

Synthesis of a Novel Fluorescent Cyanide Chemosensor Based on Photoswitching Poly(pyrene-1-ylmethyl-methacrylate-*random*-methyl methacrylate-*random*-methacrylate spirooxazine)

Hoan Minh Tran¹
 Tam Huu Nguyen¹
 Viet Quoc Nguyen¹
 Phuc Huynh Tran³
 Linh Duy Thai³
 Thuy Thu Truong¹
 Le-Thu T. Nguyen¹
 Ha Tran Nguyen^{*1,2}

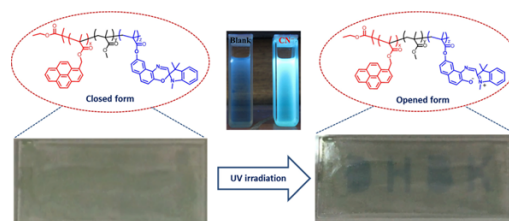
¹ Faculty of Materials Technology, Ho Chi Minh City University of Technology (HCMUT), Vietnam National University, 268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Vietnam

² Materials Technology Key Laboratory (Mtlab), Vietnam National University - Ho Chi Minh City, 268 Ly Thuong Kiet, District 10, Ho Chi Minh City 70000, Vietnam

³ Faculty of Chemical Engineering, Ho Chi Minh City University of Technology (HCMUT), Vietnam National University, 268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Vietnam

Received November 4, 2017 / Revised July 10, 2018 / Accepted August 7, 2018

Abstract: The photoswitching poly(pyrene-1-ylmethyl-methacrylate-*random*-methyl methacrylate-*random*-methacrylate spirooxazine) was synthesized *via* atom transfer radical polymerization and characterized by proton nuclear magnetic resonance (¹H NMR), gel permeation chromatography (GPC), Fourier transform infrared (FTIR) spectroscopy, UV-visible spectroscopy, and differential scanning calorimetry (DSC). The obtained copolymer exhibited the capability of erasable and rewritable photoimaging, making it a potential candidate for optical data storage materials. Moreover, the copolymer also showed the sensing ability for cyanide anions effect in aqueous solutions.



Keywords: photoswitching polymers, spirooxazine, atom transfer radical polymerization, chemosensor.

1. Introduction

The creation of functional optical materials having photoactive properties has become one of the most promising objects in advanced materials science. These materials are used in the fabrication of several optoelectronic devices such as optical memories, optical switches, and hologram memory devices.¹ These integrated systems are basically formed by two components: the support media and the photoactive material; most of them are functionalized polymers containing photoactive molecules.² In particular, photochromism has attracted great attraction due to their optical application which relies on refractive index or absorbance changes.³

The photochromism of spiropyrans was reported by Fischer and Hirshberg⁴ in 1952 and since then these organic compounds have been extensively studied.^{5,6} Subsequent to spiropyrans, spirooxazine compounds were synthesized in 1970 and being a class of photochromic compounds are potentially applicable such as data recording and storage, optical switches, displays, and non-linear optics.⁷⁻¹² In addition, they can also be incorporated into materials for UV sensitive food packaging products.^{13,14} A spirooxazine structure is composed of an imide and a chromene moiety which were linked by a spirocarbon atom. Irradiation of spirooxazine with UV light induces heterolytic cleavage of the

spiro-carboneoxygen bond to give the ring-opened form referred as coloured merocyanine (MC), which returns to the initial ring-closed form by visible light irradiation.¹⁵⁻¹⁸ However, the use of spirooxazine derivatives in practical optical information storage is challenging due to the difficulty in making the MC form of spirooxazine molecules stable enough to ensure that optical recorded data can be maintained for a relatively long time. Thus, the requirement to further improve the stable high-density optical storage materials is necessary. Various methods to stabilize the photomerocyanine form have been developed¹⁹⁻²¹ including the synthesis of spirooxazine polymers containing photocrosslinkable chalcone unit in the side chain,²² modification of spirooxazine by the substitution of several groups on its benzopyran ring,¹⁵ incorporation of spirooxazine unit in polymeric structures and the formation of complexes of spirooxazine with metals.²³⁻²⁶ Grafting of spirooxazine compound to polymethyl methacrylate (PMMA) has been reported to enhance the photoresponse and slower bleaching in dichloromethane solution.²⁷

The chemical incorporation of spiropyran and spirooxazine chromophores into polymer structures has been performed by various pathways at different steps of the polymerization: i) after polymerization *via* covalent coupling with a chromophore derivative, ii) at the very beginning *via* a chromophore-functional initiator or chain transfer agent, and iii) during copolymerization of a functional monomer with other monomers.²⁸⁻³¹ Among the controlled polymerization methods reported, atom transfer radical polymerization (ATRP) is of interest because of great versatility, efficiency and wide monomer scope. For instance, spirooxazine-containing ATRP initiators have been employed to prepare

Acknowledgments: This research was fully supported by the Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number "104.02-2016.56".

***Corresponding Author:** Ha Tran Nguyen (nguyentranha@hcmut.edu.vn)

poly(meth)acrylates and polystyrenes bearing one spirooxazine group at one polymer chain end.³²⁻³⁴ Spiropyran-containing polymers have been synthesized by copolymerization of a spiro-oxazine-functional methacrylate with 2-(dimethylamino)ethyl methacrylate using ATRP.^{35,36} Rod-coil diblock copolymers of a conjugated polymer and PMMA with spirooxazine side units along the coil block have been obtained by ATRP of MMA with spirooxazine-methacrylate using a polythiophene macroinitiator.³⁷

It has been reported that the spirooxazine and spirooxazine groups behave as sensitive cyanide anion (CN⁻) receptors.^{38,39} One of the approaches used to create sensor probes to detect CN⁻ has been to combine the photochromic spirooxazine moiety with a fluorescent unit in the same structure.^{37,40} The fluorophore moiety emits fluorescence which is only observed when the photochromic compound is in the ring-closed form. In contrast, emission is severely quenched when the photochromic compound is in the MC form under UV irradiation, as a result of fluorescence resonance energy transfer (FRET) from the excited state of the fluorophore to the MC form of the photochromic compound. However, the degree of fluorescence quenching of the irradiated solution could significantly decrease when the spirooxazine MC form interacts with cyanide anion. Based on this phenomenon, copolymers containing fluorophore and photochromic spirooxazine compounds have been designed and probed as cyanide sensors based on fluorescent quenching. To the best of our knowledge, only a few types of fluorophores, including coumarin, nitrophenyl azo group and polythiophenes, have been combined with spirooxazine to develop FRET-based sensors for cyanide detection.^{37,40-42} For example, a polythiophene having spirooxazine groups in the side chains has been developed and applied to the detection of cyanide anion.⁴⁰ Prakash *et al.* have synthesized a nitrophenyl azo substituted spirooxazine for sensitive and selective colorimetric detection of cyanide ions.⁴¹ Shiraiishi *et al.* have synthesized a copolymer consisting of *N*-isopropylacrylamide and coumarin-conjugated spirooxazine (CS) units and studied for selective fluorometric detection of cyanide anion (CN⁻) in water.⁴² A rod-coil copolymer of a polythiophene and PMMA bearing spirooxazine side units has been synthesized and investigated as a sensor probe for cyanide anions.³⁷

