Preparation and Photochromic Performance of Homogeneous Phase Nitrocellulose Membrane Grafting Spirooxazine Moieties

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Received: 23 May 2020; Accepted: 15 June 2020; Published: 17 June 2020

Abstract: The synthesis of 1,3,3-trimethyl-9’-acryloxyspiro[indoline-2,3′(3H)naphtho[2,1-b][1,4]-oxazine] (AISO) was carried out by catalytic esterification of 1,3,3-trimethyl-9’-hydroxyspiro-indoline-2,3′(3H)naphtho[2,1-b][1,4]-oxazine (SO–OH) and acrylic acid in the presence of 1,3-dicyclohexylcarbodiimide (DCC) and N-dimethylaminopyridine (DMAP). Then, the synthesis of the target copolymer (NC-g-AISO) was carried out by benzoyl peroxide (BPO)-induced graft copolymerization of the AISO monomer onto nitrocellulose (NC) in a homogeneous methyl isobutyl ketone medium. The structure of NC-g-AISO was characterized by Fourier transform infrared (IR) spectroscopy, 13C Nuclear Magnetic Resonance (NMR) spectra and thermogravimetric (TG) analysis. The photochromic properties of NC-g-AISO were investigated by examining UV–Vis spectra in ethyl acetate solution and solid membrane. Compared with the AISO monomer in ethyl acetate solution, the thermal color decay stability of the colored form of NC-g-AISO in ethyl acetate solution and in solid membrane improved significantly. The thermal color decay reaction rate constants in ethyl acetate solution and membrane at 25 °C were 1.77 \times 10^{-2} and 1.36 \times 10^{-3} s^{-1}, respectively, fitted using the first-order reaction equation. After ten photochromic cycles, the relative absorption intensity of the colored form of NC-g-AISO decreased by 0.85%, indicating that the NC-g-AISO membrane has good reversible photochromic behavior.

Keywords: nitrocellulose; spirooxazine; graft copolymer; homogeneous phase; membrane; photochromism; thermal color decay; fatigue resistance

1. Introduction

The discovery of the photochromic reactions of spiropyrans by Fischer and Hirshberg in 1952 and Hirshberg’s idea of using the phenomenon for a “photochemical erasable memory” initiated active research on photochromism [1–3]. Typical examples of photochromic reactions of spiropyrans and the closely related spirooxazines are the reversible photochemical cleavage of the spiro C–O bond and giving of an open merocyanine (MC) form. Owing to their excellent properties, these compounds have the prospect of wide applications in optical information storage [1–6], photochromic coatings [7,8] and molecular switches [9,10]. Most of the MC forms of spiropyrans and spirooxazine are thermally unstable at room temperature, hindering further commercial applications [11,12]. As a rule, incorporating them in the polymer matrices not only makes it easier
for the processing device but also improves the thermal stability of their MC form by retarding the chemical reaction because of steric hindrance [13–15].

Although the photochromic polymer materials can be obtained by blending dye into a polymer matrix, this traditional method causes a defect, in that phase separation occurs under long-term use. Photochromic materials with covalently linked photochromic moieties overcome the limitations inherent in the traditional mixed type photochromic polymer materials [16]. This type of material can be obtained by two different methods: the copolymerization of photochromic compounds carrying polymerizable groups with other vinyl monomers [16–20], and the covalent attachment of photochromic dyes to polymer chains or natural macromolecules [21–25].

There are huge reserves of the natural macromolecules represented by cellulose, starch and chitin; they are low cost and also represent great development value. Most natural macromolecules have some disadvantages, such as poor solubility, and the simple functional groups are also difficult to modify, although primary derivatives of natural macromolecules with good solubility make modification easier. Nitrocellulose (NC) is the nitration product of cellulose that can be dissoluble in some organic solvents, such as ethyl acetate and acetone. In spite of its excellent membrane-forming performance and its applications in surface coating industries [26–30], little research appeared in the literature dealing with the graft copolymerization of NC by vinyl monomer until grafting of methyl methacrylate onto NC had been reported [31–35].

The nitrated cellulose grafted by the spirooxazine group and its method for preparation have been disclosed in the form of a Chinese invention patent [36]. In this paper, we report on the preparation, characterization and photochromic properties of nitrocellulose derivatives grafting spirooxazine moieties (NC-g-AISO), especially focusing on the thermal color decay stability and the photochromic reversibility of the NC-g-AISO membrane.

