

# Synthesis and characterization of the photoswitchable poly(methyl methacrylate-*random*-methacrylate spirooxazine)

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## Abstract

The photoswitchable poly(methyl methacrylate-*random*-methacrylate spirooxazine) was synthesized via atom transfer radical polymerization with the feed mole ratio of MMA/MSP comonomer of about 5.5/1. Well-defined poly(methyl methacrylate-*random*-methacrylate spirooxazine) have been obtained with the average molecular weight ( $M_n$ ) of 6500 g/mol and polydispersity of 1.21. The structure and properties of the resulting copolymers were characterized by proton nuclear magnetic resonance (<sup>1</sup>H NMR), gel permeation chromatography, Fourier Transform infrared, UV-visible spectroscopy, and differential scanning calorimetry. Moreover, the copolymer exhibited the erasable and rewritable photoimaging on the solid state film which could be as potential candidate for optical data storage materials.

**Keywords:** *spirooxazine, controlled radical polymerization, photoswitching polymers.*

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## 1. Introduction

The creation of functional optical materials having photoactive properties has become one of the most promising objects in materials science. These materials are used in the fabrication of several optoelectronic devices such as optical memories, switches, and holograms. These integrated systems are basically formed by two components: the support media and the photoactive material, most of them are polymers functionalized with photoactive molecules<sup>[1]</sup>. Photochromism has attracted much attention recently from the viewpoint of optical applications because of interest in refractive index or absorbance changes through optical extraction.

Since the last decade, the development of such optoelectronic devices has included the photochromic compounds as the active ingredient<sup>[1]</sup>. The photochromism of spiropyrans (SP) was reported by Fischer and Hirshberg<sup>[2]</sup> in 1952 and since these organic compounds have been extensively studied due to their possible application in many fields. Following, spirooxazine compounds synthesized belonged to the spiroindolinonaphthoxazine ring system. Spirooxazine being a class of photochromic compounds are potentially applicable as chemical-UV-dosimeters for personal protection<sup>[3,4]</sup> or they can be incorporated into the materials used for packaging applications in the case

of UV sensitive products like food products. Generally, there is a great interest for the properties of photochromic compounds inserted into polymer films due to their possible use in practical applications. Spirooxazine are composed of an imide and a chromene moieties that are linked by a spirocarbon atom. Irradiation of spirooxazine with UV light induces heterolytic cleavage of the spiro-carboneoxygen bond, thus, producing the ring opened form, the intensively coloured merocyanine (MC). Merocyanine returns to the initial spirooxazine form in the dark or by visible light irradiation<sup>[5-7]</sup>. The time to resume the initial colour depends on temperature and on the nature of the compound. In recent years, photochromic and thermochromic spiropyrans and spirooxazines have been receiving considerable attention, due to their potential application in many new technologies, such as data recording and storage, optical switching, displays, and non-linear optics<sup>[8-12]</sup>. Recently, Ventura et al have reported the synthesis of new and well-defined poly(6-benzospiropyran hexylmethacrylate)s bearing a BSP moiety on the side chain of each unit of the polymer with linear, star-like and molecular brush architectures and narrow molecular weight distributions were successfully synthesized combining ATRP and click chemistry<sup>[13]</sup>. More

recently, Dübner et. al have published the copolymer brushes, composed of glycidyl methacrylate and a furanprotected maleimide-containing monomer, after postpolymerization modification, they have functioned microperoxidase-11 and photochromic spiroxan moieties, the polymer brushes catalyzed the oxidation of 3,3',5,5'- tetramethylbenzidine. Their obtained brushed copolymers exhibited the light-induced spiroxan-merocyanine transition under UV or visible-light, turnover by more than 1 order of magnitude<sup>[14]</sup>.

Here we reported the synthesis of poly(methyl methacrylate)-*r*-poly(methacrylate spirooxazine) (PMMA-*r*-PMSp) via atom transfer radical polymerization (ATRP). The well- defined copolymers were characterized via <sup>1</sup>H NMR, GPC, FTIR, DSC, UV-vis spectrum. Especially, the synthesized copolymers exhibited the spirooxazine-merocyanine transition under UV irradiation for both solution and solid film state.

## 2. Materials and Methods

### 2.1 Materials

2,7-Dihydroxynaphthalene (97%), sodium nitrite (NaNO<sub>2</sub>), sodium hydroxide (NaOH), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), hydrochloric acid (HCl), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), 1,3,3-trimethyl-2-methyleneindoline (97%), triethylamine (99%), methacryloyl chloride (97%), Copper(I) bromide (CuBr, 98%), *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA, 99%), ethyl  $\alpha$ -bromoisobutyrate (Et<sub>2</sub>BriB, 98%), 4-(Dimethylamino)pyridine (99%) were purchased from Aldrich. Methyl methacrylate (MMA, 98%) was purchased from Sigma-Aldrich passed through a plug of basic alumina before use in order to remove the hydroquinone inhibitors and stored under nitrogen atmosphere. Dichloromethane (99.8%) and tetrahydrofuran (THF, 99%) were purchased from Fisher/Acros and dried using molecular sieves under N<sub>2</sub>. Chloroform (CHCl<sub>3</sub>, 99.5%), hexane (99%), methanol (99.8%), absolute ethanol (99%) and ethyl acetate (99%) were purchased from Fisher/Acros and used as received.