In this work we report for the first time the synthesis of a copolymer combining the photochromic spirooxazine groups with pyrenyl moieties by the ATRP of spirooxazine- and pyrene-containing (meth)acrylate monomers, and evaluation of its affinity towards cyanide anions. The choice of pyrene as a fluorophore was prompted by its extensive use as a fluorescent probe in light-responsive polymers⁴³⁻⁴⁷ and the relatively simple, popular, and easy preparability of pyrene-bearing polymers. Previous reports on the ATRP of spirooxazine- and pyrene-containing (meth)acrylate monomers alone have suggested uncontrolled polymerizations, due to the incompatibility of ATRP with these functional monomers, preventing the formation of polymers of desired structures.^{6,37,48} In our work, initially the ATRP synthesis of a copolymer of pyrene-1-ylmethyl-methacrylate (PyrMMA) and methacrylate spirooxazine (MSP) was attempted but the results suggested a poorly controlled polymerization. Thus, alternatively, PyrMMA and MSP were successfully copolymerized in the pres-

ence of methyl methacrylate (MMA), resulting in poly(pyrene-1-ylmethyl-methacrylate-*random*-methyl methacrylate-*random*-methacrylate spirooxazine) (poly(PyrMMA-*r*-MMA-*r*-MSP)). Herein, we describe the ATRP process and characterization of this copolymer, as well as their photoswitching and sensitive chemosensing for cyanide anion behaviors.

2. Experimental

2.1. Materials

Potassium carbonate (K₂CO₃), triethylamine (99%), methacryloyl chloride (97%), Copper(I) bromide (CuBr, 98%), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, 99%), ethyl α -bromoisobutyrate (Et₂BrIB, 98%), 4-(Dimethylamino)pyridine (99%) were purchased from Sigma-Aldrich. Methyl methacrylate (MMA, 98%) and 1-pyrenemethanol (pyrene hydroxyl, 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. MSP was synthesized according to a previously reported procedure.^{37,49} Dichloromethane (99.8%) and tetrahydrofuran (THF, 99%) were purchased from Fisher/Acros and dried using molecular sieves under N₂. Chloroform (CHCl₃, 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

¹H NMR spectra were recorded in deuterated chloroform (CDCl₃) with TMS (δ 0.00 ppm). FTIR spectra, collected as the average of 264 scans with a resolution of 4 cm⁻¹, were recorded from KBr disk on the FTIR 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 300-800 nm.

2.3. Synthesis of pyrene-1-ylmethyl-methacrylate (PyrMMA)

To a solution of triethylamine (0.9 mL, 6.5 mmol) in 30 mL of anhydrous THF, 4-(dimethylamino)pyridine (0.26 g, 0.5 mmol) and 1-pyrenemethanol (1 g, 4.3 mmol) were added. Methacryloyl chloride (0.63 mL, 6.5 mmol) was added dropwise to this clear solution at 0 °C in 1 h. Then, the reaction was stirred at room temperature overnight. Subsequently, the reaction medium was filtered and the solvent was evaporated under reduced pressure. Afterwards, the solid residue was extracted with chloroform (100 mL) and washed with distilled water several times (3 × 100 mL). The organic phase was dried by anhydrous K₂CO₃ and the solvent was removed by rotary evaporation to give a crude product. The crude product was purified by silica gel column chromatography with the eluent of hexane/ethyl acetate (7/1: v/v)

to give a white crystalline solid.

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm): 8.32–8.00 (m, 9H), 6.15 (d, 1H), 5.91 (s, 2H), 5.56 (d, 1H), 1.97 (s, 3H). FTIR (cm^{-1}): 2971, 2958 (=C–H), 1706 (C=O), 1632, 1451, 1319, 1164, 1012, 924, 843, 764, 703, 647. Anal. Calcd. For $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_3$: C, 75.70; H, 5.82; N, 6.79. Found: C, 75.53; H, 5.77; N, 6.73. m/z : 300.12 (100.0%), 301.12 (23.0%), 302.12 (2.9%). Elemental Analysis: C, 83.98; H, 5.37; O, 10.65. Found: C, 84.78; H, 5.17; O, 10.05.

2.4. Synthesis of poly(pyrene-1-ylmethyl-methacrylate-random-methyl methacrylate-random-methacrylate spirooxazine) (poly(PyrMMA-*r*-MMA-*r*-MSp))