2. Materials and Methods

2.1. Materials and Reagents

Commercially available NC (1/2 sec grade, 11.80% nitrogen, the degree of substitution by nitro groups was calculated by the chemical formula \( \text{C}_6\text{H}_{10-x}\text{O}_5(\text{NO}_2)_x \), in which \( x \) has the value 2.20), was supplied by the Hui’an Chemical Factory in Xi’an, China. It was purified before use by being dissolved and precipitated twice; then, it was extracted in a Soxhlet apparatus (Xi’an teaching instrument factory, Xi’an, China) by refluxing in petroleum ether (60–90 °C) for 24 h and drying at 55 °C under vacuum (Xi’an teaching instrument factory, Xi’an, China) to constant weight. N-dimethylaminopyridine (DMAP, ≥99%) and 1,3-dicyclohexylcarbodiimide (DCC, ≥99%) was supplied by Sinopharm Chemical Reagent Co., Ltd. All other chemicals were analytical reagents and were used as received without purification.

2.2. Synthesis of Monomer 1,3,3-trimethyl-9’-acryloxyspiro[indoline-2,3’(3H)naphtho[2,1-b][1,4]-oxazine] (AISO)

Intermediate 1,3,3-trimethyl-9’-hydroxyspiro-[indoline-2,3’(3H)naphtho[2,1-b][1,4]-oxazine] (SO–OH) was synthesized from 1,3,3-trimethyl-2-methylene-indoline and 1-nitroso-2,7-hydroxy-naphthalene, according to the method previously described in references [37,38]. The yield was an earthy-grey solid 4.40 g (38%), m.p. 223–225 °C. IR (KBr) was 3324, 1628, 1360, 1242, 835, 746. \(^1\)HNMR (CDCl\(_3\), 400 MHz) \( \delta: \) 1.34 (s,6H,C–(CH\(_3\))\(_2\)), 2.75 (s,3H,NCH\(_3\)), 5.58 (s,1H,ArO–H), 6.50–7.90 (m,10H,ArH,CH=N).

The synthesis of monomer AISO was carried out according to the synthetic route outlined in Figure 1.

Intermediate SO–OH (3.44 g), acrylic acid (0.79 g), DCC (2.07 g), DMAP (0.10 g) and anhydrous diethyl ether (50.0 mL) were added to a 100 mL round bottom flask (Xi’an teaching instrument factory, Xi’an, China). Then, the mixture was stirred in darkness at room temperature. The reaction process was monitored by thin layer chromatography. After completion of the reaction, the precipitate was moved by filtration. The filtrate was washed twice with 100 mL 0.5 M Na\(_2\)CO\(_3\), 100 mL
brine, 100 mL 0.5 M HCl and 100 mL brine and dried with anhydrous MgSO₄ for 8 h. The final solution was evaporated under reduced pressure to produce a crude compound. The crude compound was then column chromatographed (silica gel) with the mixture of petroleum ether and acetone at 20:1 (v/v) as eluent. The yield was light yellow crystal 2.27 g (57%), m.p. 147–149°C.

IR (KBr) ν (cm⁻¹): 1743, 1622, 1508, 1362, 1248, 1154, 1083, 1030, 981, 833, 804, 742.

$^{1}$$H$NMR (CDCl₃, 400MHz) δ: 1.34, 2.74, 6.03, 6.37, 6.56, 6.64, 6.89, 6.98, 7.07, 7.16, 7.21, 7.64, 7.70, 7.76, 8.28.

$^{13}$$C$NMR (acetone-d₆, 400MHz) δ: 164.73, 151.76, 150.34, 148.16, 145.27, 136.29, 133.23, 132.83, 130.59, 129.97, 128.49, 128.38, 127.82, 122.74, 121.90, 120.28, 119.92, 116.99, 113.16, 107.64, 99.38, 52.16, 29.63, 25.29, 20.52.

The NMR spectra of AISO (Figures S1 and S2) and its assignment (Tables S1 and S2) can be seen in the Supporting Materials.

