

Synthesis of Azobenzene and Naphthopyran Based Polymers and Characterization of Their Photochromic Properties

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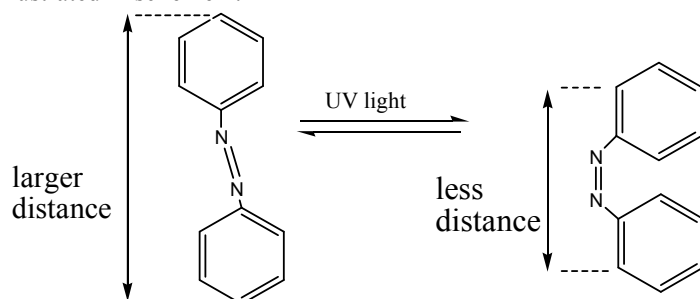
Abstract

The optically active monomer is prepared to synthesize the target polymer which contains naphthopyran and its photochromic properties and kinetics are investigated as well. Its photochromic property was studied using UV-vis absorption spectroscopy. When we stop measuring of the UV light, the decolorization of the sample changes spontaneously in the dark because of the thermal back-reaction which occurs as open form of the naphthopyran undergoes ring closure and the polymer's decoloration kinetics in films forms were analysed in the dark condition at room temperature after the optical intensity reached the maximum under UV irradiation. The naphthopyran polymer has showed the thermal bleaching tendency that the decoloration rate is very fast at the beginning of the thermal bleach and then gradually it became slow down.

Keywords- Photochromism, naphthopyran-containing polymer, kinetics, irradiation

1. INTRODUCTION

The photochromism is a remarkable development that has been drawing various attentions for several decades [1-3]. Organic materials having photochromic and nonlinear optical properties have been of prime importance [4]. They have several technological applications such as devices for the optical storage of information, waveguides, optical switches, optical modulators, surface relief gratings, holograms, chemical photoreceptors and in general as materials exhibiting photoresponsive properties when irradiated with light of suitable frequency and intensity[5]. It is a reversible photochemical reaction of a compound, which quickly changes its color when irradiated with light, such as UV light, sunlight or light from a fluorescent lamp and resumes its initial color when no irradiation [1]. Azobenzene and its derivatives undergo trans-to-cis isomerization when subjected to UV irradiation. This isomerization effectively reduces the distance between attachment points from 9.0 to 5.5 Å, as illustrated in scheme 1.



Scheme 1: The reversible isomerization of azobenzene upon UV/vis irradiation

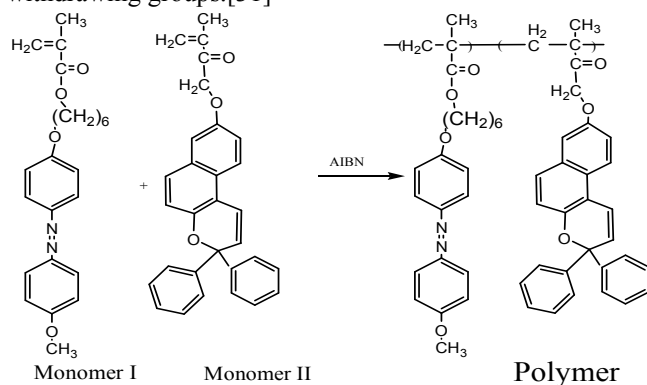
In particular, when illuminated with a polarized laser light in resonance with the electronic transitions of the azo group, the photochromic transazoaromatic groups undergo a reversible and repeated trans-cis-trans isomerization process providing orientational redistribution of the chromophores. Azobenzene and its derivatives undergo trans-to-cis isomerization when subjected to UV irradiation since azobenzene and many of its derivatives are characterized by reversible transformations from the generally more stable trans form to the less stable cis one, upon irradiation with UV or visible light[6, 7]. Under illumination with visible or UV light, corresponding to absorption band, the more stable trans form undergoes transformation to the less stable cis form. The reverse cis-trans reaction takes place as a thermal relaxation and it is relatively slow. To accelerate this transformation the illumination with light corresponding to the absorption band of the cis form is recommended [8-11]. The photoisomerization of the azobenzene group is particularly interesting because its consequence is a change of physicochemical properties of the materials such as: dipole moment, refractive index and dielectric permittivity, which can be interesting for practical applications in linear and nonlinear optics. It was found that recording of information was dependent on anisotropy of polymers which could be achieved by orientation of polymer chromophore groups by action of linearly polarized light. This mechanism is based on the selective excitation of azobenzene groups whose dipole moment vector is placed in parallel position towards direction of light polarization plane [12]. The polymer should have a proper structure to show photochromic and nonlinear optical properties. Among materials containing chromophore groups the most promising seem to be polymers because their properties can be flexibly modeled [13]. When the azobenzene molecule is attached chemically to a

