Spectroscopic studies of some photochromic compounds in polymeric thin films

By

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\section*{Introduction}

\subsection*{Definition of Chromism and Photochromism}

Chromism is a reversible change in a substance's colour resulting from a process caused by some form of stimulus. Many materials are chromic, including inorganic and organic compounds and conducting polymers, and the property can result from many different mechanisms.

\subsection*{Types of Chromism}

There are also several types of chromism, which are detailed below.

\subsubsection*{Thermochromism}

Thermochromism is the reversible colour change of a substance induced by temperature change. A large variety of substances, organic, inorganic, organometallic, supramolecular and polymeric systems exhibit this phenomenon. Examples of these include bianthrones, cobalt hexacyanoferrate, the zirconocene complex of 1,4-diphenyl-1,3-butadiene and poly(3-alkylthiophene). The organic $\beta,\beta'$-bixanthenyldiene is colourless at 0 K, yellow-green at 82 K and dark-blue when melted at 220 K.

Heating conducting polymers can cause them to change colour. This is achieved by causing conformational changes to the polymer backbone, resulting in a change in the band gap of the polymer. It has been reported that regioregular poly(3-hexylthiophene) P3HT reversibly changes colour upon heating to 200°C due to temperature-dependent conformation changes. Thermally crosslinked polymer undergoes the same colour change, but it is much less reversible. Other forms of thermochromism may be commercially important, e.g. to give a visual indication of temperature changes.

\subsubsection*{Photochromism}

Photochromism is a reversible transformation of a chemical species in one or both directions by absorption of electromagnetic radiation between two forms A and B, having different absorption behaviour. We will discuss this phenomenon with full details (see section \ref{Photochromism}).
Chirochromism and Diastereoselective Photochromism

Chirochromism is the reversible change in rotation of a plane of polarised light between two different chiral diastereomers of a photochromic compound. Diastereoselective photochromism is the photoinduced reversible change of absorption spectra between two diastereomers. The required diastereomer can be selected by exposing the material to light at particular wavelengths depending on which isomer is required. For example, if diastereomers A and B have absorption maxima at $\lambda_1$ and $\lambda_2$, respectively, then A can be converted to B by using light of wavelength at or near $\lambda_1$, and B into A at $\lambda_2$. Often, the same reaction can occur as a result of thermal energy (diastereothermochromism).

Halochromism

Halochromism is the reversible colour change due to a change in pH of a solution. Halochromic compounds include phenolphthalein and titanium dioxide. The compounds themselves are weak acids or bases and become involved in acid-base reactions. A change in the pH causes a change in the ratio of ionised and non-ionised states, and, since these two states have different colours, the colour of the solution changes. This colour change can be used in acid-base titrations where the colour change of the halochrome corresponds to the end-point of the reaction.

Piezochromism

Piezochromism is the phenomenon when crystals undergo a major change of color due to mechanical grinding. The induced color reverts to the original color when the fractured crystals are kept in the dark or dissolved in an organic solvent. The grinding generates a metastable form (see tribochromism). An example of a piezochromic organic compound is diphenylflavylene ($\nu$).

Tribochromism

Tribochromism is the phenomenon when crystals undergo a major change of color during mechanical grinding (as is the case of piezochromism), but the induced color change does not revert to the original color when the fractured crystals are kept in the dark or dissolved in an organic solvent. The crystals, prior to fracture, are in a metastable state ($\gamma$).
\subsection{Solvatochromism}

Solvatochromism is the reversible colour change induced by solvents. This often derives from changes in polarity of various solvents. This affects charge transfer mechanisms in solvatochromic compounds, causing colour changes. Poly(\(\tau\)-alkylthiophenes) are known to be solvatochromic. The effect on the polymers' colour of increasing the solvent polarity is very similar to decreasing temperature of the polymer i.e. the absorption maxima is red-shifted. This is due to the solvent being less able to intermingle with the alkyl chains and so the polymer becomes more planar, causing a decrease in the band gap. The colour of poly(\(\tau\)-hexylthiophene) solution was changed by the addition of a poor solvent. There was a crystallisation of the chains into a folded conformation \((\tau\tau)^{(\omega\omega)}\). For P\(\tau\)ATs, solvatochromism is often paralleled by a change in phase as it precipitates out of solution. However, insoluble crosslinked P\(\tau\)HT also changes from red to orange when chloroform is added due to chloroform's ability to penetrate the polymer matrix, causing it to swell.

\subsection{Halosolvatochromism}

Halosolvatochromism is the reversible change in colour brought on by a change in ionic strength without a change in the structure of the chromophore. An example of a halosolvatochromic compound is the dye, \(\tau,\tau\)-diphenyl-\(\tau\)-(\(\tau,\tau,\tau\)-triphenyl-\(\tau\)-pyridino)phenoxide. Upon addition of salts such as KI, Ca(SCN)\(\tau\), or Mg(ClO\(\tau\))\(\tau\) to solutions containing the dye to undergo a shift in the electronic absorption spectrum that increases with a change in cation density.