### 2.2 Characterization

<sup>1</sup>H NMR spectra were recorded in deuterated chloroform (CDCl<sub>3</sub>) with TMS ( $\delta$  0.00 ppm). The following abbreviations are used to describe the NMR signals: s (singlet), d (doublet), t (triplet), q (quartet), and br (broad). FT-IR spectra, collected as the average of 264 scans with a resolution of 4 cm<sup>-1</sup>, were recorded from KBr disk on the FT-IR Bruker Tensor 27. Size exclusion chromatography (SEC) measurements were performed on a Polymer PL-GPC 50 gel permeation chromatograph system equipped with an RI detector, with THF as the eluent at a flow rate of 1.0 mL/min. Molecular weight and molecular weight distribution were calculated with reference to polystyrene standards. UV-vis absorption spectra of polymers in solution and polymer thin films were recorded on a Shimadzu UV-2450 spectrometer over a wavelength range of 250-800 nm.

### 2.3 Synthesis of 1-nitrosonaphthalene-2,7-diol

After dissolving NaOH (2.5 g, 62.4 mmol) in 100 mL of H<sub>2</sub>O, 2,7-dihydroxynaphthalene (1) (10 g, 62.4 mmol) and Na<sub>2</sub>NO<sub>2</sub> (4.3 g, 62.4 mmol) were added to the solution.

The reaction solution was heated for 1 h at 60 °C and then cooled to 0 °C. The mixture of 8 mL of concentrated H<sub>2</sub>SO<sub>4</sub> and 15 mL of distilled water was added dropwise to the reaction solution with the temperature remained at 0 °C. The reaction continued for 1 h. After the reaction, the precipitate was isolated by vacuum filtration and washed with 0.1 M aqueous HCl followed by cold water to obtain compound 2 as a dark brown powder solid. Yield: 11.22 g, 95%.

<sup>1</sup>H NMR, (500 MHz, methanol-d<sub>4</sub>),  $\delta$  (ppm): 7.42 (d, 1H), 7.59 (d, 1H), 7.56 (d, 1H), 6.8 (d, 1H), 6.18 (s, 2H). FT-IR (cm<sup>-1</sup>): 3143 (O-H), 1301 (N=O).

### 2.4 Synthesis of 1,3,3-trimethylspiro[indoline-2,3'-naphtho[2,1-b][1,4]oxazin]-9'-ol (spirooxazine-hydroxyl)

To a suspension of 2,7-dihydroxy-1-nitrosnaphthalene (compound 1) (2.84 g, 15 mmol) in absolute ethanol (50 mL) was added dropwise, under refluxing a solution of 1,3,3-trimethyl-2-methyleneindoline (2.59 g, 2.65 mL, 15 mmol) in absolute ethanol (20 mL). After continuous refluxing under a N<sub>2</sub>-stream, the obtained brown solution was purified over silica column with ethyl acetate/hexane (2:1) to obtain the crude product. Then, solvents were evaporated under vacuum to give a black powder. The black powder was washed with distilled water and extracted with CHCl<sub>3</sub>. Finally, the product was crystallized in hexane to obtain the pure white powder of SP. The product (2.74 g, yield: 53%) was dried in a vacuum oven at RT and was characterized by <sup>1</sup>H NMR and FT-IR.

<sup>1</sup>H NMR, (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 1.35 (s, 6H), 2.77 (s, 3H), 6.58 (t, 1H), 6.84 (d, 1H), 6.9 (d, 1H), 7.02 (d, 1H), 7.09 (d, 1H), 7.23 (t, 1H), 7.58 (d, 1H), 7.65 (d, 1H), 7.71 (s, 1H), 7.88 (s, 1H), 10.04 (s, 1H, OH). FT-IR (cm<sup>-1</sup>): 3313 (O-H), 3065 (=C-H), 1627 (C=N), 1301 (N=O).