![Reaction Scheme](image)

**Figure 1.** Synthetic route to obtain monomer AISO.

### 2.3. Preparation and Purification of NC-g-AISO

A 100 mL three necked round-bottomed flask filled with a stirrer in a temperature-controlled water bath (Xi’an teaching instrument factory, Xi’an, China) was used in the dark for the copolymerization. A known weight of NC was dissolved in methyl isobutyl ketone. The desired quantity of AISO monomers was added. After purging with purified nitrogen for 30 min, the mixture was stirred and heated slowly to 70 °C; the required amount of benzoyl peroxide (BPO) was added into the flask (Xi’an teaching instrument factory, Xi’an, China). When the appropriate reaction time had elapsed, the contents of the flask were cooled using the water bath to arrest the reaction and the contents of the flask were precipitated by pouring them into an excess of petroleum ether (60–90 °C). The gross polymer was filtered and dried for 24 h under vacuum at 60 °C.

Then, the gross polymer was extracted with benzene in a Soxhlet extractor (Xi’an teaching instrument factory, Xi’an, China) for 72 h to remove the homopolymer. Some benzene obtained from the Soxhlet extractor was added dropwise onto test paper. After exposure to UV light, if the paper color remained the same, it indicated that the homopolymer was completely removed. Subsequently, the purified NC-g-AISO was dried at 60 °C under vacuum to constant weight.

The percentage of grafting ($G\%$) was determined by the following equation (Equation (1)):

$$G\% = \frac{w_1 - w_0}{w_0} \times 100\%$$

where $w_0$ and $w_1$ denote the weights of NC and NC-g-AISO, respectively.

### 2.4. Preparation of Membrane

At room temperature, 0.5 g NC-g-AISO was dissolved in 5 mL acetone. After stirring and dissolving, it was poured into a circular glass plate placed horizontally. After the solvent volatized in darkness for 48 h at about 30 °C, the membrane was peeled, cut and fixed on a quartz sheet for investigation.

### 2.5. Characterization and Properties Testing

The FT-IR spectra of NC and NC-g-AISO were recorded by NEXUS-670 Fourier transform infrared spectrophotometer (Thermo Nicolet Co., Madison, WI, USA), and samples were scanned from 4000 to 400 cm⁻¹ using KBr pallets (Sinopharm Chemical Reagent Co., China).
The NMR spectra of NC and NC-g-AISO were recorded on a Varian Mercury plus-300 MHz spectrometer, using acetone-\textit{d}{6} as the solvent and tetramethylsilane as the internal standard.

TG analysis was performed by SDT Q600 synchronous thermal analyzer (TA Instruments, New Castle, DE, USA) under a nitrogen flow rate of 100 mL/min; NC and NC-g-AISO samples were heated from 30 to 800 °C with a heating rate of 10 °C/min.

The UV–Vis absorption spectra of target polymer were determined by an Agilent-8453 spectrometer (Agilent Technologies, Stevens Creek, CA, USA). The samples were scanned from 200 to 800 nm.

A ZF7c UV analysis apparatus (16 W, table lamp type, made in Kanghua Biochemical Co., Ltd., of Shanghai, China) was used as the UV light source; the wavelength selected was 254 nm. The optical filter area was 50 × 150 mm\textsuperscript{2}. The transparent side of the cuvette with the sample to be tested was facing the center of the optical filter, and the distance between them was about 3 mm. This UV light source and the test scenarios (Figure S3) can be seen in Supporting Materials.

2.6. Kinetics of Photochromism

The thermal color decay of samples was studied in ethyl acetate solution at 25 °C; the concentration was 0.2 mg/mL (0.2 mg target copolymer in 1 mL solvent). After the samples were irradiated by UV light for 10 min in order to generate the MC form, they were put in the measurement chamber for thermal color decay and the absorption spectra were determined at different times until the absorbance became constant.

The reaction rate constant (\(k\)) of the thermal color decay was calculated by the first-order reaction in Equation (2):

\[
\ln(A_t - A_{\infty}) = kt + \ln(A_0 - A_{\infty})
\]  

where \(A_0\), \(A_t\) and \(A_{\infty}\) are the absorbance at \(\lambda_{\text{max}}\) at time zero, any time \(t\) and time \(\infty\), respectively.

The half-life time (\(t_{1/2}\)) was calculated by Equation (3):

\[
t_{1/2} = 0.693/k
\]

The absorption spectra of NC-g-AISO membrane (the thickness is 30 μm) were determined and the thermal color decay reaction rate constant (\(k'\)) and half-life time (\(t'_{1/2}\)) were calculated using the same method.