polymer chain, photoinduced isomerization can result in conformational change being induced in the polymer chains. This can cause significant changes to physical properties such as the dipole moment, refractive index, and solution viscosity. Many of these changes can be reversed by heat or visible irradiation. Viscosity changes in polymer solution associated with photoinduced conformational change of the macromolecules were reported by Lovrien in 1966. Lovrien reported that, under the influence of UV light, the solution of a copolymer of methacrylic acid and azocompounds exhibited an increase in the reduced specific viscosity. The same author also investigated the photoviscosity effect of poly(methacrylic acid) and chrysophenine in water, reporting a decrease in viscosity of 50% due to UV irradiation. Following on from Lovrien's work, many more studies have been conducted into the photoviscosity effect in azobenzene-based polymers [14]. Irie and coworkers synthesized a range of polyamides containing azobenzene groups in the backbone. All of the polyamides exhibited a degree of the photoviscosity effect. The authors investigated the influence of spacer groups in the polymer backbone and speculated that the magnitude of the photoinduced change in the viscosity decreases with the addition of flexible units such as methylene chains [15-18]. Kumar and co-workers investigated a range of polyureas with azobenzene groups in the polymer backbone in DMSO at 35 °C. In 1920 Staudinger [19] was the first to report on the nature of olefin polymerizations leading to high polymers. A great many of his studies were carried out on the polymerization of styrene. These studies led to recognition of the relationship between relative viscosity and molecular weight [20,21]. The radical nature of these reactions was later elucidated by Taylor [22], Paneth and Hofeditz [23], and Haber and Willstatter [24]. The understanding of the mechanism of polymerization was greatly aided by Kharasch *et al* [25], Hey and Waters [26], and Flory [27, 28].

Continued studies in to photochromic polymers have been invaluable, proposing new concepts, solutions and applications for photochromism. These have evolved from a deeper understanding of how photochromics interact in a polymeric environment. Prior to the polymerization process the important monomers are prepared via several methods [29].

The synthesis of polymer can be carried out using controlled radical polymerization technique and By using this technique, polymers with defined architectures and functionalities can be accessed with controlled molecular weights (M_n and M_w) and polydispersities ($PDI = M_w/M_n$) and hence, with adjustable compositions and properties[30].

Now the interest of this work has been aimed on the study of synthesis on naphthopyran and azobenzene based compounds and studying the photochromic properties of polymer formed from naphthopyran and azobenzene. As it was discussed by another author, compared to other photochromic families, the naphthopyran compounds have the advantages of the low initial color, low solvachromism, high color density and large color gamut provided by the ring open form when substituted with various electron donating and withdrawing groups.[31]



Scheme 2: Synthesis of poltmer matrix

2. Synthesis of monomer (II)

3,3-diphenyl-3H-benzo[f]chromen-8-yl methacrylate is synthesized by using the following steps:

2.1. Synthesis of 1,1-diaryl-prop-2-yn-1-ol (1a) In the dried flask 6ml of THF and 18ml of n-butyllithium in hexane (2.5Mwith 45mmol) followed by addition of trymethyl silyl acetylene (45mmol) and stirred for at least an hour. The benzophenone, slurred or dissolved in anhydrous THF, was added and then cooled for at least four hours. Finally KOH (2.52gram) added and the solution is cooled to 0°C during the addition of KOH. Then the solution flask is removed from the cooling bath and cooled to room temperature. The result was measured and obtained as the pure product for the following procedures.

2.2 Synthesis of 6-(2-hydroxyethoxy) naphthalen-2-ol (1b)

In the three necked flask naphthalenediol and K_2CO_3 together and then DMF added to dissolve the above two compounds to form 6-hydroxynaphthalen-2-olate ion.

Then the formed ion solution is refluxed for an hour using the condenser at temperature $25^{\circ}C$. The condenser is attached to the boiling flask and cooling water is circulated to condense escaping vapors. One should use always a boiling stone or a magnetic stirrer to keep the boiling solution from bumping. After the given time of refluxing 6.87g of 2-bromoethanol added drop by drop then a small amount of KI is added and temperature rose to $85^{\circ}C$ kept for three days. The reflux is stopped after four day and water is added to dissolve the remained K_2CO_3 and acetic acid is added to neutralize the reaction which becomes the pH value ~ 7 . Then it is filtered while adding water and ethyl acetate. The organic layer is separated and washed several times by ethyl acetate. The separated organic layer is washed with water to remove the remained DMF. The organic layer is condensed for further separation to get the solid product; and then the solid product dissolved with methyl dichloride and again condensed. To make the product more dry the silicone gel is added and dissolved with methyl dichloride and again condensed to the dry solid product.