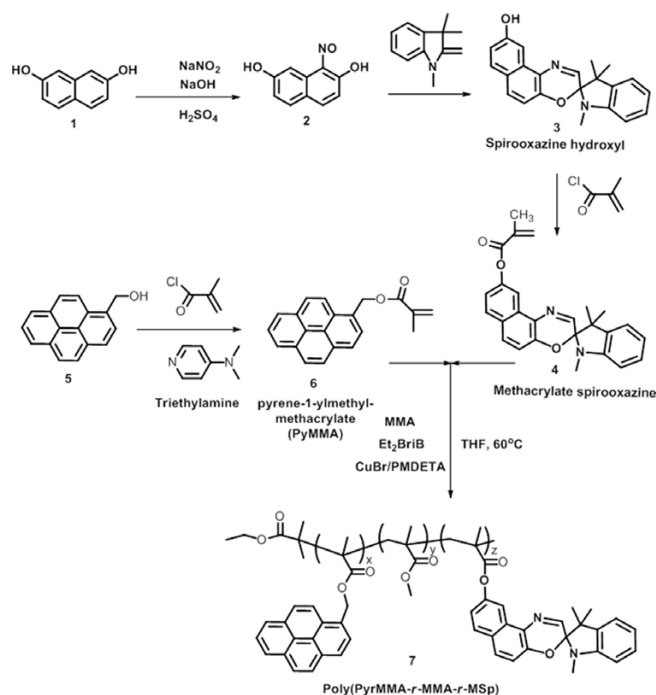
Poly(PyrMMA-*r*-MMA-*r*-MSp) copolymers were synthesized with a ratio of [MMA]:[MSp]:[PyrMMA]:[Et₂BriB]:[CuBr]:[PMDETA] = 50:4:8:1:1:2 *via* ATRP method using CuBr and PMDETA as catalytic system. Into a dried glass tube with a magnetic bar, CuBr (2.15 mg, 0.015 mmol) and ligand PMDETA (5.2 mg, 0.03 mmol) were added. Then, monomer MMA (97 mg, 0.97 mmol), MSp (61.87 mg, 0.15 mmol), PyrMMA (45.05 mg, 0.15 mmol), and anhydrous THF (2 mL) were added under nitrogen atmosphere. The mixture was degassed *via* three freeze-pump-thaw cycles and purged with nitrogen. The Et₂BriB initiator (2.93 mg, 0.015 mmol) was added to the solution, and the polymerization was carried out at 65 °C in oil bath for 24 h. Then, the poly(PyrMMA-*r*-MMA-*r*-MSp) copolymer solution was diluted with extra chloroform and passed through an alumina column to remove copper catalyst. The solution mixture was concentrated and precipitated in 80 mL of cold methanol to obtain the poly(PyrMMA-*r*-MMA-*r*-MSp) copolymer. Finally, the copolymer was dried under vacuum at 60 °C until a constant weight was achieved. Yield 83%, $M_{n(\text{GPC})}$ = 7,000 g/mol, \bar{D} = 1.23.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm): 0.8–1.3 (s, 18H), 1.35 (s, 6H), 1.6–2.4 (s, 6H), 2.75 (s, 3H), 3.60 (s, 3H), 4.09 (m, 2H), 5.74 (s, 2H), 6.57 (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), 8.00–8.32 (m, 9H), 8.24 (d, 1H). FTIR (cm^{-1}): 2971, 2948 (=C–H), 1727 (C=O), 1630 (C=N), 1448, 1240, 1148, 970, 843, 764.

3. Results and discussion

3.1. Monomer and polymer synthesis

The synthesis of monomers and poly(PyrMMA-*r*-MMA-*r*-MSp) copolymer was described in Scheme 1. Methacrylate spirooxazine (MSp) monomer was prepared and purified following the previously reported procedure.^{37,49} Pyrene-1-ylmethyl-methacrylate (PyrMMA) monomer has been prepared *via* the esterification reaction of 1-pyrenemethanol and methacryloyl chloride in the presence of 4-(dimethylamino)pyridine and triethylamine as the catalytic system. The obtained monomers were characterized *via* FTIR (ESI) and $^1\text{H NMR}$ spectroscopy to determine their structures. In $^1\text{H NMR}$ spectrum of MSp monomer (Figure 1(A)), the peaks at 5.7 and 6.3 ppm correspond to the methacrylate double bond group. In addition, the peak at 8.4 ppm is assigned for the imine group of MSp.²¹ The $^1\text{H NMR}$ spectrum of PyrMMA monomer is shown in Figure 1(B). The peaks at 5.56 and 6.15 ppm



Scheme 1. Synthesis of poly(PyrMMA-*r*-MMA-*r*-MSp).

and the peak at 5.91 ppm are assigned to the methacrylate double bond group and the methyl group, respectively. The peaks in the range of 8.0–8.32 ppm are assigned to aromatic pyrene protons.⁵⁰

The poly(PyrMMA-*r*-MMA-*r*-MSp) copolymer was synthesized from MSp, MMA and PyrMMA co-monomers *via* ATRP method. In this polymerization, ethyl α -bromoisobutyrate and CuBr/PMDETA were used as an initiator and catalyst/ligand system, respectively. The feed ratio of MMA/MSp/PyrMMA comonomers was established to be 12.5/1/2 for good control over the ATRP process. We performed the polymerization of comonomers in THF at 60 °C for 24 h under nitrogen atmosphere. The polymerization was stopped by cooling the reaction mixture and the mixture was diluted with THF and purified over aluminum column to remove CuBr catalyst. Then, the copolymer was precipitated in cold *n*-heptane, filtered and dried under vacuum. The obtained poly(PyrMMA-*r*-MMA-*r*-MSp) was characterized by FTIR to determine its functional groups. In the FTIR spectrum (Figure S2, Supporting information), the signal at 1727 cm^{-1} is attributed to the carbonyl (C=O) vibrational absorption and the peak at 1630 cm^{-1} is assigned to the N=C linkage vibration of MSp moieties.

The chemical structure of the obtained copolymer was confirmed by $^1\text{H NMR}$ spectroscopy. The $^1\text{H NMR}$ spectrum of poly(PyrMMA-*r*-MMA-*r*-MSp) is shown in Figure 2. The broad proton signals in the regions of 8.5–7.5, 6.5–7.2, 3.7–3.1, 2.5–1.6, and 1.4–0.8 ppm are assigned to the aromatic protons of PyrMMA, aromatic protons of MSp, methyl groups, side chain methylene and backbone methylene, respectively. In addition, the peak at 5.74 ppm corresponds to CH_2 of PyrMMA, and the peaks at 2.75 and 3.6 ppm are assigned to the methyl groups in MSp ring and methyl group of MMA moieties, respectively. These results indicate the successful synthesis of poly(PyrMMA-*r*-MMA-*r*-MSp).