\subsection{Ionochromism and Acidichromism}

Ionochromism is the reversible colour change caused by the addition of ions. It can occur in addition to photochromism and can trigger an alteration in conductivity. When ionochromism does occur along side photochromism, both the relaxed and excited states can undergo ionochromism, i.e., in the photochromic reaction \(A \rightarrow B\), \(A\) can react to form \(AM^{\tau}\) and \(B\) can react to form \(BM^{\tau}\). All four of these compounds can have different colours, producing a four-colour system. A variation to ionochromism is acidichromism, where \(M = H\). Some phenols and aromatic amines are display this phenomenon. One possible use for acidichromism is in non-destructive readout systems where one form is used for readout and the others for writing and erasing \((\Lambda\tau\tau\tau)\).
\subsection{Electrochromism}

This is potentially the most commercially useful form of chromism. Electrochromic materials have been known since ٨٦٨١ (١٦). Three classes of electrochromic materials are known. These are metal oxide films, molecular dyes and conducting polymers. While some of these systems are all-solution, and some are solution-to-solid electrochromes, most electrochromes are all-solid systems. They have a number of potential uses, including displays, smart mirrors and windows, active optical filters and computer data storage (١٥).

The key properties of electrochromic materials are the switching times, the contrast ratios, coloration efficiency, electrochromic memory and long term stability. The switching time may be defined as the time for the colour change to become \( \% \) of the ultimate change in transmittance. The contrast ratio is the difference in transmittance in the visible spectrum. The electrochromic memory is the ability of the material to hold its colour with no current. The coloration efficiency (CE) is the change in optical density (\( \Delta \text{OD} \)) per unit area of the electrode (Qd) for a given wavelength. For amorphous tungsten trioxide films fabricated by thermal evaporation, a CE of \( \times \) \( \text{cm}^2 \text{C}^{-1} \) (٣٣٦ nm) can be achieved (١٥). The long term stability is the ability of the material to retain its electrochromic properties over a large number of switching cycles.
المستخلص

لقد تم في هذه الرسالة دراسة الخواص الفوتوكرومية لمركبات الفولجايد والسبيرو بيران والسبيرو اوكرزازين في أغشية رقيقة من المبلمرات مثل:

polyurethane , polymethylmethaacrylate, polystyrene, polyacrylic acid, epoxy polymer

وإجراء دراسات طيفية عليها للتعرف على خصائصها التي قد تفيد في بعض الصناعات مثل صناعة النظارات الشمسية، أقراص الكمبيوتر، العدسات، شاشات الجوال ومجالات أخرى.

وقد اجريت عليها بعض الدراسات الطيفية تركزت على المطبافية الإلكترونية باستخدام جهاز الأشعة فوق البنفسجية والمرئية وذلك لدراسة الخواص الفوتوكرومية، وتتبع عمليات التلوين الضوئي تفاعلات الرتبة الأولى. حيث تم تشغيل المركبات السابقة وتمت دراسة سرعة التلوين ودراسة سرعة إزالة اللون وقياس فترة نصف العمر لها بغرض معرفة أي المواد صالح للتطبيقات الضوئية مثل العدسات الشمسية وغيرها.

كما تم دراسة تأثير المادة المضادة على الخواص الفوتوكرومية لمركبات الفولجايد والسبير وبيران وقد وجد أن زمن نصف العمر لتفاعل الفوتوكرومي يتغير حسب تأثير المادة المضادة على المركب الفوتوكرومي. وقد لوحظ أن هذه التغيرات في زمن نصف العمر تتأثر بقابلية المادة المضادة لمنح الإلكترونات، فيزيتة قابلية المادة المضادة للمنح يزداد زمن نصف العمر وبالتالي ينقص معدل التفاعل الفوتوكرومي.

كما تم تحضير أحد مشتقات مركب الفولجايد وكذلك تحضير بعض مركبات السبيرو اوكرزازين ودراسة خواصها الفوتوكرومية. وقد وجد أن أحد مركبات السبيرو اوكرزازين يملك خواص فوتوكرومية جيدة ولكن يتطلب ذلك توفر وسط من النيتروجين السائل حيث تم بواسطةه قياس سرعة التلوين لة.
Abstract

The purpose of this research is to study the photochromic properties of fulgide, spiropyran and spirooxazine in thin films of polyurethane, polymethylmethaaceylate, polystyrene, polyacrylic acid and epoxy polymer.

Spectral studies have been carried out to investigate the properties of photochromic compounds that can be used in many industries such as CD, floppy disks, sunglasses, lenses, mobile screens and some other fields.

The photocoloration processes of these compounds were studied by using ultraviolet-Visible spectroscopy.

These compounds were irradiated in presence of additive and their photocoloration and kinetics were determined.

We also investigated the effect of the additive on there photochromic compounds. The half-life of photocoloration with additive was found to change, with concentration and the donor ability of the additive.

We synthesized new fulgides and spirooxazines. the latter showed better properties when cooled in liquid nitrogen.
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