Still the solid product is not pure so it needs further purification, and it further purified by using column chromatography. The appropriate solvents used are ethyl acetate and petroleum ether. After separation finally the purified solution is condensed and get solid pure product. It again dissolved with methyl dichloride to get more products that is called 6-(2-hydroxyethoxy) naphthalene-2-ol.

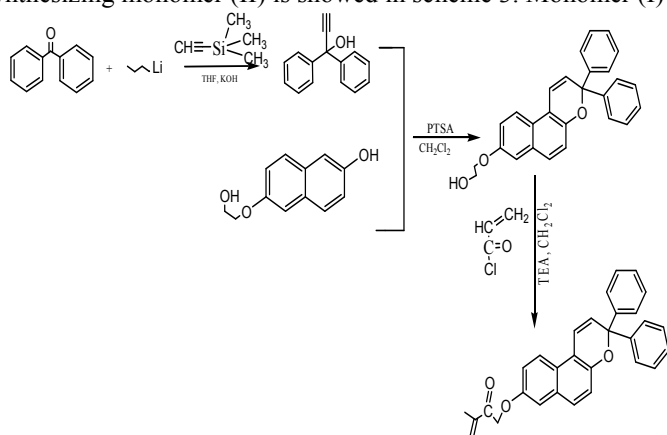
2.3. Synthesis of 2-(3, 3-diphenyl-3H-benzo[f]chromen-8-yloxy)ethanol(1c)

In the clean flask 3gm of (1a) and 0.43gm of (1b) added and then 0.1gm of PTSA mixed. The solvent CH_2Cl_2 is added thoroughly to dissolve the mixtures. Then it refluxed for 3 days in room temperature until TLC examination indicated that none of the prop-2-yn-1-ol remained. The refluxing stopped, distilled and dried by using drying agent. Then the product is further purified by the same fashion as previous by column chromatography. The purity of product is checked by TLC, weight and used for further producers.

2.4. Synthesis of the final product

2.4.1. 1-(3,3-diphenyl-3H-benzo[f]chromen-8-yloxy)-3-methylbut-3-en-2-one

In the dried three necked flask a small amount of CH_2Cl_2 and 0.531ml of TEA is added inside hood since it most poisonous compound and then (1c) is added. It kept for 30 minutes. Then acryloyl chloride is added slowly drop wise by using the side neck. And finally it is washed with CH_2Cl_2 and the flask kept in low temperature below $0^{\circ}C$. It was reacted for at least 20 hours until the product is formed which is checked by TLC frequently. Then after the conformation of having the target product, the reaction is stopped and transferred to another flask washed by CH_2Cl_2 . If there is any remained product it washed by NaOH solution then the small amount of NaOH(10%) added to the product solution. The product solution should be the pH range between 6-5 by adding HCl, then the organic layer and water portion is separated by using different the separation method. Finally the separated product solution is dried by adding anhydrous magnesium sulfate in it and mixed for 1 or 2 hrs then the organic product is separated from the solid one and distilled to obtain the solid form of the product. To get the pure product we have to use the further separation method. The column chromatography is used for further separation. The final pure product is used as the monomer for the synthesis of polymer. The entire process of synthesizing monomer (II) is showed in scheme 3. Monomer (I) is used as it is taken.



Scheme 3: Synthesis of 1-(3,3-diphenyl-3H-benzo[f]chromen-8-yloxy)-3-methylbut-3-en-2-one

3. Synthesis of polymer

Homo- and copolymerization reactions were carried out in glass vials using AIBN as free radical thermal initiator (2% w/w with respect to monomer) in dry THF solutions (12 ml) containing 0.6g of both monomer I and II. Feed having the molar composition is taken as 50 to 50 mole ratio were prepared and introduced into the vials under nitrogen atmosphere, submitted to several freeze-thaw cycles in order to eliminate any trace of dissolved oxygen and heated at 70°C for 72 h. The crude product was precipitated from the solution by pouring the reaction mixture into a large excess of methanol (100 ml) and collected by filtration. The solid polymeric products were repeatedly redissolved in DMF and precipitated again with methanol. The last traces of unreacted monomer were eliminated from the product by Soxhlet extraction with methanol followed by acetone. The purified products were finally thoroughly dried to constant weight under vacuum at 70°C for several days. The dried polymers were sufficiently soluble in THF and CHCl₃ as well as in strongly polar solvents such as nitrobenzene, DMF, DMA or dimethylsulfoxide (DMSO) and it illustrated in scheme2. And then product is characterized by GPC and determined the value of M_n which is reported in the table 1.