### 2.5 Synthesis of the methacrylate spirooxazine monomer (MSP)

Spirooxazine-hydroxyl (1.03 g, 3.00 mmol) was added to 25 mL of anhydrous dichloromethane in a 50 mL round bottomed flask. After cooling the solution to 0 °C, triethylamine (0.46 g, 0.627 mL, 4.5 mmol) was added and the reaction was stirred for an hour. Then, methacryloyl chloride (0.47 g, 0.44 mL, 4.5 mmol) was dissolved in 5 mL of anhydrous dichloromethane and added dropwise to the reaction mixture under N<sub>2</sub> atmosphere, cooled to 0 °C. The reaction was continuously stirred for 24 h at room temperature. The solvent was rotary evaporated and the crude product was recrystallized in hexane. This crude product was purified over column silica hexane/ethyl acetate (v:v = 30/1) to obtain the pure white powder of Msp. The product was dried in a vacuum oven at RT and was characterized by <sup>1</sup>H NMR and FT-IR. Yield: 75%.

<sup>1</sup>H NMR, (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 1.35 (s, 6H), 2.1 (s, 3H), 2.77 (s, 3H), 5.6 (s, 1H), 6.3 (s, 1H), 6.58 (dd, 1H), 6.84 (dd, 1H), 6.9 (s, 1H), 7.02 (d, 1H), 7.09 (d, 1H), 7.23 (d, 1H), 7.66 (d, 1H), 7.72 (s, 1H), 7.78 (d, 1H), 8.28 (d, 1H). FT-IR (cm<sup>-1</sup>): 2971 (=C-H), 1728 (C=O), 1627 (C=N), 1121, 740.

## 2.6 Synthesis of Poly(methyl methacrylate-*co*-methacrylate spirooxazine) (Poly(MMA-*co*-MSP))

Copolymer Poly(MMA-*co*-MSP) were synthesized using a ratio of [MMA]:[MSP]:[Et<sub>3</sub>BriB]:[CuBr]:[PMDETA] = 55:10:1:1:2. Into a dried glass tube with a magnetic bar, CuBr (2.15 mg g, 0.015 mmol) and ligand PMDETA (26 mg, 0.15 mmol) were added, then monomer MMA (82.60 mg, 0.75 mmol), MSP (61.87 mg, 0.15 mmol), and anhydrous THF (2 mL) were added under nitrogen. The mixture was degassed by three freeze-pump-thaw cycles and purged with nitrogen. Et<sub>3</sub>BriB (2.93 mg, 0.015 mmol) was added before the polymerizations were carried out at 65 °C oil bath for 24 h. The flask was then opened and exposed to air. The copolymer was recovered by removing the solvent under reduced pressure, re-dissolving the polymer in chloroform, passing the polymer solution through an alumina column to remove excess copper catalyst and was then concentrated by using a rotary evaporator. The concentrated solution was added in drops into an approximately 80 mL of cold methanol. The precipitation product was filtered through a medium frit funnel. Finally, the polymer was dried under vacuum at 60 °C for 24 h until a weight constant. Yield 75%, M<sub>n</sub> = 8000 g/mol, M<sub>w</sub>/M<sub>n</sub> = 1.34, as obtained by gel permeation chromatography.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 0.8-1.3 (s, 15H), 1.35 (s, 6H), 1.6-2.4 (s, 4H), 2.76 (s, 3H), 3.60 (s, 3H), 4.09 (m, 2H), 6.58 (dd, 1H), 6.84 (dd, 1H), 6.9 (s, 1H), 7.02 (d, 1H), 7.09 (d, 1H), 7.23 (d, 1H), 7.66 (d, 1H), 7.72 (s, 1H), 7.78 (d, 1H), 8.24 (d, 1H).

## 3. Results and Discussions

### 3.1 Monomer synthesis

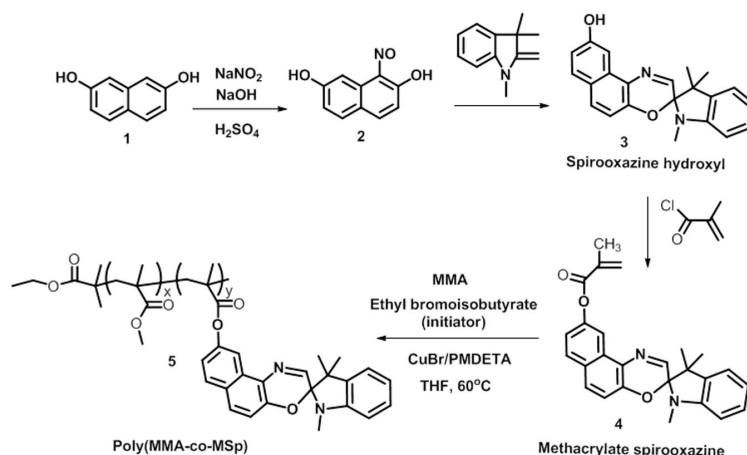
First, 2,7-Dihydroxynaphthalene (compound 1) was nitrated by NaNO<sub>2</sub> in presence of NaOH and H<sub>2</sub>SO<sub>4</sub> to obtain 1-nitronaphthalene-2,7-diol (compound 2, Scheme 1). Then, 1-nitronaphthalene-2,7-diol reacted with 1,3,3-trimethyl-2-methyleneindoline to form spirooxazine-hydroxyl (compound 3, Scheme 1), which subsequently reacted with methacryloyl chloride to give methacrylate-spirooxazine

(MSP) (compound 4, Scheme 1). Finally, the synthesis of poly(MMA-*co*-MSP) (compound 5, Scheme 1) was performed via atom transfer radical polymerization using CuBr and PMDETA as catalyst system. The synthesis of poly(MMA-*co*-MSP) was described as Scheme 1.

