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ORGANIC PHOTO-CATALYST FOR CONTROLLED SYNTHESIS OF POLY(METHYL METHACRYLATE) USING SPIROOXAZINE INITIATOR

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ABSTRACT

Photoinitiated metal-free controlled living radical polymerization of methyl methacrylates was investigated using the nuclear aromatic compound of pyrene. In the presence of photoredox catalysts and UV irradiation, spirooxazine initiator was used as initiator for polymerization of methyl methacrylate with good control over molecular weight in range of 10000 – 14000 g/mol and polydispersity below 1.5. Moreover, the obtained polymer also exhibited photochromic properties under UV irradiation both in solution and in solid state film. We are reliable believe that organic-based photoredox catalysts will enable new applications for controlled radical polymerizations in both small molecules and polymer chemistry.

Keywords: ATRP, methyl methacrylate, metal-free ATRP, polymerization, spirooxazine.

TÓM TẮT

Xúc tác hữu cơ cho quá trình polymer hóa poly(methyl methacrylate) sử dụng chất khơi mào spirooxazine

Quá trình polymer hóa methyl methacrylate được khảo sát sử dụng hợp chất vòng pyrene. Dưới quá trình chiếu sáng của tia UV và sự có mặt của hợp chất xúc tác quang và hợp chất khơi mào phản ứng polymer hóa spirooxazine, quá trình polymer hóa methyl methacrylate được thực hiện. poly(methyl methacrylate) được tổng hợp đạt trọng lượng phân tử trung bình khối trong khoảng 10.000 – 14.000 g/mol với độ đa phân tán của polymer thấp hơn 1.5. Hơn nữa polymer được tổng hợp thể hiện tính chất đổi màu dưới tác động của tia UV trong dung môi. Việc sử dụng xúc tác quang cho quá trình polymer hóa mở ra một hướng ứng dụng tiềm năng cho nhiều loại phân tử hữu cơ và trong lĩnh vực hóa học polymer.

Từ khóa: ATRP, methyl methacrylate, phản ứng ATRP không sử dụng kim loại, quá trình polymer hóa, spirooxazine.

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1. Introduction

The introduction of the controlled/living radical polymerization (CLRP) concept to synthetic polymer chemistry made it possible to synthesize various polymeric architectures with narrow molecular weight distribution, controlled average molecular weight and controlled chain-end functionality.[1] The most common methods for controlled polymerization include the atom transfer radical polymerization (ATRP),[2,3] Nitroxide-mediated radical polymerization (NMRP),4, 6 and reversible addition− fragmentation chain transfer (RAFT),[7,8] processes. Among them, ATRP is one of the most commonly used methods due to the availability of a broad scale of initiators and the application of a higher number of monomers.[9]

Traditional ATRP requires a low-oxidation state transition metal complex including CuX/L, X = Cl or Br and L = ligand in conjunction with an alkyl halide (R−X). The initiation mechanism involves a fast equilibrium of halogen abstraction/donation between CuX and R−X, where CuX_2 and radical of Rˆ are reversibly formed. In this fast equilibrium state, monomers can add to the alkyl radical, and the growing chains become dormant by halogen abstraction to yield CuX and Pn−X. In this equilibrium, the reverse reaction is favored and yields chains with R as the α-chain and halide as the ω-chain-end functionalities. Because of the fast initiation and the reversibility of the fast halide abstraction-donation steps, this process delivers polymers of target molecular weight with narrow molecular weight distribution.

Photochemical strategies have common advantages with respect to the other approaches as they facilitate possibility for temporal and spatial control over the polymerization processes. To take such advantages, light induced processes were often applied to controlled light radical polymerization (CLRP) techniques. Initially, the positive effect of light on ATRP systems was examined by Guan and Smart who performed ATRP by photochemical means with lower Cu(X) concentrations.[9-12] Following this study, several other approaches were reported to produce ATRP polymers using reduced amounts of inorganic catalyst.[13] In a more recent study, many research groups were also shown to display favorable thermodynamic characteristics to catalyze the syntheses of polymers with tunable molecular weights and low dispersities by metal-free photo ATRP. Miyake and co-workers used organic photoredox catalysts (perylene, diaryl dihydrophenazines) to mediate ATRP of methyl methacrylate (MMA) under visible light.[14-15] Recently, Cheng and co-workers used fluorescein as an organic catalyst for controlled polymerization of MMA.[16]

Herein we report metal-free ATRP of MMA using spirooxazine as initiator and its application in sensitive UV light materials. We also investigated the polymerization of MMA using pyrene as pho-organic catalyst under UV irradiation. The obtained polymers were characterized via gel permeation chromatography (GPC), nuclear magnetic resonance spectroscopy (1H NMR), UV-Vis and differential scanning calorimetry (DSC).

