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Solvatochromic and Photochromic behavior of 1',3',3'-trimethyl-8-nitrospiro[chromene-2,2'-indoline]

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Abstract

1',3',3'-trimethyl-8-nitrospiro[chromene-2,2'-indoline] is one of the spiropyran derivatives. In recent years, the spiropyran derivatives have been studied numerously for their photochromic properties.We know these compounds as an isomeric system. The closed-ring spiropyran (SP) could be converted into the open-ring merocyanine (MC) upon UV irradiation. In this work, 1',3',3'-trimethyl-8-nitrospiro[chromene-2,2'-indoline] is prepared, and subsequently, characterized by the FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopic techniques. In order to confirm its molecular structure, the UV–visible spectroscopic analysis of its solutions is studied in different solvents in the spectral range of 250-750 nm before and after exposure to a UV lamp. The 1',3',3'-trimethyl-8-nitrospiro[chromene-2,2'-indoline]chromophore shows a solvatochromism behavior: the spiropyran solution in acetonitrile is completely colorless, while its solution is pale blue in DMF and dark purple in ethanol and methanol. The visible spectra of the spiropyran solutions show that the solvents methanol and ethanol are capable of stabilizing the MC form better than the solvents DMF and acetonitrile, and that this photochromic compound has a higher absorption intensity in the visible region.

Keywords: Photochromism, Spiropyran, 3-nitrosalicylaldehyde, Solvatochromism.

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Introduction

In photochromism, two isomers are reversibly interconverted via a photochemical reaction. The absorption spectra of these isomers are different. The molecular structures of most photochromic compounds such as spiropyrans change from colorless to a colored compound upon exposure to UV irradiation; these compounds display a positive photochromism. (Some spiropyrans show a negative photochromism.) They are colored in the dark and lose their color upon exposure to UV light [1]. Spiropyran is one of the most intensive photochromic compounds that have been widely studied in the past decade. The spiropyran derivatives can exist in two forms: the colorless closed-ring spiropyran (SP) and the colored open-ring merocyanine (MC). The C-O bond in the benzopyran ring is cleaved after exposure to the UV irradiation, and the unconjugated SP is transformed into the conjugated MC, which demonstrates a broad absorption in the visible region. The open-ring MC state is polar, and returns to the closed-ring SP state by another irradiation (Figure 1) [2-4]. Owing to their excellent properties, the spiropyran derivatives have wide applications in optical information storage devices [5-7], photochromic coatings [8-10], and molecular switches [11-13].

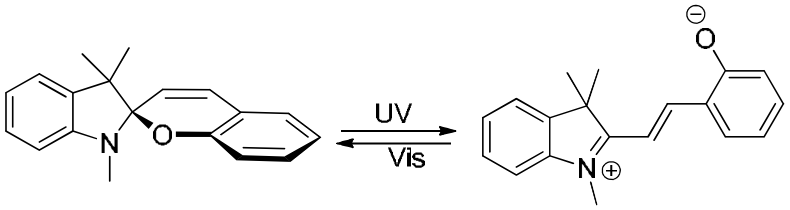

Figure 1. SP-MC interconversion.

The spiropyran derivatives display different behaviors: in addition to being photochromic, their reversible isomerization can take place in the presence of different external stimuli such as solvents (solvatochromism) [14-15], acid/base (acidochromism) [16-18], heat (thermochromism) [19-20], and water (hydrochromism) [21]. Besides, the spiropyran derivatives can complex with some ions in order to form relatively stable blue-shift metal complexes (ionchromism) [22-24]. So far, there have been numerous reports on switching between the spiropyran compounds; most of these reports are based on their solutions, and few reports are based on their solid states. We believe that the solid-state study of spiropyran photochromism is important, and is a challenging topic among chemical researchers. Thus we became interested in carrying out some research works in this field. Herein, we present the synthesis of the spiropyran derivative, its solvatochromism and photochromism in the solid state, in the mixture with polystyrene, and in covalent bonding with polystyrene. For this purpose, 1',3',3'-trimethyl-8-nitrospiro[chromene-2,2'-indoline] and the spiropyran-functionalized polystyrene were prepared (Figure 2).