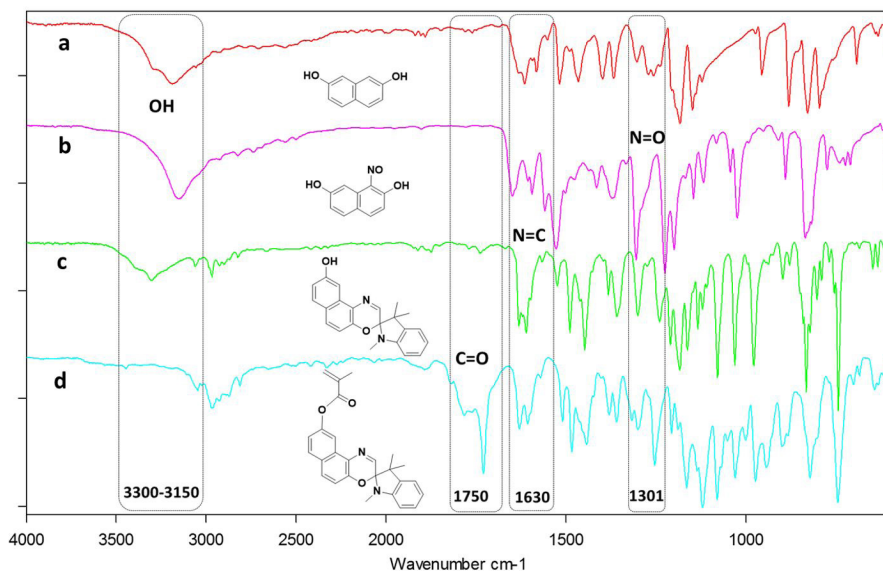
The FTIR was used to characterize the spirooxazine hydroxyl (compound 3) and methacrylate spirooxazine (MSP) (compound 4) to determine the chemical functional groups in their structure. Figure 1 showed the FTIR of spirooxazine hydroxyl and methacrylate-spirooxazine, the vibration peaks at 1630 cm<sup>-1</sup> corresponding to N=C linkage and the broad peaks at 3300 cm<sup>-1</sup> assigned to OH group in spirooxazine hydroxyl (green line c, Figure 1). Following, Spirooxazine-hydroxyl was reacted with methacryloyl chloride to give methacrylate-spirooxazine (MSP) in the presence of triethylamine as catalytic. The reaction was performed in 24 hours. The obtained product was purified over column using heptane/ethyl acetate as eluent, and the purified product was recrystallized in methanol in the yield of 75%. The obtained methacrylate spirooxazine exhibited the vibration peaks at 1750 cm<sup>-1</sup> corresponding to C=O linkage, and the peaks of OH group at 3300 cm<sup>-1</sup> disappears completely that confirmed that the esterification of spirooxazine hydroxyl with methacryloyl chloride was taken place successfully (cyan line d, Figure 1).