4. UV-vis spectrophotometry

The photochromic properties of the polymeric films were recorded using an Agilent Technologies, Varian Cary 500 UV-vis spectrophotometer with the characteristic time of recording ca. 1 s. To measure wavelength of the dark reactions with the characteristic time of several seconds, samples were placed on the position of sample in the cuvette box of the spectrophotometer and their absorbance spectra were measured. The samples were then irradiated to a constant intensity with UV light to measure wavelength of open form in the visible spectra region. A CHF-XM35 parallel light system with a 500 W xenon lamp with 5 cm beam diameter was used as the ultraviolet source of irradiation. The wavelength of the maximum absorption (λ_{max}) of the ring-opened form (coloured) of the polymer was obtained by plotting the UV spectrum of the sample. All of the experiments were carried out at room temperature.

5. Materials

Methacryloyl chloride (Aldrich) was distilled (bp 95 °C) under inert atmosphere in the presence of traces of 2,6-di-tert-butyl-p-cresol as polymerization inhibitor before use. Tetrahydrofuran (THF), N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMA) were purified and dried and stored over molecular sieves (4 Å) under nitrogen.

Triethylamine (Aldrich) was refluxed over dry CaCl₂ for 8 h then distilled (bp 89°C) under nitrogen atmosphere. 2, 20-Azobisisobutyronitrile (AIBN) (Aldrich) was crystallized from abs. ethanol before use. The molecular weight of the polymer was determined by gel permeation chromatography (GPC)

¹H NMR spectra were recorded on a Varian Unity Inova Spectrometer (500 MHz) at room temperature and d-chloroform was used as solvent.

All other reagents and solvents were used as received.

6. Preparation of thin films

Polymer (0.3 g) was added to THF (15 ml) under stirring. The mixture of solution well stirred and became clear then it was poured into a quartz glass and kept at room temperature for several hours to remove all traces of solvent. After staying at 50°C for at least 1 h in a vacuum, the resulting films were kept in the dark to prevent their degradation by direct sunlight prior to the spectroscopic measurements.

7. Results and discussion

7.1. Synthesis of monomer and characterization of polymers

7.1.1. The synthesis of monomer,

1-(3,3-diphenyl-3H-benzo[f]chromen-8-yloxy)-3-methylbut-3-en-2-one, was carried out starting from benzophenone through coupling with **1,1-diaryl-prop-2-yn-1-ol** and **6-(2-hydroxyethoxy) naphthalen-2-ol** to give the main intermediate,

2-(3, 3-diphenyl-3H-benzo[f]chromen-8-yloxy)ethanol. Then this intermediate is allowed to react with acryloyl chloride thus affording the desired novel optically active monomer. The optical activity of the monomer is confirmed that it is mirror image and non-superimposable. This indicates that an enantiomeric property is present in these compounds thus excluding the possibility of racemization of the chiral center in the course of the synthesis. This allows to reasonably attributing an analogous optical purity to the monomer.

The radical homo- and copolymerization reactions of monomer I with Monomer II afforded in all cases polymeric products in high yields with comparable average molecular weights and polydispersity values, as determined by GPC (Table 1).

GPC Result, Table 1

	Mn	Mw	Mp	Polydispersity	The total area	Retention time (minutes)
Polymer	3727	4896	4232	1.313477	1968132	10.241

7.2. UV-vis properties in polymer film.

All the obtained products exhibit in the UV-vis spectra in THF (in figure 1) two absorption bands in the spectral region 200–700 nm. The former one, more intense and significant, located about 470 nm, is related to the n- π^* , π - π^* and internal charge transfer electronic transitions of the conjugated azoaromatic chromophore, the latter, located around 362 nm, is related to the π - π^* electronic transition of the aromatic ring.