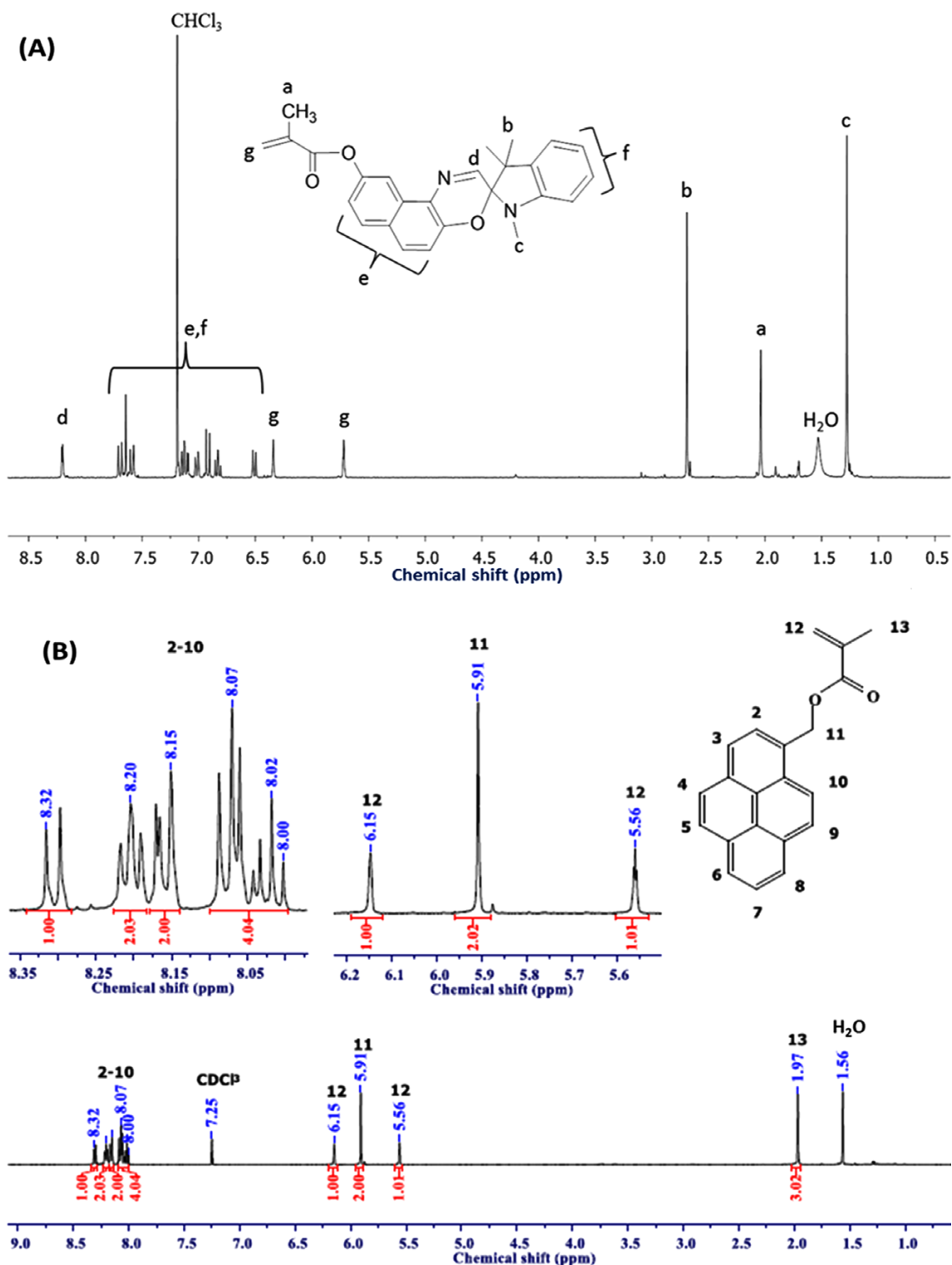


Figure 1. ^1H NMR spectra of methacrylate spirooxazine (MSP) (A) and pyrene-1-ylmethyl-methacrylate (PyrMMA) (B).

The polymerization degrees (DPs) of MSP, MMA, and PyrMMA were calculated by comparing the relative signal intensities of the methyl group in MSP (peak “m”, $\delta=2.75$ ppm, Figure 2), the methyl group in MMA at 3.6 ppm (peak “f”, Figure 2) and methylene group in PyrMMA at 5.74 ppm (peak “11”, Figure 2) with that of the CH_2 group of initiator (peak “b”, $\delta=4.09$ ppm, Figure 2), respectively. The DPs of MSP, MMA, and PyrMMA were estimated to be 3, 44 and 6, respectively. This gives the weight compositions

of 59.2%, 24.2% and 16.6% of MMA, PyrMMA, and MSP, respectively, in poly(PyrMMA-*r*-MMA-*r*-MSP) copolymer.

As seen from Table 1, the poly(PyrMMA-*r*-MMA-*r*-MSP) was obtained with a relatively good approximation between theoretical and experiment molar masses, indicating an initiation efficiency close to 1. A narrow molecular weight distribution of poly(PyrMMA-*r*-MMA-*r*-MSP) was recorded by GPC, with $D_M=1.23$.