### 3.2 Polymer synthesis

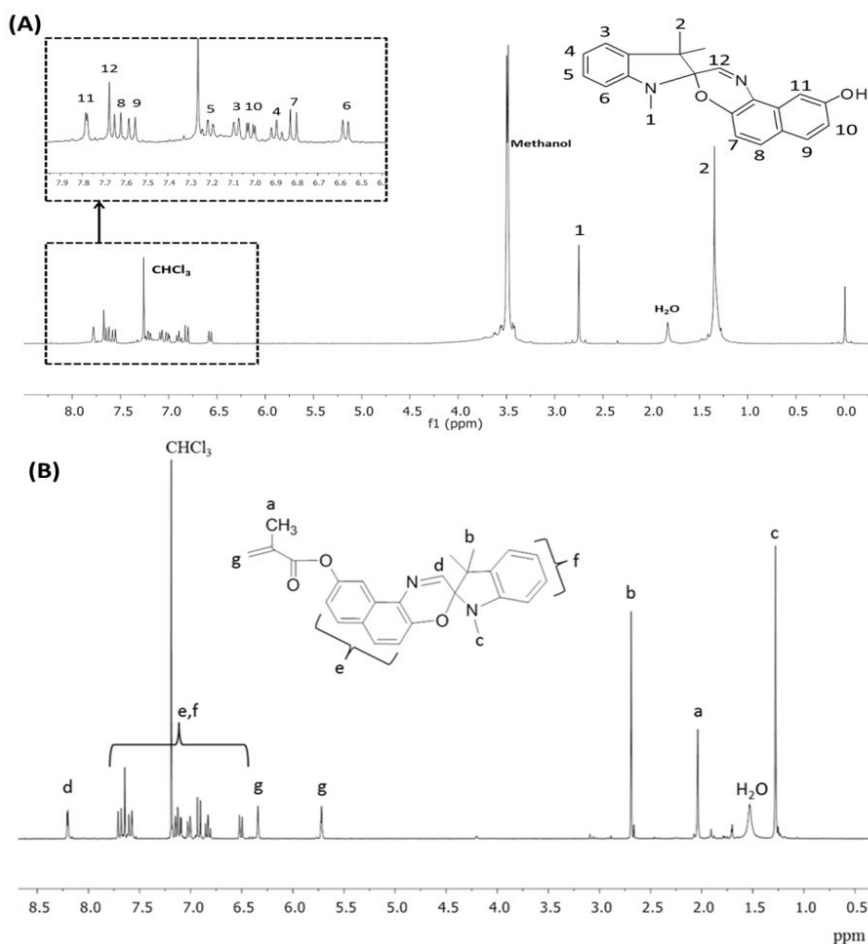
The <sup>1</sup>H NMR spectrum of spirooxazine hydroxyl showed the proton resonance of imine linkage at 7.65 ppm. Moreover, the signals at 2.65 ppm and 1.42 ppm exhibited for the methyl groups of 1,3,3-trimethyl-2-methyleneindoline in spirooxazine hydroxyl moieties. The <sup>1</sup>H NMR spectrum of MSP (Figure 2) showed the proton resonance of methylene linkage of methacrylate at 5.70 ppm and 6.30 ppm. The <sup>1</sup>H NMR spectrum of MSP also showed the imine linkage in methacrylate - spirooxazine ring at 8.4 ppm which was shifted from 7.65 ppm in spirooxazine-hydroxyl. All other proton resonances appear in the reasonable intensities and are correlated to spirooxazine structure, thus confirming the expected molecular structure of MSP. The attribution



**Scheme 1.** Synthesis of poly(methyl methacrylate-*co*-methacrylate spirooxazine).



**Figure 1.** FTIR of monomer compounds: (a) FTIR of 2,7-dihydroxynaphthalene compound; (b) FTIR of 1-nitrosonaphthalene-2,7-diol compound; (c) FTIR of spirooxazine-hydroxyl; (d) FTIR of methacrylate spirooxazine monomer.



**Figure 2.** The  $^1\text{H}$  NMR of spirooxazine hydroxyl and methacrylate spirooxazine (MSp): (A)  $^1\text{H}$  NMR of spirooxazine hydroxyl; (B)  $^1\text{H}$  NMR of methacrylate spirooxazine).



of the  $^1\text{H}$  NMR signals of spirooxazine hydroxyl and MSp is presented in Figure 2<sup>[15]</sup>.

In final step, the MSp and MMA comonomers were polymerized via ATRP using ethyl  $\alpha$ -bromoisobutyrate in the presence of CuBr and PMDETA as catalyst and ligand, respectively. The feed ratio of MMA/MSp comonomer of about 5.5/1 was established for achieving a good control over ATRP ( $[\text{MMA}]/[\text{MSp}]/[\text{Initiator}]/[\text{CuBr}]/[\text{PMDETA}] = 55:5:1:1:2$ ). The polymerization was performed in THF at 60 °C for 24 h under nitrogen atmosphere. The polymerization was stopped by cooling the reaction mixture followed by dilution with extra volume of THF, then the mixture was purified over aluminium column to remove CuBr catalyst. The copolymers were obtained by precipitation in cold *n*-heptane, the copolymers were filtered and dried under vacuum until constant mass.

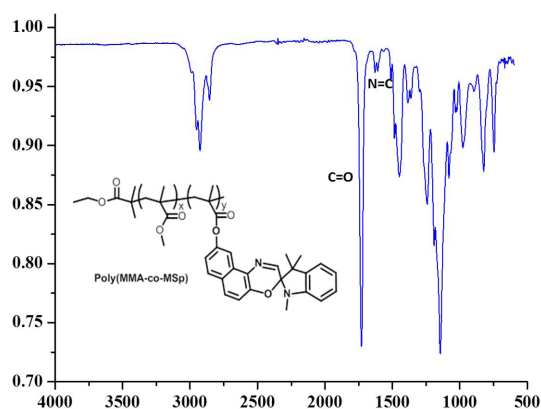


Figure 3. The FT-IR of copolymers Poly(MMA-*r*-MSp).