2.7. Fatigue Resistance Testing

The fatigue resistance of the NC-g-AISO membrane was tested at 25 °C. The NC-g-AISO membrane was irradiated by UV light for 10 s and kept in the dark for 2 h, in repeat cycles. For the nth photochromic cycle (before UV irradiation, immediately after 10 min of UV irradiation and 2 h after UV irradiation), the absorbance at \(\lambda_{\text{max}}\) before UV irradiation (\(A_{\text{closed,n}}\)), immediately after 10 s of UV irradiation (\(A_{\text{open,n}}\)) and 2 h after UV irradiation (\(A_{\text{closed,n+1}}\)) were determined and relative absorbance change (η) of the nth photochromic cycle was calculated by Equation (4):

\[
\eta_n = \left[1 - \frac{(A_{\text{open,n}} - A_{\text{closed,n}})}{(A_{\text{open,1}} - A_{\text{closed,1}})}\right] \times 100\%\]

3. Results

3.1. Synthesis

SO–OH is a common hydroxy substituted spirooxazine compound which can be synthesized by condensation of 1,3,3-trimethyl-2-methylene-indoline and 1-nitroso-2,7-hydroxy-naphthalene [37,38]. AISO (acrylate of SO–OH) and methacrylate of SO–OH are common monomers with in a vinyl group. By copolymerizing with other monomers, lots of interesting copolymers have been prepared and investigated [39–41]. In this paper, we synthesized AISO monomer by catalytic esterification of SO–OH and acrylic acid in the presence of DCC and DMAP, instead of the method using acryloyl chloride [21], and achieved many good results, such as avoiding the use of acryloyl
chloride which irritates the nose and eyes, and improving the synthesis efficiency (yield improved from 32% to 57%).

In order to improve the value and function of cellulose, attempts to graft polymerize vinyl monomer onto cellulose or its primary derivates have aroused interest [42–44]; however, grafting copolymerization onto NC is rare. This may be because NC is flammable and explosive. The groups of Sudhakar [31–34] and Tang [35] completed a lot of research on NC graft copolymerization with methyl methacrylate. Using methyl isobutyl ketone as the medium and BPO as the initiator, the synthesis of NC-g-AISO was carried out by graft copolymerization of AISO onto NC in a homogeneous medium. This is shown in Figure 2 according to the literature [31].

Several NC-g-AISO samples with different G% were prepared by changing reaction conditions. A representative reaction condition was 0.50 g NC, 50.0 mL methyl isobutyl ketone, 1.20 g AISO monomer and 0.10 g BPO, with a reaction time of 3.0 h. The G% of the resulting NC-g-AISO sample was 82%, and its structure was analyzed by IR, 13CNMR, TG and UV–Vis spectra.

![Figure 2. Synthetic route to NC-g-AISO.](image)

3.2. Characterization

Figure 3 shows the IR spectra of NC. The absorption band at 3560 cm⁻¹ is assigned to the stretching vibration of OH; the blue shift is due to the formation of hydrogen bonds between the hydroxyl groups and nitro groups. The band at 1659 cm⁻¹ is assigned to the anti-symmetric stretching vibration of the nitro group and the band at 1280 cm⁻¹ is assigned to the symmetric stretching vibration of the nitro group [45], while the bands at 841, 750 and 689 cm⁻¹ correspond to vibrations of the nitrate groups of valence ν(NO₂), wagging γ(NO₂) and scissoring δ(NO₂), respectively [46]. The narrowed band for OH and stronger bands for nitro groups imply that the NC has a high degree of substitution of nitro groups. The absorption bands around 1207–1003 cm⁻¹ were assigned to the stretching vibration of C–O [47].
In the IR spectra of NC-g-AISO (Figure 4), the characteristic bands of NC all appear, but with slightly different wavenumbers and different intensities, such as the absorption band at 3485 cm$^{-1}$ for OH (compared with the wavenumber 3560 cm$^{-1}$ in NC, the red shift is related to the annihilation of hydrogen bond by graft copolymerization); the absorption bands at 1630 and 1288 cm$^{-1}$ for anti-symmetric and symmetric stretching vibration of the nitro group, respectively; the bands at 835, 743, 686 cm$^{-1}$ for vibrations of the nitrate groups valence $\nu$(NO$_2$), wagging $\gamma_w$(NO$_2$) and scissoring $\delta$(NO$_2$), respectively; the absorption band around 1205–984 cm$^{-1}$ assigned to the stretching vibration of C–O.