Experimental

All the chemicals except polystyrene (commercial) were supplied from the Merck, and used as received.

Preparation of 1',3',3'-trimethyl-8-nitrospiro[chromene-2,2'-indoline] **(1)**

3-nitrosalicylaldehyde was prepared via the classical nitration of salicylaldehyde with nitric acid according to the literature [25-26]. 1,3,3-trimethyl-2-methyleneindoline (1.8 mL, 10 mmol) was then added dropwise to the solution of 3-nitrosalicylaldehyde (1.67 g, 10 mmol) in 15 mL of acetonitrile. The reaction mixture was refluxed for 3 h. TLC (2:5 ethyl acetate and n-hexane) monitored the reaction progress. After the reaction was complete, the solvent was evaporated. Ethanol (5 mL) was then added, and stirring was continued at room temperature for 2 more h. The precipitate formed was filtered off and then dried in the air. 2.2 g (68%) of the pure product was obtained. mp, 117-119 °C; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm): 1.26 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 2.80 (s, 3H, CH_3), 5.91 (d, J = 9 Hz, 1H), 6.59 (s, J = 9 Hz, 1H), 6.91 (t, J = 7.5 Hz, 2H), 6.97 (d, J = 6 Hz, 1H), 7.12 (d, J = 6 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.31 (d, J = 9 Hz, 1H), 7.71 (d, J = 6 Hz, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 20.09, 26.04, 28.88, 52.16, 106.63, 107.10, 119.11, 119.81, 121.28, 121.45, 121.63, 125.21, 127.71, 128.50, 131.13, 136.10, 137.16, 147.55, 148.27; FT-IR (KBr), ν (cm^{-1}): 3060, 2962, 2925, 2865, 1654, 1606, 1527, 1461, 1459, 1363, 1303, 1265, 1182, 1105, 1074, 1024, 921, 809, 742.; m/z: 332 $[M]^+$. Anal. Calcd. for $C_{19}H_{18}N_2O_3$: C, 70.80; H, 5.59; N, 8.70; Found: C, 70.91; H, 5.46; N, 8.64.

Preparation of functionalized polystyrene **(2)**

3-nitro-5-chloromethylsalicylaldehyde was prepared according to the literature [27-31]. Polystyrene (2 g) and 3-nitro-5-chloromethylsalicylaldehyde (0.38 g, 0.1 eq.) were dissolved in nitrobenzene (25 mL). $AlCl_3$ (0.01 g) was dissolved in nitrobenzene (5 mL) and added dropwise to the reaction mixture under an inert atmosphere (Ar), and the mixture was stirred for 3 days at room temperature. The reaction progress was monitored by TLC (1:3 ethyl acetate and n-hexane). After completion of the reaction, the reaction mixture was poured into methanol, filtered, and washed with 40 mL of 50% (v/v) methanol/HCl (aq), a dilute solution of Na_2CO_3, distilled water and methanol, respectively, and dried overnight in a vacuum oven at 50 °C. An insoluble pale-yellow polymer was obtained. FT-IR (KBr), ν (cm^{-1}): 3062, 3023, 2917, 2850, 1654, 1594, 1519, 1490, 1444, 1340, 1074, 1025, 946, 906, 754, 700, 1543. Anal. found: C, 68.48; H, 4.67; N, 4.8.

Preparation of spiropyran-functionalized polystyrene **(3)**

3-nitrosalicyladehyde-functionalized polystyrene **(2)** (1 g) was stirred in toluene (50 mL) for 30 min. 2,3,3-trimethyl-3*H*-indole (0.5 mL) was added dropwise to the reaction mixture under an inert atmosphere (Ar). The reaction mixture was refluxed overnight, and precipitated in petroleum ether. The precipitate formed was washed with methanol, and then dried in the dark at 50 °C under vacuum for 24 h. An insoluble pale pink polymer was obtained. FT-IR (KBr), ν (cm^{-1}): 3033, 3027, 2925, 1852, 1650, 1602, 1533, 1488, 1450, 1367, 1024, 914, 748, 698, 541.

Preparation of a thin film of polystyrene mixed with spiropyran

A thin film of polystyrene and spiropyran was prepared from a solution of polystyrene (0.5 g) and 1',3',3'-trimethyl-8-nitrospiro[chromene-2,2'-indoline] (0.02 g) in DMF (10 mL).

