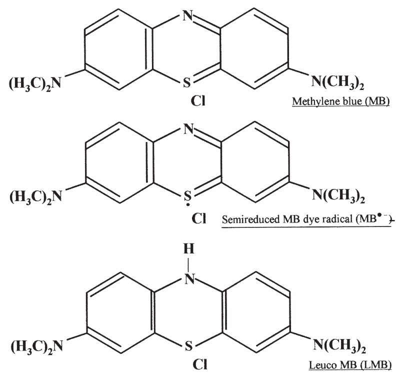

Figure 3. Formula structure of methylene blue and its common reduced forms.

The absorbance peak as a function of exposure time at different dye concentrations is then plotted in Figure 4. Each of the curves shows a gradual decay of absorbance as a result of photobleaching for MB-PMMA sample. The absorbance of the MB-PMMA sample at the lower concentration shows a significant decrease when compared with that at the higher concentration for the first 60 s. The color change (% of bleaching) of the irradiated samples could be estimated using a sample relationship proposed by Barakat *et al.* (2001). From Figure 4, after the irradiation for the first 60 s, the percentage of bleaching are 63.64, 60.29 and 54.9% for 6.3x10^{-4}, 1.9x10^{-3} and 3.1x10^{-3} mol/l, respectively. This indicates that the sample with lower MB concentration bleached much faster when compared with that at higher concentration.

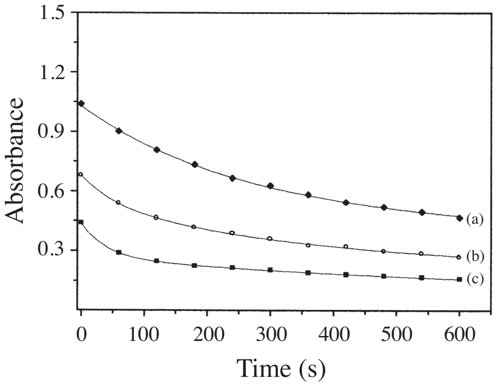

Figure 4. Absorption peak versus irradiation time of MB-PMMA samples at three different dye concentration: 3.1x10^{-3} M (a); 1.9x10^{-3} M (b) and 6.3x10^{-4} M (c).

It is a well-known phenomenon that higher dye concentration doped in polymer matrices may lead to the lower of photobleaching rate, which is mainly due to the ground state quenching (non-radiative deactivation of an excited dye molecule by a nearby dye molecule in the ground state) (Hartmann *et al.,* 1998). Solano *et al.* (1987) reported that by increasing the concentration of dye molecules, the possibility of the dye-dye interaction between the excited dye molecule (^{3}MB* and ^{1}MB*) and the nonexcited dye molecule (MB) increases and produces the non-bleached molecules in the electronic ground state. Consequently, this leads to a decrease in the rate of bleaching at higher concentration of MB doped PMMA matrix.

Conclusion

The photodegradation of the methylene blue (MB) embedded in the solid matrix PMMA [poly (methyl methacrylate)] has been investigated using the UV-visible fibre optics spectrophotometer. The absorbance peak of the sample centered at 658 nm decayed with time under continuous UV-visible light exposure. A faster photobleaching process occurred at the lower dye concentration when compared with that at the higher concentration. This is mainly due to the dye-dye interaction between two neighbors excited dye molecule and nonexcited dye molecule resulting in the return to the ground state of the excited molecule.

Acknowledgements

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