At the same time, some absorption peaks not belonging to NC also appear, such as the characteristic absorption band at 1742 cm$^{-1}$ for the stretching vibration of C=O in an ester structure and the absorption band at 1508 cm$^{-1}$ for the skeleton vibration of C=C in a benzene ring. The shoulder band (at about 870 cm$^{-1}$) for the bending vibration of C–H in 1,2,4-trisubstituted benzene and the shoulder band (at about 805 cm$^{-1}$) for the bending vibration of C–H in 1,2,3,4-tetrasubstituted benzene were submerged in the strong band for valence $\nu$(NO$_2$) which appears at 835 cm$^{-1}$. The absorption band for the bending vibration of C–H in 1,2-disubstituted benzene overlaps with wagging $\gamma_w$(NO$_2$) and appears at 743 cm$^{-1}$. The absorption band (at about 1651 cm$^{-1}$) for the stretching vibration of C=N in the oxazine ring overlaps with the anti-symmetric stretching vibration of the nitro group and appears at 1630 cm$^{-1}$. As the homopolymer of AISO was initially removed by extraction with benzene, the presence of the above absorption bands provides evidence of grafting.
There are six carbon atoms in the repeat unit of cellulose and three hydroxyl groups linked with C-2, C-3 and C-6. In NC, which has high degree of substitution of nitro groups, most of the hydroxyls are nitrated. The carbon atom linked with the hydroxyl group that is nitrated is labeled as C-2′, C-3′ and C-6′ in this paper. The $^{13}$C NMR spectra of NC are shown in Figure 5. This includes seven peaks. The peaks with chemical shifts at 98.67–103.9, 83.42, 81.76, 79.22, 77.56, 76.40 and 70.80 ppm originate from C-1, C-2′, C-3′, C-2, C-4, C-5 and C-6′ in turn [48–52]. The absence of a peak originating from C-3 in the groups of C-2, C-4, C-5 may be due to the complete nitrification on the hydroxyl group which is linked with C-3, or overlaps with that of C-2.

![Figure 5. $^{13}$C NMR spectra of NC.](image)

The $^{13}$CNMR spectra of NC-g-AISO are shown in Figure 6. It shows all the peaks which belong to the carbon atoms of NC with a slight chemical shift. At the same time, the spectra of NC-g-AISO show carbon of the carboxylate ester group at $\delta$ 174.22 ppm, the carbons of benzene rings and C=N in the oxazine ring at $\delta$ 157.25–107.13 ppm, the quaternary carbon of spirooxazine moieties at $\delta$ 51.93 ppm, the carbons of dimethyl linked with quaternary carbon at $\delta$ 24.82 and 20.07 ppm and the carbons of the polyolefin chain at $\delta$ 24.17 and 21.82 ppm. The carbon peak of N-CH$_3$ overlaps with solvent at $\delta$ 29.20 ppm, while the spiro carbon peak at $\delta$ 99.50 ppm submerged in that of C-1 of the NC backbone. Before polymerization, the chemical shift of carbon atoms of C=C double bond and benzene rings are basically in the same range; after polymerization, the C=C double bond vanished, and polyolefin chain formed. The carbons of polyolefin chain appear at $\delta$ 24.17 and 21.82 ppm. Before polymerization, the carbon of unsaturated carboxylate ester group in AISO monomer appear at $\delta$ 164.73 ppm; after polymerization, the carbon of the saturated carboxylate ester group moves to $\delta$ 174.22 ppm. Before polymerization, the aromatic carbon, which directly links with the unsaturated carboxylate ester group in AISO monomer, appears at $\delta$ 151.76 ppm; after polymerization, it appears at $\delta$ 158.19 ppm. From the above spectra data, it can be concluded that copolymer NC-g-AISO has an NC backbone with the grafted spirooxazine moieties.
The TG curves for the thermal degradation of NC and NC-g-AISO are shown in Figure 7. In the case of NC, three distinct weight-loss zones are observed from 30 to 800 °C. Before reaching 185 °C, the weight loss of NC is slow and is mainly due to the removal of residual methyl isobutyl ketone and petroleum ether (the NC sample was purified by these solvents before use), and the release of NO₂ gas from the denitration reaction. In the 185–189 °C range, especially 188–189 °C, the weight of NC drops sharply, and the remaining weight fraction is 2.23 wt %. After this, the weight loss of NC is very slow until reaching 600 °C, when weight lost is almost 100.00 wt %, and the NC sample is decomposed into gas and released completely.