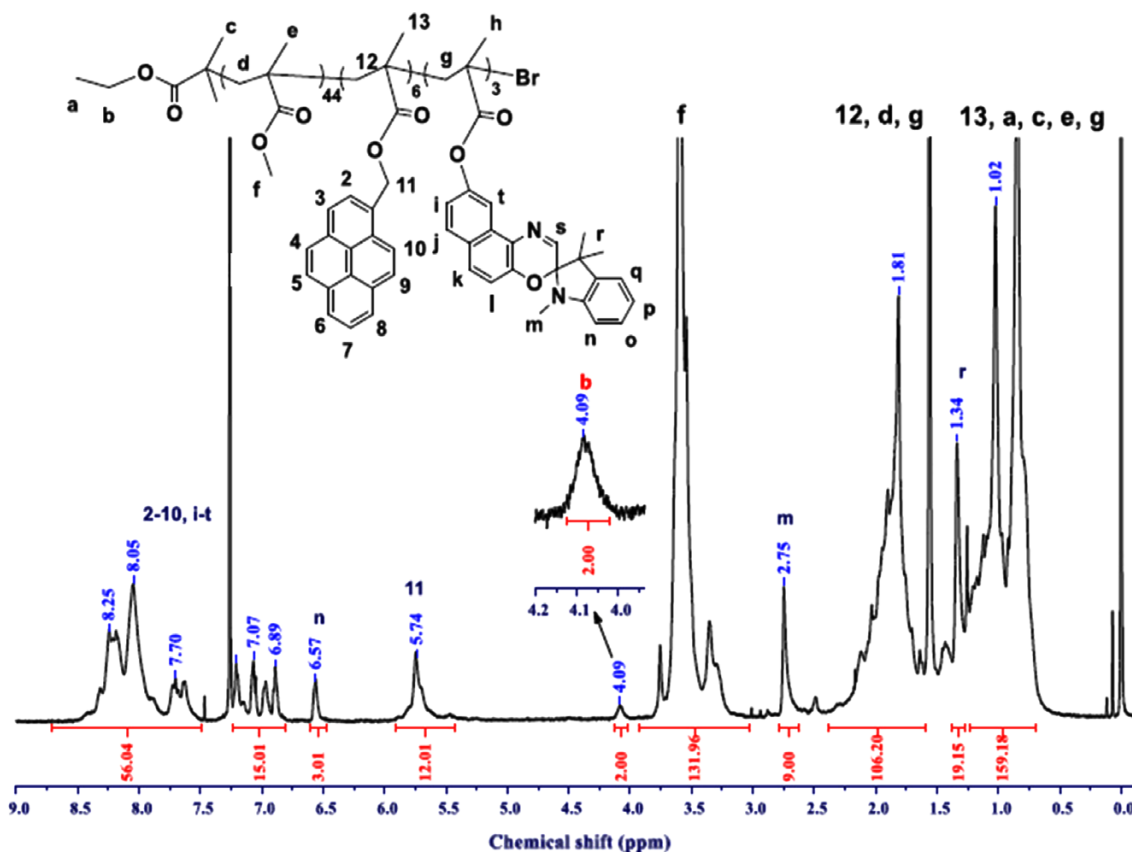


Figure 2. The ^1H NMR spectrum of poly(PyrMMA-*r*-MMA-*r*-MSp).

Table 1. Macromolecular characteristics of poly(PyrMMA-*r*-MMA-*r*-MSp) synthesized by ATRP using α -bromoisobutyrate initiator and CuBr/PMDETA ([CuBr]/[PMDETA]=1/2) as the catalytic complex^a

No	Conv ^b (%)	PyrMMA		MMA		MSp		f ^e	Poly(PyrMMA- <i>r</i> -MMA- <i>r</i> -MSp)	\mathcal{D}^f
		$M_{n\text{ theo}}^c$	$M_{n\text{ exp}}^d$	$M_{n\text{ theo}}^c$	$M_{n\text{ exp}}^d$	$M_{n\text{ theo}}^c$	$M_{n\text{ exp}}^d$			
1	83	1,994	1,802	4,155	4,405	1,370	1,237	1	7,445	1.23
2	81	1,946	1,772	4,055	4,205	1,336	1,220	1	7,197	1.28

^aEntry 2 was a repeat experiment of Entry 1, confirming the reproducibility of the results. ^bConversion as determined after precipitation in cold *n*-heptane: $\text{Conv.} = (m - m_i - m_{cu} - m_l) / m_M$ where *m* denotes the weight of product, and *m_i*, *m_{cu}*, *m_l*, *m_M* the weights of the initiator, copper catalyst, ligand (PMDETA) and monomers, respectively. ^cPyrMMA, MMA, and MSp theoretical number-average-molar mass as calculated by $[\text{PyrMMA}]_0$, $[\text{MMA}]_0$, or $[\text{MSp}]_0$ / $[\text{Initiator}]_0 \times \text{Conv}(\%) \times M_{w\text{ PyrMMA}}$ (or $M_{w\text{ MMA}}$ or $M_{w\text{ MSp}}$) assuming a living process. ^dPyrMMA, MMA or MSp experimental number-average molar mass as determined by ^1H NMR spectroscopy: $\bar{M}_{n\text{ exp}} = DP_{\text{exp}} \times M_{w\text{ PyrMMA}}$ (MMA or MSp) where DP_{exp} is the experimental degree of polymerization, as calculated from the relative intensities of methyl protons of MMA ($\delta=3.6$ ppm), methyl group in MSp ($\delta=2.75$ ppm) and methylene group in PyrMMA ($\delta=5.74$ ppm) with methylene protons of initiator group (4.09 ppm). ^eInitiation efficiency as calculated from $\bar{M}_{n\text{ theo}}$ of poly(PyrMMA-*r*-MMA-*r*-MSp) / $\bar{M}_{n\text{ exp}}$ of poly(PyrMMA-*r*-MMA-*r*-MSp). ^fDispersity index as determined by GPC in THF using polystyrene standards.

3.2. Properties of Poly(PyrMMA-*r*-MMA-*r*-MSp) Copolymer

Photoisomerization properties of poly(PyrMMA-*r*-MMA-*r*-MSp) were studied in solvents and in solid state film. Figure 3(A) and (B) demonstrate the color changing of a copolymer solution (3 mg mL⁻¹) measured at 25 °C under UV irradiation (365 nm) and the corresponding UV spectra are revealed in Figure 3(C). Without UV irradiation, the polymer shows almost insignificant absorption in the visible region indicating that the spirooxazine units exist in a closed form. Under UV irradiation (365 nm), the spirooxazine moieties were converted to the MC open form resulting in a solution color change from transparent to blue and correspondingly a distinctive absorption band centered at 470 nm. In addition, the color change of poly(PyrMMA-*r*-MMA-*r*-MSp) in solid state film was further demonstrated. A colorless film of

poly(PyrMMA-*r*-MMA-*r*-MSp) was spin-coated on a transparent glass substrate, followed by drying at 60 °C for 2 h. The film color was changed to blue upon UV irradiation and back to colorless by visible light (sunlight) exposure.

To further demonstrate the potential application of poly(PyrMMA-*r*-MMA-*r*-MSp) as a data recording material, UV writing and erasing experiments on the poly(PyrMMA-*r*-MMA-*r*-MSp) film was performed with masks of different patterns. As shown in Figure 4, upon UV irradiation, the unmasked regions turned to blue color, which still remained after removal of the mask. Two patterns, one with "ĐHBK" letters and the other of the flag of South Korea, were illustrated. Upon sunlight exposure for 60 min, the blue patterns were completely erased. The optical writing and erasing cycle was repeated for more than 30 times without any polymer degradation.

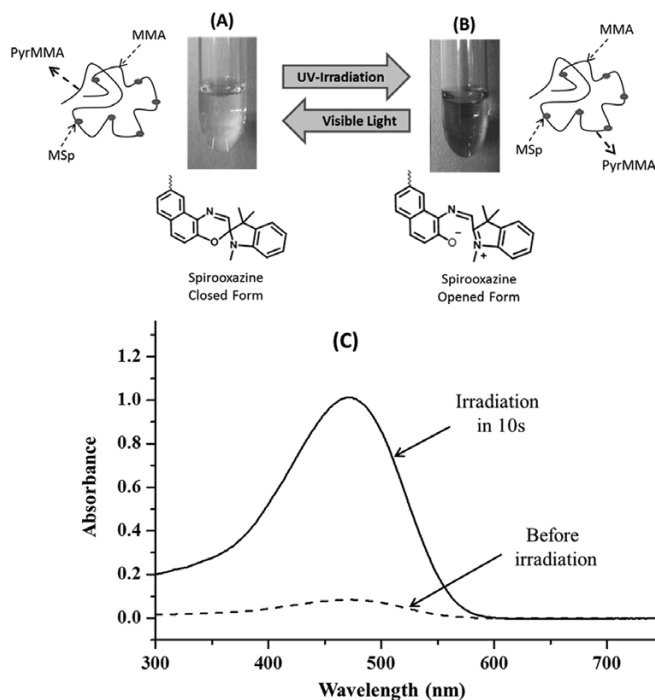


Figure 3. Poly(PyrMMA-*r*-MMA-*r*-MSp) in THF solution with MSp in closed form (A), poly(PyrMMA-*r*-MMA-*r*-MSp) in THF solution with MSp in opened form after UV irradiation (B), UV-Vis spectra of poly(PyrMMA-*r*-MMA-*r*-MSp) under UV-irradiation (C).