The FT-IR spectra was used to characterize the copolymers Poly(MMA-*r*-MSp) as Figure 3. The appearance of the high intensity signal observed at 1728  $\text{cm}^{-1}$  that attributed to carbonyl vibrational ( $\text{C}=\text{O}$ ) of Poly(MMA-*r*-MSp). In addition, the  $\text{N}=\text{C}$  linkage of MSp in Poly(MMA-*r*-MSp) was also exhibited at 1651  $\text{cm}^{-1}$ .

The polymer structure of Poly(MMA-*r*-MSp) was also confirmed by  $^1\text{H}$  NMR. The Figure 4 exhibited all characteristic peaks of copolymers Poly(MMA-*r*-MSp). The polymerization degree of the Poly(MMA-*r*-MSp) was calculated from recorded  $^1\text{H}$  NMR spectrum by comparing the relative signal intensities of the imine proton of the MSp and methylene protons of the MMA residue at  $\delta = 8.24$  ppm (peak “s”, Figure 4) and  $\delta = 3.6$  ppm (peak “f”, Figure 4), respectively, with that of the methylene protons of initiator at 4.09 ppm (peak “b”, Figure 4). The molecular weight of the copolymers Poly(MMA-*r*-MSp) was determined to be 6500 g/mol and to comprise 52 and 3 of MMA and MSp units, respectively. These results give the weight compositions of 80% and 20% of MMA and MSp, respectively in copolymers Poly(MMA-*r*-MSp).

As seen from Table 1, the Poly(MMA-*r*-MSp) was obtained with a relatively good approximation between theoretical and experiment molar masses that approved for an initiation efficiency close to 1. A narrow molecular weight distribution of the copolymers Poly(MMA-*r*-MSp) was recorded by GPC, with  $\bar{M}_w = 1.21$ .

### 3.3 Photoisomerization properties of polymers

Photoisomerization property of poly(MMA-*r*-MSp) was studied in THF. Figure 5A and Figure 5B show the color changing of polymer solution (0.1 g/L; pH 9.0) measured at 25 °C under UV irradiation. Without UV irradiation, the

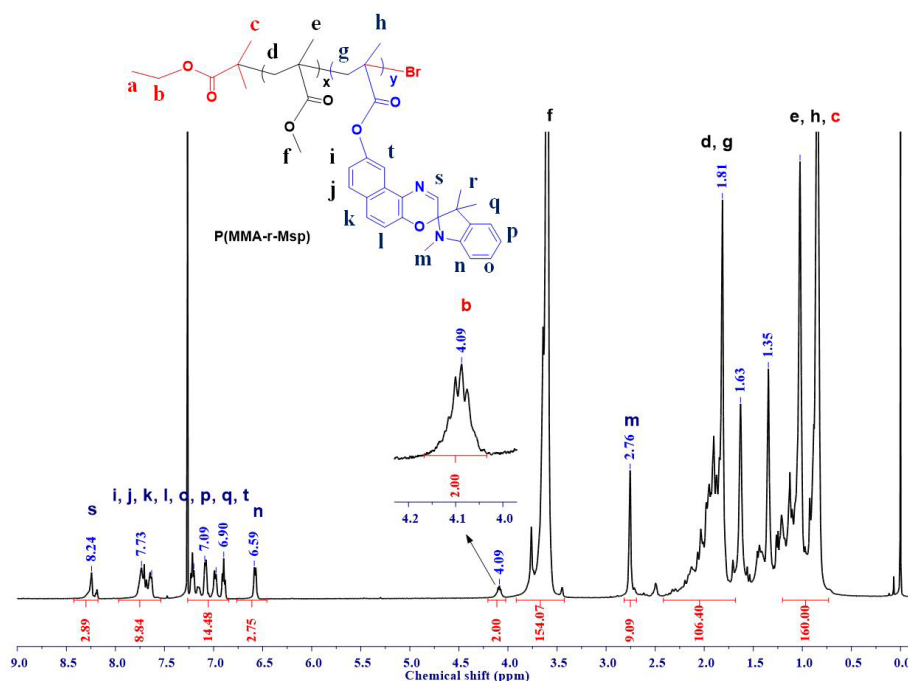
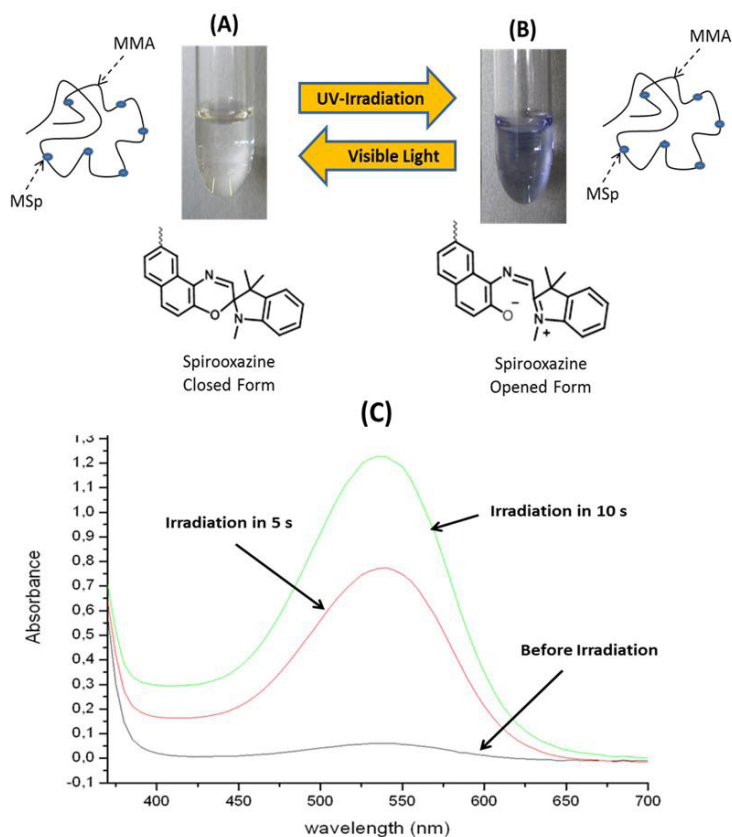