Comparing the TG curves of NC with different nitrogen content [53–56], the majority of the thermal decomposition of NC occurred within the 100–200 °C range, where the overall process was completed in minutes or seconds. When comparing NC with different nitrogen contents, the weight drop occurs sharply at different temperature ranges; for one NC sample, this temperature range is very narrow, instead of exhibiting sustained slow weight loss. When NC decomposes under heat, the O–NO₂ bond breaks first and NO₂ is produced. Most NO₂ is retained in the NC sample.
framework, which can further catalyze the decomposition of NC. At last, when the heating temperature reaches a certain critical value, the molecular chain framework breaks suddenly and small molecular gases such as CO, CO\textsubscript{2}, NO, NO\textsubscript{2}, HCHO and HCOOH escape, resulting in a sharp decrease in mass.

In the case of NC-g-AISO, the first weight loss (less than 180 °C) was slightly smaller than that of NC. This phenomenon can be interpreted as the weakening of the network structure by graft copolymerization; thus, the small residual molecules trapped in the NC framework reduced. After 180 °C, the weight loss of the NC-g-AISO entered an acceleration period, but it was not like the vertical decline of NC, and the remaining weight fraction was 49.00 wt % at 227 °C. This rapid weight loss of NC-g-AISO can mainly be attributed to the NC main chain. It starts at 180 °C, which is lower than that of NC (starts at 185 °C) because the main chain entanglement state is loosened after the grafting copolymerization. After reaching 227 °C, the weight loss of the NC-g-AISO enters a relatively slow phase compared to the rapid weight loss from 180 to 227 °C. This weight loss stage can mainly be attributed to the side chain. Until reaching 372 °C, the weight loss almost stopped, and the remaining weight fraction was 9.88 wt %. This phenomenon is similar to that of the NC derivatives grafted by polyethylene glycol, although the latter is grafted by the esterification of the bridging compound (dibutyltin dilaurate) with the hydroxyl groups on polyethylene glycol and residual hydroxyl groups on NC [57]. NC with a high degree of nitration has enough oxygen content for all carbon elements in the NC macromolecule to be released in the form of gas, so the weight loss of NC in this study was complete. In NC-g-AISO, the grafted side chains had high carbon content, and the element composition of NC-g-AISO was not sufficient to release carbon completely in the form of gas, so the weight loss of NC-g-AISO was incomplete.

4. Discussion

The color of the AISO monomer in ethyl acetate solution with a concentration of 2 \times 10^\text{-4} mol/L changed from colorless to blue upon UV irradiation, but the color faded quickly when the UV light was turned off. It is difficult to measure the complete UV–Vis absorption spectra of the MC form of AISO at 25 °C since its thermal decay from the colored form to the colorless form is fairly rapid [58].

At 25 °C, the NC-g-AISO in ethyl acetate solution with a concentration of 0.2 mg/mL (0.2 mg target copolymer in 1 mL solvent) was irradiated by UV light (254 nm) for 2 min. It significantly becomes blue, indicating the translation of spirooxazine moieties from the closed form to the open form (Figure 8). The larger the concentration of the solution, the more intense the color. After UV light is removed, the color fades slowly at room temperature, indicating the translation of spirooxazine side groups from the open form to the closed form. The larger the concentration of the solution, the longer the time until the color fades.

Comparing the speed at which the color faded with the naked eye was enough to find that the thermal decay stability of spirooxazine groups was improved by being grafted onto the NC
macromolecular chain. Due to the large conformational change in the photochromic reaction, isomerization is depressed by incorporating spirooxazine groups into the polymer matrices with intertwined macromolecular chains. The reaction from the colored form to the colorless form is retarded, which improves the thermal color decay stability of spirooxazine groups grafted onto the NC macromolecular chain [13–15].

The change of absorption spectra of the colored form of NC-g-AISO in ethyl acetate solution during the thermal color decay was recorded and is shown in Figure 9A. It has a maximum at 605 nm and a shoulder around 570 nm. As time passes, the intensity of the absorption peak decreases.

![Figure 9. Absorption spectra during thermal color decay of the colored form of NC-g-AISO in ethyl acetate (A), in solid membrane (C) and the first-order thermal color decay kinetic curve in ethyl acetate (B), in solid membrane (D).](image)

During the thermal color decay process, the shape of the spectra remained unchanged and the spectra measured were at any time proportional to each other in the visible region. This allowed the absorption to be monitored at $\lambda_{\text{max}}$ as a function of time to obtain the thermal color decay rate constant ($k$) from a first-order reaction kinetic equation [59–63]. Figure 9B shows the first-order thermal color decay kinetic curves. The rate constant ($k$) for thermal color decay was $1.77 \times 10^{-2}$ s$^{-1}$. The half-life time $t_{1/2}$ is 39.15 s.