To investigate the sensing ability of poly(PyrMMA-*r*-MMA-*r*-MSp) toward CN⁻ in aqueous solution, 3 mg/mL aqueous solutions of poly(PyrMMA-*r*-MMA-*r*-MSp) containing CN⁻ at various concentrations (0.01 M HEPES buffer, pH 7.2) were prepared following the WHO guideline. As seen in Figure 5, the solutions containing CN⁻ turned to yellow color after UV irradiation (365 nm)

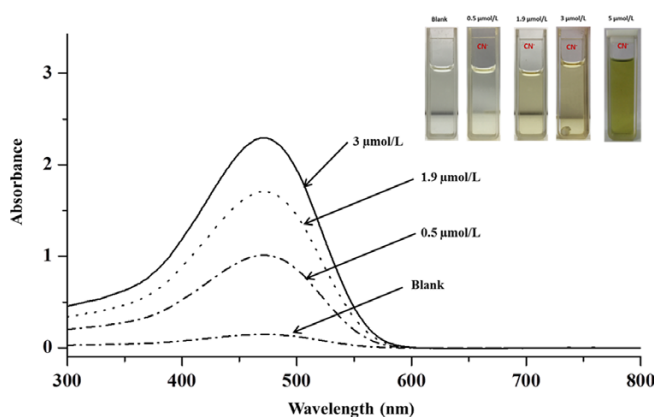


Figure 5. UV-vis spectra of aqueous solutions of poly(PyrMMA-*r*-MMA-*r*-MSp) in the presence of CN⁻ at different concentrations after UV irradiation, and corresponding images of the UV irradiated solutions.

as a result of the complexation of the MC form of spirooxazine with CN⁻, whereas the blank solution in the absence of CN⁻ remained colorless. The strength of the yellow color increased with increasing cyanide concentration (from 0.5 to 3 μmol/L). This was in accordance with increases in intensity of the absorbance at 483 nm.

The emission spectra of poly(PyrMMA-*r*-MMA-*r*-MSp) solutions before and after UV irradiation, when excited at the absorption maxima, were compared in Figure 6. The poly(PyrMMA-*r*-MMA-*r*-MSp) solution before UV irradiation displayed a fluorescence quantum yield of 0.62. The emission was quenched considerably when the solution was irradiated with UV light, attributed to FRET effect. The solution containing 1.9 μmol/L of CN⁻ after UV irradiation showed a quantum yield of 0.52, suggesting the adduct formation of the spirooxazine MC form with CN⁻ that

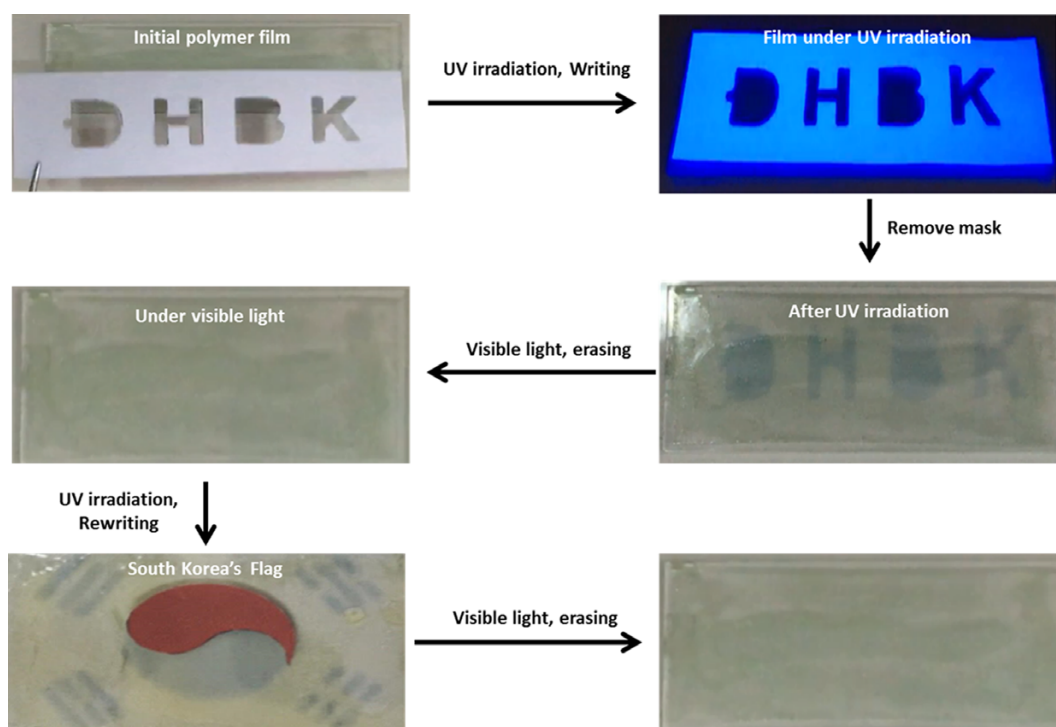


Figure 4. Optical writing and erasing experiments on a poly(PyrMMA-*r*-MMA-*r*-MSp) film spin-coated on a glass substrate (the red color was a piece of red sticker put on the surface to mimic the flag symbol, which was then removed in the subsequent erasing step).