Results and discussion

In this work, 1',3',3'-trimethyl-8-nitrospiro[chromene-2,2'-indoline] was prepared from the reaction of 3-nitrosalicyladehyde with 1,3,3-trimethyl-2-methyleneindoline (Figure 2).

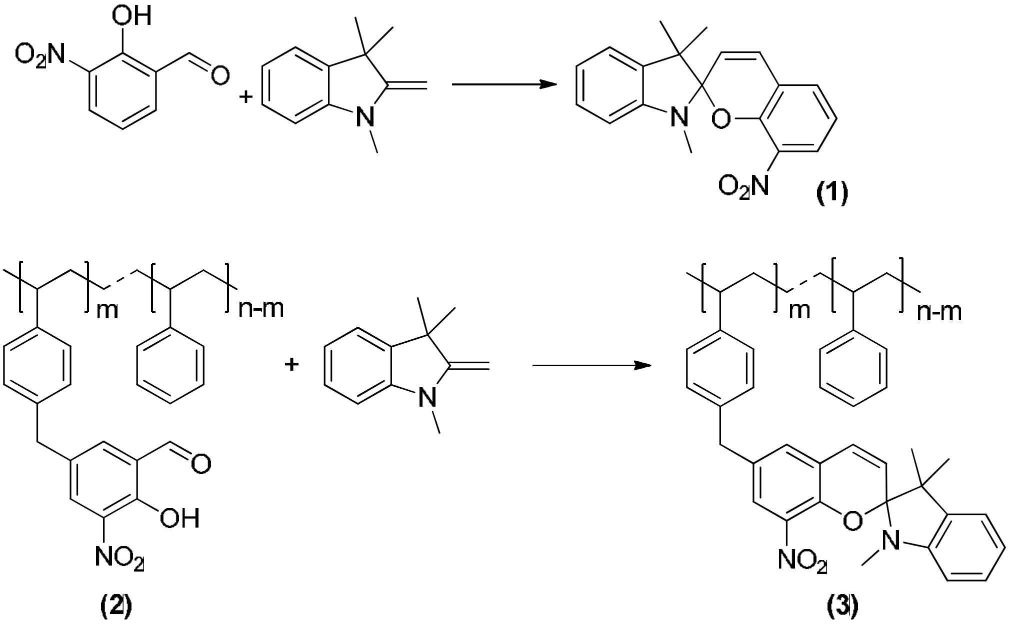

Figure 2. Synthesis of 1',3',3'-trimethyl-8-nitrospiro[chromene-2,2'-indoline] and 1',3',3'-trimethyl-8-nitrospiro[chromene-2,2'-indoline]-functionalyzed polystyrene.

The FT-IR spectrum of the product showed an absorption band at 1654 cm^{-1}, related to the stretching resonance of the C=C bond at the pyran ring, and two absorption bands at 1527 cm^{-1} and 1363 cm^{-1}, related to the $-NO_2$ group (asymmetric and symmetric stretching modes, respectively). The proton resonance of the aliphatic protons (9H) was observed at 1.26 ppm and 1.42 ppm for two

-CH_3 groups, and at 2.80 ppm for the N-CH_3 group. The proton resonance of the other 9 protons (aromatic and pyran ring) was observed in the range of 5.71-7.71 ppm in the ^{1}H-NMR of this spiropyran derivative. The appearance of 19 peaks in the ^{13}C-NMR spectrum of this compound confirms the structure of the synthesized spiropyran. Polystyrene was functionalized with 3-nitro-5-chloromethylsalicylaldehyde in the presence of $AlCl_3$. The functionalized polymer obtained was insoluble in most solvents (polar and non-polar). According to the elemental analysis, 7.24% of the repeating units of polystyrene was functionalized with the salicylaldehyde functional group. In the FT-IR spectrum of the functionalized polystyrene **(2)** (Figure 3), the absorption band at 1654 cm^{-1} is related to the stretching resonance of the C=O bond of the aldehyde group. The absorption bands at 1519 cm^{-1} and 1340 cm^{-1} are related to the -NO_2 group (asymmetric and symmetric stretching modes, respectively). Finally, the insoluble functionalized polystyrene was suspended in toluene and reacted with 1,3,3-trimethyl-2-methyleneindoline to produce the final product. In the FT-IR spectrum of the spiropyran-functionalized polystyrene **(3)** (Figure 3), the disappearance of the absorption band at 1654 cm^{-1} (related to the stretching resonance of the C=O bond) is an important evidence for the success of the reaction.