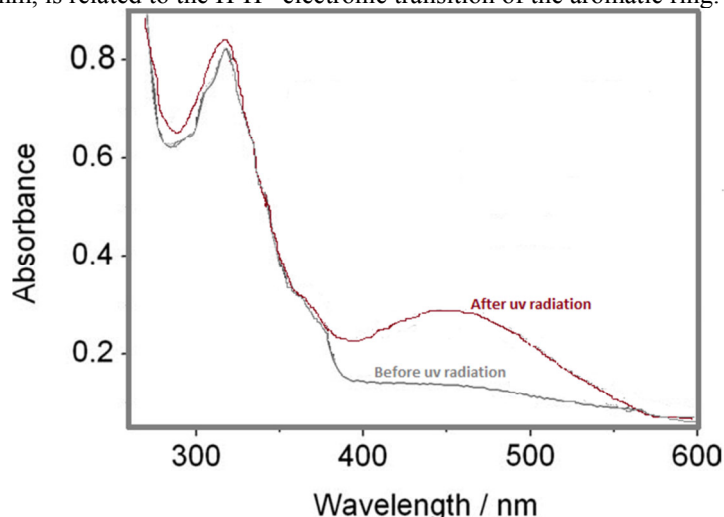


Figure 1: UV-vis absorption spectra of polymer II in film form before and after UV light irradiation

8. The photochromic properties of polymer

In the reversible transformation upon exposure to UV radiation (Scheme1), our target polymer compound in the open form indicated the typical absorption peaks in the visible area round 362nm shown in Fig 1 and its photochromic characteristics of the colored forms (open forms) were listed in Table1. However, it can be seen that no peak were observed at all in the range of 400-500 nm before UV irradiation. Fig.2 indicates that the optical absorbance change during coloration of polymer by the irradiation of UV light (365 nm). When we increase the irradiation time, we observed that the optical intensity at 470nm increases exponentially. The intensity of the 470 nm absorption band nearly reaches a plateau after irradiation for long time, indicating long irradiation time can cause saturation of the optical intensity. Upon stopping of the UV light, the samples decolorize spontaneously in the dark due to the thermal back-reaction which occurs as open form of the naphthopyran undergoes ring closure, this process is accompanied by decreasing of absorbance band of ring-opened naphthopyran.

The molecular weight of a polymer is of prime importance in the polymer's synthesis and application [5]; however, as it was listed in table 1 the value of molecular weight of both polymers is not such a high value that is because of the contaminants and impurities during the synthesizing process.

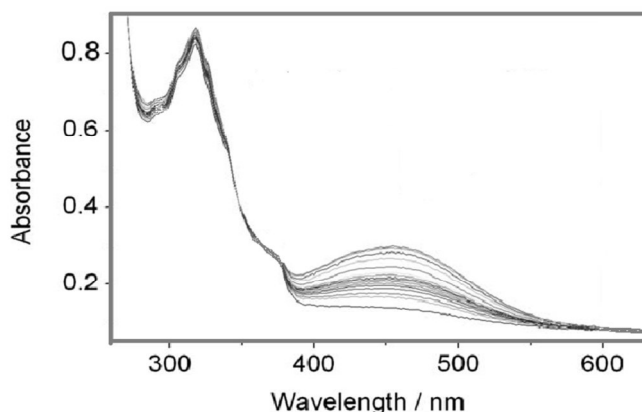


Figure 2: Optical absorbance spectra change during coloration of polymer I in the film form by irradiation of UV light versus irradiation time. The absorbance intensity increase at 470 nm is shown in the inset.

9. The decoloration Kinetics

The colored form that tending to return to an earlier state; to the thermodynamically stable closed form, with decay kinetics strongly dependent on the environment and kinetics in solid media is normally quite complex due to the rigidity of the environment [32].

The thermal decoloration of naphthopyran polymer films was examined scientifically in the dark at room temperature after the optical intensity reached the maximum under UV irradiation. The decoloration happened spontaneously in the dark due to the thermal back reaction from merocyanine form to closed naphthopyran form. The kinetic properties of spectra decaying were studied by monitoring the absorption intensity against the time at the maximum wavelength (455 nm) of the merocyanine form. For naphthopyran, the decoloration rate of opened form (TC) and (TT) to closed form are fast and slow, respectively, (Scheme 1).

Naphthopyran in polymer has the bleaching trend; the decoloration rate is very fast at the beginning of thermal bleach, which is accompanied by ring-close reaction from TC to ring-closed naphthopyran. After the most of TC isomer transformed to the closed form, the transforming of TT isomer to ring-closed naphthopyran is dominating thermal bleach process that is the latter part on the curves in Figure 2.

Acknowledgment: I would like to express my gratitude to Professor Guang Wang who generously helped me by his technical advice, suggestion and his valuable criticism with his time, knowledge and expertise.

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