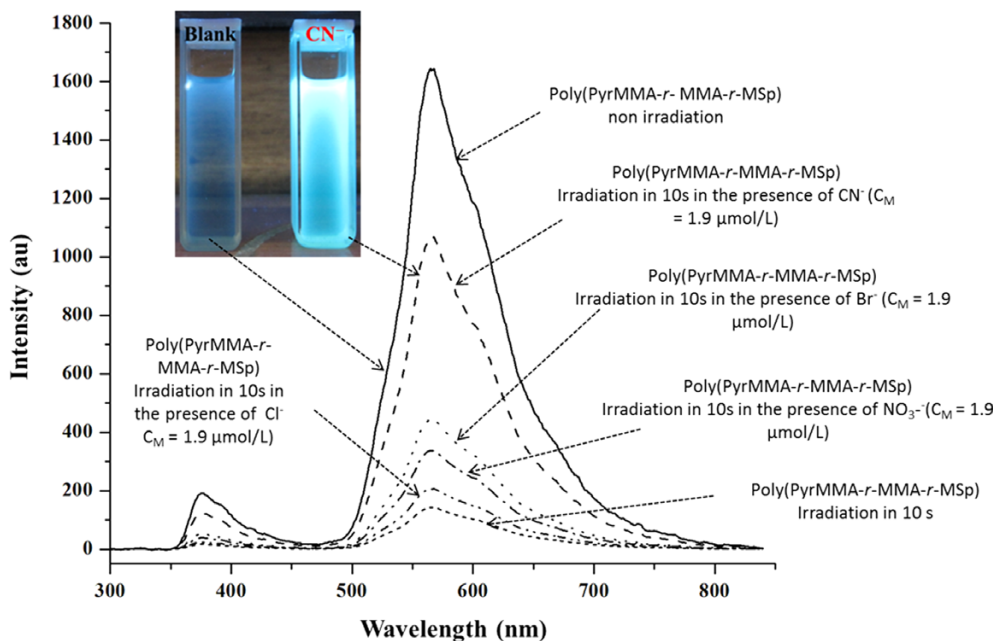


Figure 6. Emission spectra of the poly(PyrMMA-*r*-MMA-*r*-MSp) solutions before and after UV-irradiation for 10 s, and those containing 1.9 $\mu\text{mol/L}$ of anions (CN^- , Br^- , Cl^- , NO_3^-) after UV irradiation for 10 s.

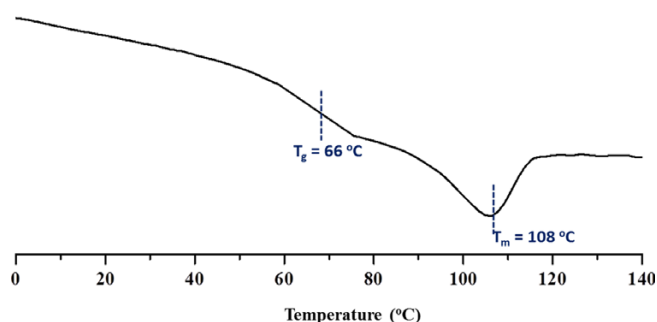


Figure 7. The DSC thermogram (second scan, exo up) of poly(PyrMMA-*r*-MMA-*r*-MSp).

prevents the FRET process.

Furthermore, the affinities of poly(PyrMMA-*r*-MMA-*r*-MSp) towards other anions, such as Br^- , Cl^- and NO_3^- were accessed. The emission spectra of the copolymer solutions in the presence of the corresponding anions displayed quantum yield values of ~ 0.23 , which is much smaller than the case of CN^- . This suggests that the spirooxazine MC form did not bind Br^- , Cl^- and NO_3^- efficiently, and hence the FRET quenching process still occurred. These results suggest the selective sensing ability of the copolymer for cyanide anions.

Last but not least, the DSC measurement of poly(PyrMMA-*r*-MMA-*r*-MSp) was performed to determine its thermal transitions. The DSC second-heating trace in the range from 0 to 150 $^\circ\text{C}$ of the poly(PyrMMA-*r*-MMA-*r*-MSp) showed a glass transition temperature (T_g) of around 66 $^\circ\text{C}$ and a melting transition (T_m) at about 108 $^\circ\text{C}$ (Figure 7).

4. Conclusions

In conclusion, we have successfully designed and synthesized a novel photoswitching poly(PyrMMA-*r*-MMA-*r*-MSp) via ATRP

method. The obtained copolymer has the average molecular weight of 7445 g mol^{-1} with polydispersity index of around 1.23. The poly(PyrMMA-*r*-MMA-*r*-MSp) copolymer exhibited excellent photochromic behavior in solid film under UV irradiation. Erasable and rewritable photoimaging on the solid film was successfully demonstrated. Poly(PyrMMA-*r*-MMA-*r*-MSp) could be a promising candidate for fundamental studies and eventual technical applications as optical data storage materials. Moreover, the poly(PyrMMA-*r*-MMA-*r*-MSp) copolymer also exhibited the sensing ability for cyanide anions in aqueous solution as revealed by the fluorescence spectrometry results.

Supporting information: Information is available regarding the experimental procedure for the synthesis and characterization of the methacrylate spirooxazine monomer and the FTIR spectrum of poly(PyrMMA-*r*-MMA-*r*-MSp). The materials are available *via* the Internet at <http://www.springer.com/13233>.

References

- (1) O. Emanuele and S. Paolo, *Adv. Mater.*, **26**, 1827 (2014).
- (2) T. Mizokuro, H. Mochizuki, A. Kobayashi, S. Horiuchi, N. Yamamoto, N. Tanigaki, and T. Hiraga, *Chem. Mater.*, **16**, 3469 (2004).
- (3) Z. Junji, Z. Qi, and T. He, *Adv. Mater.*, **25**, 378 (2013).
- (4) E. Fischer and Y. Hirshberg, *Royal Soc. Chem.*, 4522 (1952).
- (5) M. Dübner, V. J. Cadarso, T. N. Gevrek, A. Sanyal, N. D. Spencer, and C. Padeste, *ACS Appl. Mater. Interfaces*, **9**, 9245 (2017).
- (6) C. Ventura, P. Thornton, S. Giordani, and A. Heise, *Polym. Chem.*, **5**, 6318 (2014).
- (7) M. R. di Nunzio, P. L. Gentili, A. Romani, and G. Favaro, *J. Phys. Chem. C*, **114**, 6123 (2010).
- (8) V. A. Lokshin, A. Samat, and A. V. Metelitsa, *Russ. Chem. Rev.*, **71**, 893 (2002).
- (9) H. Bouas-Laurent and H. Dürr, *Pure Appl. Chem.*, **73**, 639 (2001).
- (10) A. J. Myles, T. J. Wigglesworth, and N. R. Branda, *Adv. Mater.*, **15**, 745 (2003).