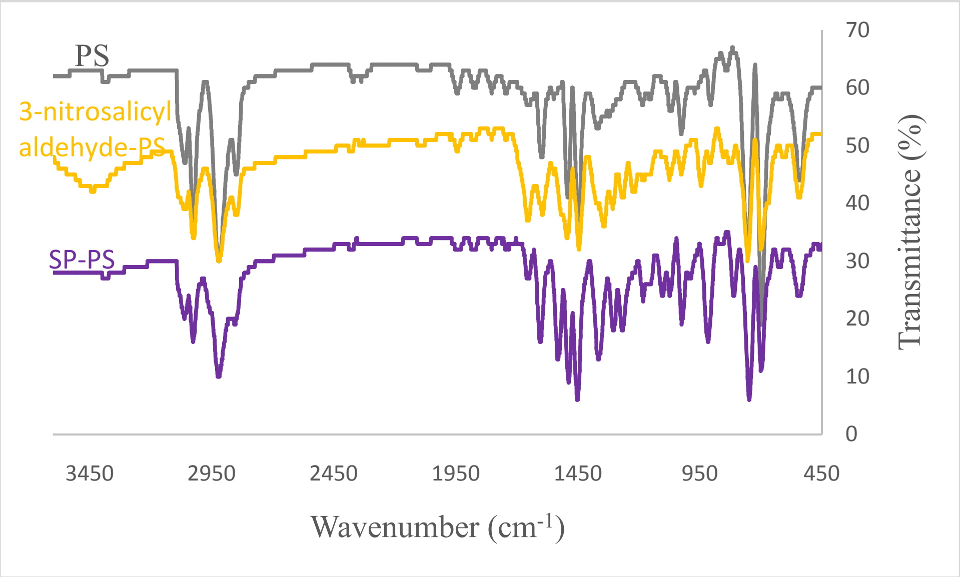

Figure 3. Comparison of the FT-IR spectra of polystyrene, 3-nitrosalicyladehyde-functionalized polystyrene and spiropyran-functionalized polystyrene.

Photochromism of spiropyran

In the recent years, the study of photochromic compounds has been an attractive field of research works for the chemists. Among the photochromic compounds, the spiropyran derivatives have attracted the attention of more researchers. As stated earlier, the spiropyran compounds can exist in the forms of closed-ring spiropyran (SP) and opened-ring merocyanine (MC), and various external stimuli such as UV irradiation, metal ions, and bases and acids cause these two forms to be converted into each other. We were interested in studying the effects of various solvents and UV irradiation on such transformations. For this purpose, the solutions of 1',3',3'-trimethyl-8-nitrospiro[chromene-2,2'-indoline] (1mM) in various solvents including acetonitrile, DMF, methanol, and ethanol were prepared and kept in the dark for 2 h at 25 °C (Figure 4).

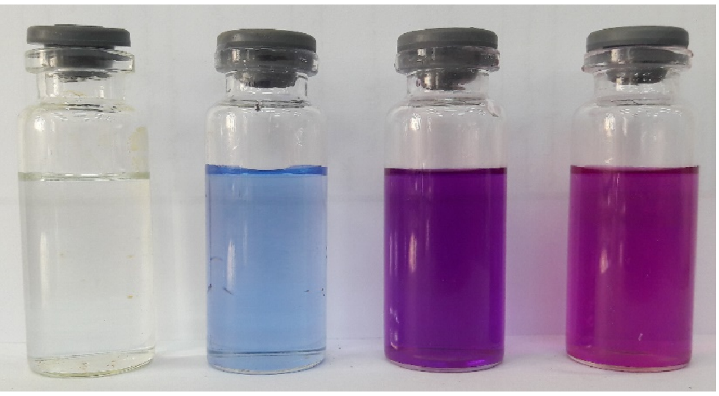

Figure 4. Spiropyran solutions in acetonitrile, DMF, methanol, and ethanol (left to right vials).