Figure 4. The  $^1\text{H}$  NMR spectrum of copolymers Poly(MMA-*r*-MSp).

**Table 1.** Macromolecular characteristics of Poly(MMA-*r*-MSP) synthesized by ATRP using  $\alpha$ -bromoisobutyrate initiator and CuBr/PMDETA ([CuBr]/[PMDETA] = 1/2) as the catalytic complex.

Diblock copolymers	T °C	Conversion (%) <sup>(a)</sup>	MMA		MSP		f <sup>(d)</sup>	Poly(MMA- <i>r</i> -MSP)	
			$\overline{M}_{n\ the}^{(b)}$ (g/mol)	$\overline{M}_{n\ exp}^{(c)}$ (g/mol)	$\overline{M}_{n\ the}^{(b)}$ (g/mol)	$\overline{M}_{n\ exp}^{(c)}$ (g/mol)		$\overline{M}_{n\ MMR}$ (g/mol)	D <sup>(e)</sup>
1	60	92	5060	5200	2150	1300	1	6500	1.21
2	60	87	4785	5100	2150	1300	1	6400	1.25

<sup>(a)</sup>Conversion as determined after precipitation in cold *n*-heptane:  $Conv. = (m - m_{Cu} - mL) / m_M$ , where *m* denotes the weight of product, and *m<sub>P</sub>*, *m<sub>Cu</sub>*, *m<sub>L</sub>*, *m<sub>M</sub>* the weights of the initiator, copper catalyst, ligand (PMDETA), and monomers, respectively; <sup>(b)</sup>MMA and MSP theoretical number-average-molar mass as calculated by  $[MMA]_0 / [Initiator]_0 \times Conv(\%) \times M_{w\ MMA(or\ MSP)}$  assuming a living process; <sup>(c)</sup>MMA (or MSP) experimental number-average molar mass as determined by <sup>1</sup>H NMR spectroscopy (see Figure 3):  $\overline{M}_{n\ exp} = DP_{EXP} \times M_{w\ MMA(or\ MSP)}$  where  $DP_{EXP}$  is the experimental degree of polymerization, as calculated from the relative intensities of methylene protons of MMA ( $\delta = 3.6$  ppm), imine proton of MSP ( $\delta = 8.24$  ppm) and methylene protons of initiator (4.09 ppm); <sup>(d)</sup>Initiation efficiency as calculated from  $\overline{M}_{n\ the\ of\ P(MMA-R-MSP)} / \overline{M}_{n\ exp\ of\ P(MMA-R-MSP)}$ ; <sup>(e)</sup>Dispersity index as determined by GPC in THF at 35 °C.