The newly synthesized NC-g-AISO has good membrane forming performance. When the NC-g-AISO membrane was irradiated by UV light, it exhibited good photochromic behavior. The absorption spectra resulting from UV irradiation of NC-g-AISO in solid membrane and in ethyl acetate are similar (Figure 9C). The visible absorption peaks at 598 nm and the first-order thermal color decay rate constant of NC-g-AISO membrane, $k'$, is $1.36 \times 10^{-3}$ s$^{-1}$ (Figure 9D). The half-life time $t'_{1/2}$ is 8.49 min. The thermal color decay of NC-g-AISO occurs more slowly in solid membrane than in solution. As a rule, photochromic reactions are retarded by the solid polymer matrix as compared with liquid. This effect is usually attributed to the confining of configuration translation in solid membrane with a limited free volume.
Another limiting factor regarding the industrial application of spiro ring photochromic compounds is the fatigue phenomenon after long-term use. Spirooxazine derivatives exhibit a better fatigue resistance than spiropyran derivatives [64–67]. One of the ways to investigate the fatigue resistance of spirooxazine derivatives is to monitor the change in relative absorption intensity at $\lambda_{\text{max}}$ in every photochromic cycle [68,69]. As shown in Figure 10, the photochromic cycles were conducted ten times, and a maximum decrease of 0.85% in relative absorption intensity of the colored form of NC-g-AISO membrane indicated that NC-g-AISO membrane has good reversible photochromic behavior.

![Figure 10](image)

**Figure 10.** Absorbance of NC-g-AISO membrane at 598 nm during photochromic cycles.

### 5. Conclusions

A photochromic polymer was prepared by graft copolymerization of a spirooxazine side group onto nitrocellulose macromolecules and its structure was characterized by IR, $^{13}$CNMR, TG and UV–Vis spectra. By grafting copolymerization, the thermal color decay stability of the colored form of spirooxazine groups grafted onto nitrocellulose was improved significantly. The thermal color decay in ethyl acetate solution and in the solid membrane fitted the first-order reaction equation, the rate constants of which at 25 °C were $1.77 \times 10^{-2}$ s$^{-1}$ and $1.36 \times 10^{-3}$ s$^{-1}$, respectively. The thermal color decay of NC-g-AISO occurs more slowly in the solid membrane than in solution, a finding attributed to the confining of configuration translation in the solid membrane with a limited free volume. After ten photochromic cycles, the NC-g-AISO membrane shows good reversible photochromic behavior. The improved thermal color decay stability and good reversible photochromic behavior of the target copolymer make it have more potential in the application fields of optical information storage and so on.

**Supplementary Materials:** The following are available online at www.mdpi.com/2079-6412/10/6/569/s1, Figure S1: $^{1}$HNMR spectrum of AISO (400 MHZ, CDCl$_3$), Table S1: Peak assignments in the $^{1}$HNMR spectrum of AISO, Figure S2: $^{13}$CNMR spectrum of AISO (400 MHZ, Acetone-d$_6$), Table S2: Peak assignments in the $^{13}$CNMR spectrum of AISO, Figure S3: The UV light source and the test scenarios.

**Author Contributions:** Conceptualization, B.-H.Y.; methodology, B.-B.S.; validation, B.-H.Y. and B.-B.S.; formal analysis, B.-B.S. and Y.-Q.H.; investigation, B.-B.S., B.-H.Y. and B.Y.; resources, B.-H.Y.; data curation, B.-B.S.; writing—original draft preparation, B.-B.S. and Y.-Q.H.; writing—review and editing, B.-B.S. and B.-H.Y.; visualization, B.-B.S.; supervision, B.-H.Y.; project administration, B.-H.Y.; funding acquisition, B.-H.Y. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by Xi’an University of Technology of China for Doctoral Thesis Innovation, grant number 207-002J1303 and Shaanxi Provincial Education Department of China for Scientific Research Program, grant number 18jk0067.
Acknowledgments: Thanks are due to Zheng-Sheng Fu from Northwest Normal University of China and Jing Han from Xi’an University of Technology of China for valuable discussion.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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