The solution of spiropyran in acetonitrile was completely colorless, while its solution was pale blue in DMF and dark purple in ethanol and methanol. It can be concluded that the polar solvents stabilize the opened-ring MC form, and the protic polar solvents such as methanol and ethanol have a stronger effect on this stability by forming a hydrogen bond with the phenolic moiety of MC. The dilute solutions of spiropyran (0.1 mM) were prepared in the mentioned solvents, and their UV-visible spectra were studied (Figure 5). The UV-visible spectrum of spiropyran showed the highest absorption in the visible region for methanol and ethanol. The visible spectra of the spiropyran solutions showed that methanol and ethanol were able to stabilize the MC form better than DMF and acetonitrile, and that this photochromic compound had a higher absorption intensity in the visible region.

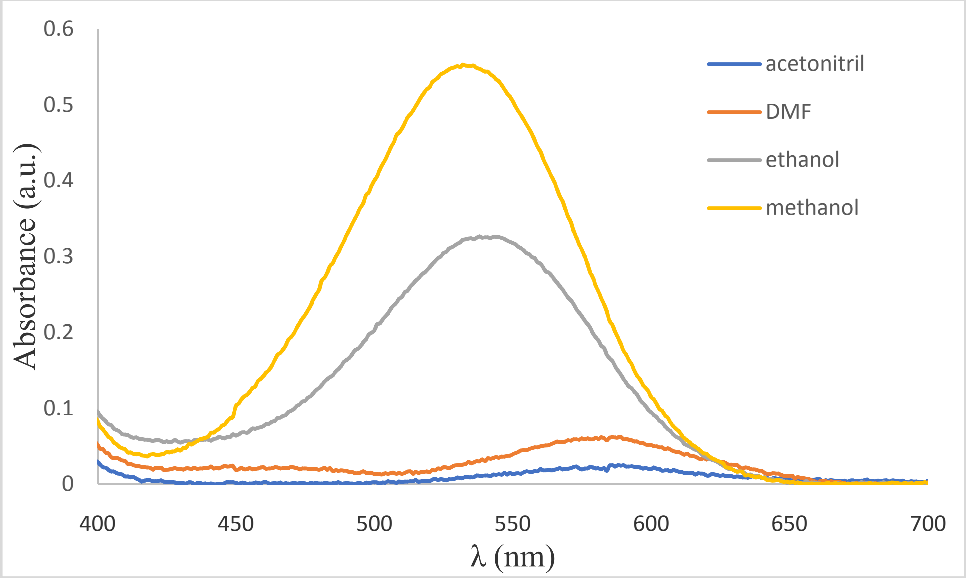

Figure 5. UV-visible spectrum of dilute solutions (0.1 mM) of 1',3',3'-trimethyl-8-nitrospiro[chromene-2,2'-indoline].

We were also interested in studying the photochromic behavior of this spiropyran derivative in the crystal state. For this purpose, the synthesized spiropyran was crystallized in ethanol and exposed to a UV irradiation (360-400 nm) for 10 min. The color of the crystals became dark after UV irradiation, and these colored crystals returned to their previous state after being in the dark for 24 h (Figure 6).