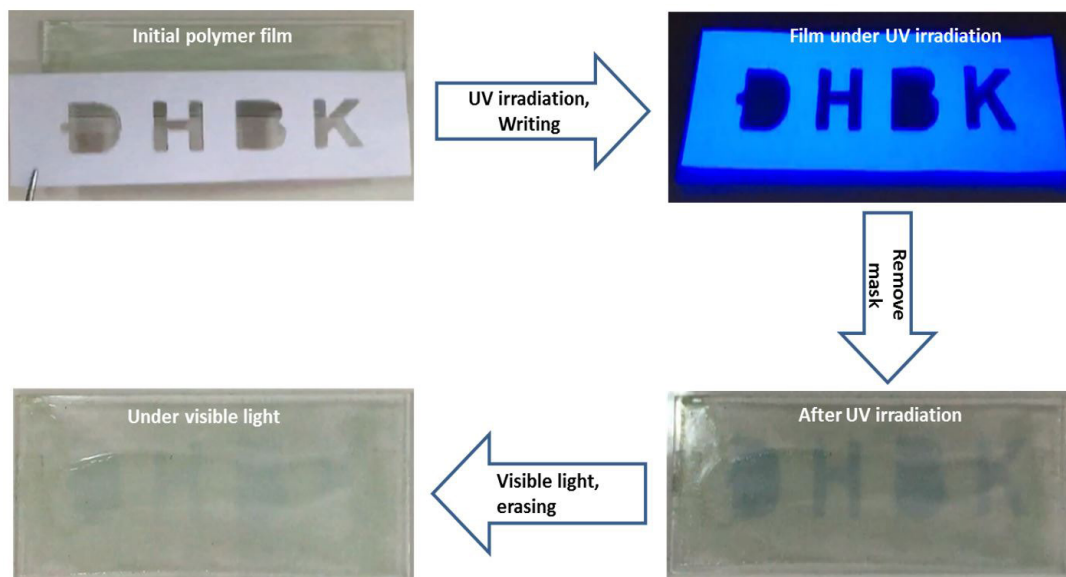
**Figure 5.** Poly(MMA-*r*-MSP) in THF solution with MSP in closed form (A), Poly(MMA-*r*-MSP) in THF solution with MSP in opened form after UV irradiation (B), UV-Vis spectra of poly(MMA-*r*-MSP) under UV-irradiation (C).

polymer shows almost no absorption in the visible region (blue line, Figure 5C) indicating that the spirooxazine units exist as a closed form, as shown in Figure 5C. However, UV irradiation of the solution (334 nm), creates a distinctive absorption band centered at 540 nm, assigned to the generation of opened form of spirooxazine.

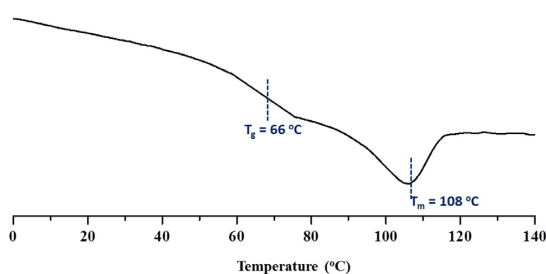
In addition, we measured the absorption spectra changes of poly(MMA-*r*-MSP) to obtain an insight into their photochromic properties in the solid state film which shows similarly photochromic performance in solution. The copolymers poly(MMA-*r*-MSP) solution was coated on transparent glass substrate via spin coating method, then

the obtained polymer film was dried in oven at 60 °C in 2 hours. Irradiation a colorless poly(MMA-*r*-MSP) film, the colorless poly(MMA-*r*-MSP) turned to blue and a new absorption band appears at around 550 nm and gradually increased and reached a photostationary state.

The inherent characteristics of poly(MMA-*r*-MSP) film make it possible to use such materials for data recording. A possible procedure for data recording and erasing is presented in Figure 6. Upon UV light irradiation through the mask, the optical data were recorded on poly(MMA-*r*-MSP) film irradiation region, when irradiation with visible light on irradiation region, the optical data were erased. In solid



**Figure 6.** Principle scheme of the optical data recording on poly(MMA-*r*-MSp) film.



**Figure 7.** The DSC diagram of poly(MMA-*r*-MSp).

state, the practical capability of rewritable photoimaging on solid state investigated by patterned illumination through photomasks. The word ‘ĐHBK’ (Ho Chi Minh City University of Technology, Vietnamese abbreviated) was recorded as a first image (Figure 6), which was subsequently erased and followed by the recording of a second image. The cycles of writing and erasing was repeated more than 30 times.

Last but not least, the thermal properties of poly(MMA-*r*-MSp) ( $M_n = 6500$  g/mol,  $\bar{D} = 1.21$ ) was characterized to determine the glass transition of copolymers by DSC. The DSC second-heating traces in the range from 0 to 150 °C of the poly(MMA-*r*-MSp) are shown in Figure 7. For such studied molecular weight, the glass transition temperature ( $T_g$ ) value of poly(MMA-*r*-MSp) is around 66 °C. Otherwise, the melting point ( $T_m$ ) of poly(MMA-*r*-MSp) is observed at ca. 108 °C which is similar to the DSC results of pure homopolymer PMMA in the same of average molecular weight.

#### 4. Conclusions

In conclusion, we have successfully designed and synthesized a novel photoswitching poly(MMA-*r*-MSp) via controlled polymerization method. The obtained

copolymer poly(MMA-*r*-MSp) has the average molecular weight of 6500 g/mol with polydispersity index of around 1.2-1.3. The copolymer exhibited excellent photochromic behavior in solid film under UV irradiation. Erasable and rewritable photoimaging on the solid film was successfully demonstrated. This optical data storage materials based on photochromic poly(MMA-*r*-MSp) could to be as candidate for fundamental studies and eventual technical application for all-photo mode – high density optical data.

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