- (11) S.-J. Lim, J. Seo, and S. Y. Park, *J. Am. Chem. Soc.*, **128**, 14542 (2006).
- (12) S.-J. Lim, B.-K. An, and S. Y. Park, *Macromolecules*, **38**, 6236 (2005).
- (13) T. Feczko, O. Varga, M. Kovács, T. Vidóczy, and B. Voncina, *J. Photochem. Photobiol. A: Chem.*, **222**, 293 (2011).
- (14) W. Shaodong, L. Xinghai, Y. Mei, Z. Yu, X. Keyu, and T. Rong, *Packaging Technol. Sci.*, **28**, 839 (2015).
- (15) G. Berkovic, V. Krongauz, and V. Weiss, *Chem. Rev.*, **100**, 1741 (2000).
- (16) J.-S. Lin, *Eur. Polym. J.*, **39**, 1693 (2003).
- (17) K. Ock, N. Jo, J. Kim, S. Kim, and K. Koh, *Synth. Met.*, **117**, 131 (2001).
- (18) P. J. Castro, I. Gómez, M. Cossi, and M. Reguero, *J. Phys. Chem. A*, **116**, 8148 (2012).
- (19) T. Suzuki, F.-T. Lin, S. Priyadashy, and S. G. Weber, *Chem. Commun.*, 2685 (1998).
- (20) M. Tomasulo, S. Sortino, A. J. P. White, and F. M. Raymo, *J. Org. Chem.*, **70**, 8180 (2005).
- (21) X. Meng, W. Zhu, Z. Guo, J. Wang, and H. Tian, *Tetrahedron*, **62**, 9840 (2006).
- (22) S.-H. Kim, C.-H. Ahn, S.-R. Keum, and K. Koh, *Dyes Pigm.*, **65**, 179 (2005).
- (23) M. M. Paquette, B. O. Patrick, and N. L. Frank, *J. Am. Chem. Soc.*, **133**, 10081 (2011).
- (24) M. Tanaka, K. Kamada, H. Ando, T. Kitagaki, Y. Shibutani, S. Yajima, H. Sakamoto, and K. Kimura, *Chem. Commun.*, 1453 (1999).
- (25) J. T. C. Wojtyk, E. Buncel, and P. M. Kazmaier, *Chem. Commun.*, 1703 (1998).
- (26) M. Tanaka, M. Nakamura, M. A. A. Salhin, T. Ikeda, K. Kamada, H. Ando, Y. Shibutani, and K. Kimura, *J. Org. Chem.*, **66**, 1533 (2001).
- (27) Y.-Y. Shi, L. Wu, J. Gao, and M. Shi, *J. Macromol. Sci., Part A*, **54**, 853 (2017).
- (28) M. Beija, M.-T. Charreyre, and J. M. G. Martinho, *Prog. Polym. Sci.*, **36**, 568 (2011).
- (29) S. Yitzchaik, J. Ratner, F. Buchholtz, and V. Krongauz, *Liq. Cryst.*, **8**, 677 (1990).
- (30) X. Li, C. Li, S. Wang, H. Dong, X. Ma, and D. Cao, *Dyes Pigm.*, **142**, 481 (2017).
- (31) F. Krohm, J. Kind, R. Savka, J. Alcaraz, D. Herold, H. Plenio, C. M. Thiele, and A. Andrieu-Brunsen, *J. Mater. Chem. C*, **4**, 4067 (2016).
- (32) G. K. Such, R. A. Evans, and T. P. Davis, *Mol. Cryst. Liq. Cryst.*, **430**, 273 (2005).
- (33) G. K. Such, R. A. Evans, and T. P. Davis, *Macromolecules*, **39**, 1391 (2006).
- (34) G. K. Such, R. A. Evans, and T. P. Davis, *Macromolecules*, **37**, 9664 (2004).
- (35) D. S. Achilleos and M. Vamvakaki, *Macromolecules*, **43**, 7073 (2010).
- (36) S. Chen, H. Liu, H. Cui, J. Hu, and H. Cai, *Des. Monomers Polym.*, **18**, 574 (2015).
- (37) H. T. Nguyen, L.-T. T. Nguyen, and T. V. Le, *Des. Monomers Polym.*, **18**, 271 (2015).
- (38) Y. Shiraishi, K. Adachi, M. Itoh, and T. Hirai, *Org. Lett.*, **11**, 3482 (2009).
- (39) S. Zhu, M. Li, L. Sheng, P. Chen, Y. Zhang, and S. X.-A. Zhang, *Analyst*, **137**, 5581 (2012).
- (40) I. S. Park, Y.-S. Jung, K.-J. Lee, and J.-M. Kim, *Chem. Commun.*, **46**, 2859 (2010).
- (41) K. Prakash, P. Ranjan Sahoo, and S. Kumar, *Sens. Actuators B*, **237**, 856 (2016).
- (42) Y. Shiraishi, S. Sumiya, K. Manabe, and T. Hirai, *ACS Appl. Mater. Interfaces*, **3**, 4649 (2011).
- (43) G. Lin, H. Ding, D. Yuan, B. Wang, and C. Wang, *J. Am. Chem. Soc.*, **138**, 3302 (2016).
- (44) J. Chao, H. Wang, Y. Zhang, C. Yin, F. Huo, J. Sun, and M. Zhao, *New J. Chem.*, **42**, 3322 (2018).
- (45) M. Shyamal, P. Mazumdar, S. Maity, G. P. Sahoo, G. Salgado-Morán, and A. Misra, *J. Phys. Chem. A*, **120**, 210 (2016).
- (46) A. Senthamizhan, A. Celebioglu, S. Bayir, M. Gorur, E. Doganci, F. Yilmaz, and T. Uyar, *ACS Appl. Mater. Interfaces*, **7**, 21038 (2015).
- (47) B. K. Rani and S. A. John, *Biosens. Bioelectron.*, **83**, 237 (2016).
- (48) T. H. Nguyen, L.-T. T. Nguyen, V. Q. Nguyen, L. Ngoc Tan Phan, G. Zhang, T. Yokozawa, D. Thuy Thi Phung, and H. Tran Nguyen, *Polym. Chem.*, **9**, 2484 (2018).
- (49) J. Berthet, S. Delbaere, L. M. Carvalho, G. Vermeersch, and P. J. Coelho, *Tetrahedron Lett.*, **47**, 4903 (2006).
- (50) J. You, J. A. Yoon, J. Kim, C.-F. Huang, K. Matyjaszewski, and E. Kim, *Chem. Mater.*, **22**, 4426 (2010).