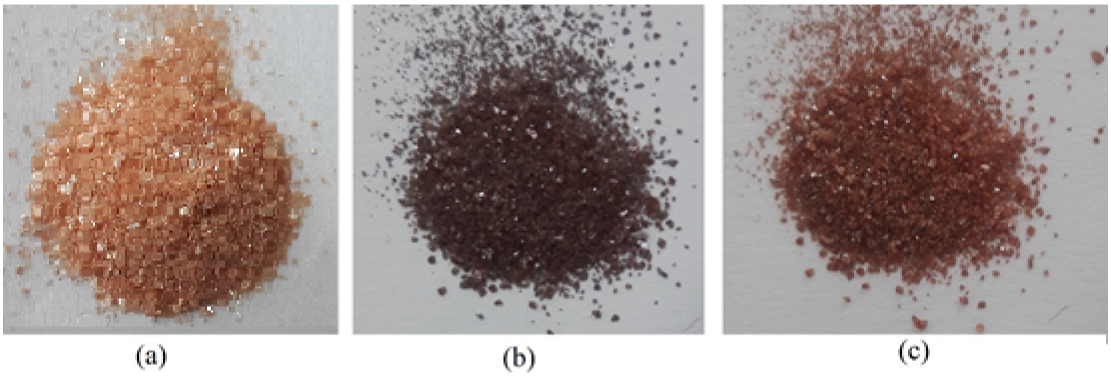

Figure 6. Crystals of spiropyran before UV irradiation (a), after UV irradiation (b), and 24 h after UV irradiation (c).

The UV-visible spectrum of the crystals of spiropyran showed an increase in absorption after UV irradiation in the visible region due to the conversion of the SP form to the MC form (Figure 7).

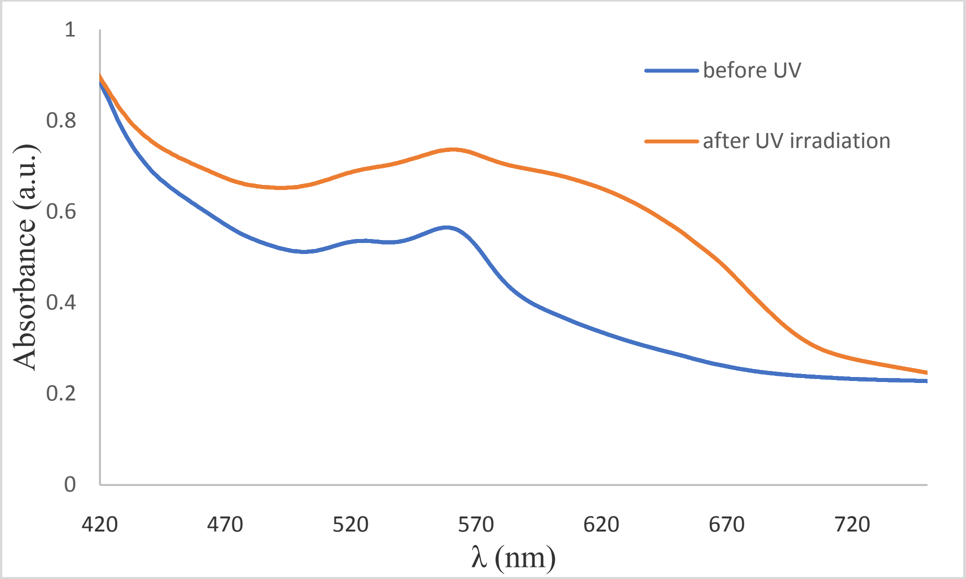

Figure 7. UV-visible spectrum of crystals of 1',3',3'-trimethyl-8-nitrospiro[chromene-2,2'-indoline] before and after UV irradiation.

It was interesting for us to study the photochromic properties of this spiropyran derivative in covalent binding to polystyrene. For this purpose, polystyrene was functionalized with the spiropyran derivative and exposed to a UV irradiation (360-400 nm) for 10 min (Figure 8).

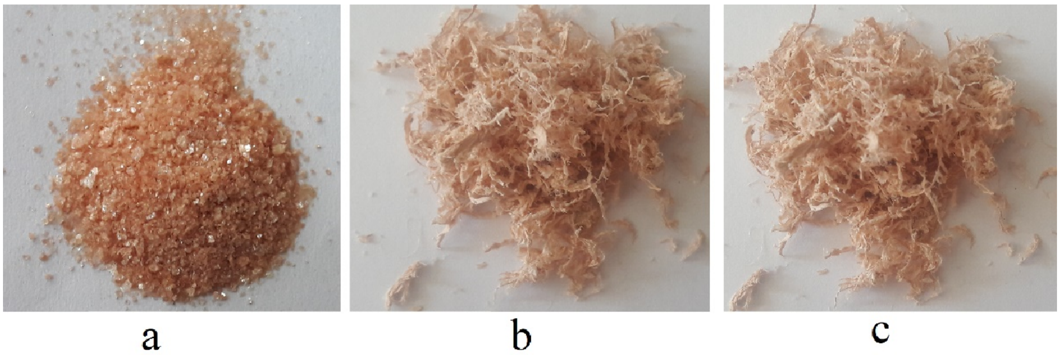

Figure 8. 1',3',3'-trimethyl-8-nitrospiro[chromene-2,2'-indoline] (a). Spiropyran-functionalized polystyrene before UV irradiation (b) and after UV irradiation (c).

Since 1',3',3'-trimethyl-8-nitrospiro[chromene-2,2'-indoline] in the solid state also showed photochromic properties, it was unexpected that the color of the spiropyran-functionalized polystyrene did not change upon UV irradiation. Also its absorption did not increase in the visible region of the electromagnetic spectra of the spiropyran-functionalized polystyrene after UV irradiation.

At last, we decided to investigate the effect of the UV irradiation on a mixture of polystyrene and 1',3',3'-trimethyl-8-nitrospiro[chromene-2,2'-indoline]. For this purpose, a thin film of the polystyrene and spiropyran mixture was prepared and exposed to a UV irradiation (360-400 nm) for 10 min (Figure 9).

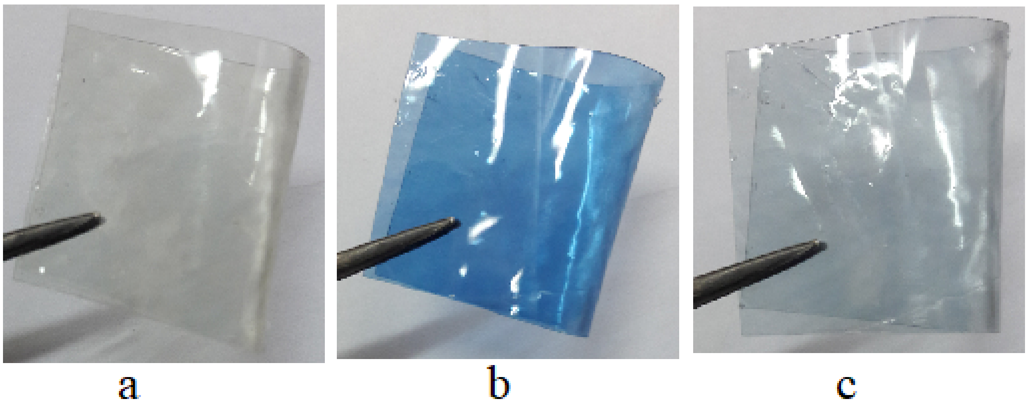

Figure 9. Thin film of polystyrene and spiropyran mixture before UV irradiation (a), after UV irradiation (b), and after 2 h in the dark (c).

After exposure to the UV irradiation, the color of the thin film turned blue, and it returned to its original colorless state after 2 h of darkness. It can be said that in the thin film of the polystyrene and spiropyran mixture, the spiropyran is readily converted to the MC form but in the spiropyran-functionalized polystyrene, the spiropyran is not easily converted to the open-ring MC, probably due to the high polarization of the MC form, which is not accommodated in the non-polar medium of polystyrene. However, the non-bonded polystyrene-spiropyran mixture eventually shows photochromism due to the agglomeration of chromophore molecules in the polymer contexture, which could provide a suitable medium for the MC formation.

Conclusion

The photochromic behavior of 1',3',3'-trimethyl-8-nitrospiro[chromene-2,2'-indoline] was investigated in different solvents in the crystal state, in binding to polystyrene by covalent bonding, and in the mixture with polystyrene. In the polar protic solutions, it shows the more stable merocyanine (MC) form, and has a stronger absorption in the visible region. It also shows a good photochromic behavior in the crystal form and in the mixture with the polymer. However, it does not exhibit a photochromic behavior in covalent binding to polystyrene, probably due to the high polarization of the MC form, which is not accommodated in the non-polar medium of the polystyrene, and thus is not formed. However, the non-bonded polystyrene-spiropyran mixture eventually shows photochromism due to the agglomeration of the chromophore molecules in the polymer contexture, which could form the MC form in an insular polar medium.We believe that the information obtained from the photochromism of the described spiropyran derivative will pave the way for further experiments to apply such light-sensitive compounds in various sciences.

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