2. Experiment

2.1. Materials

2,7-dihydroxynaphthalene (97%, Sigma Aldrich), 1,3,3-Trimethyl-2-methyleneindolin (97%, Sigma Aldrich), methacryloyl chloride (97%, Sigma Aldrich), 2-Bromoisobutyryl bromide (Br-iBuBr), triethylamine (NEt_3, 99.9%) and pyrene was orderred from Sigma Aldrich. Methyl methacrylate (99% purity, Aldrich) was purified by vacuum distillation. Triethylamine (98%), $MgSO_4$ anhydrous, sodium hydroxide, acid sulfuric and sodium nitrite were purchased from Daejung. All other reagents and solvents unless otherwise stated were obtained from Aldrich at the highest purity and used without further purification.

2.2. Characterization

^1H NMR spectra were recorded in deuterated chloroform ($CDCl_3$) with TMS as an internal standard, on a Bruker Avance 500 MHz. 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– 700 nm. Differential scanning calorimetry (DSC) measurements were carried on a DSC Q20 V24.4 Build 116 calorimeter under nitrogen flow, at a heating rate of 10 ^oC/min. 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 weights and molecular weight distributions were calculated with reference to polystyrene standards.

2.3. Synthesis of 2,7-Dihydroxy-1-nitrosonaphthalene

After dissolving NaOH (2.5 g, 62.4 mmol) in 100 ml of H_2O, 2,7-dihydroxynaphthalene (1) (10 g, 62.4 mmol) and Na_2NO_2 (4.46 g, 64.6 mmol) were added to the solution and stirred for 1 hour at 60^{o}C. This solution was then cooled to 0^{o}C. The mixture of 8 ml of concentrated H_2SO_4 and 15 ml of distilled water was added dropwise to the reaction solution with the temperature remained at 0^{o}C. The reaction was continued for 1 h. After the reaction, compound 2 as a brown powder was obtained. Yield: 93%. ^1H NMR, 500 MHz, methanol-d_4, δ (ppm): 7.42 (d, 1H), 7.59 (d, 1H), 7.56 (d, 1H), 6.8 (d, 1H), 6.18 (s, 2H). IR (cm^{-1}): 3143 (O-H); 1301 (N=O).

2.4. ynthesis of 1,3,3-trimethylspiro[indoline-2,3'-naphtho[2,1-b][1,4]oxazin]-9'-ol (spirooxazine) (SP)

To a suspension of 2,7-dihydroxy-1-nitrosonaphthaline (compound 2) (1.88 g, 10 mmol) in absolute ethanol (50 ml) was added dropwise, under refluxing a solution of 1,3,3-

trimethyl-2-methyleneindoline (10 mmol) in absolute ethanol (5 ml). After continuous refluxing under a N_2-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 chloroform. Finally, the product was crystalized in methanol to obtain the pure white powder of spirooxazine. Yield: 53%. ^{1}H NMR, 300 MHz, $CDCl_3$, δ (ppm): 1.35 (s, 6H), 2.77 (s, 3H), 6.58 (t, 1H), 6.84 (d, 1H), 6.9 (t, 1H), 7.02 (d, 1H), 7.09 (d, 1H), 7.23 (t, 1H), 7.58 (d, 1H), 7.65 (d, 1H), 7.69 (s, 1H). FT-IR (cm-1): 3313 (O-H), 3065 (=C-H), 1627 (C=N).

2.5. Synthesis of spirooxazine initiator

The reaction was carried out in the nitrogen atmosphere. After dissolving spirooxazine-OH (compound 4),(34.4 mg, 0.1mmol) in 2 mL THF, the solution was cooled to 0°C. To the solution was added 2-bromo-2-methylpropionyl bromide (25μL) and 15μL triethylamine (Et_3N) as catalyst. Then the resulting purple solution was kept stirring for about 30 minutes at 0°C. After that, the temperature was allowed to arise to room temperature and the reaction was kept for 24 h. After the reaction finished, chloroform was added to the solution and diluted $NaHCO_3$ was poured into it, then shaked vigorously. Repeat this step 3 times. Then the organic phase was separated and the solvent was allowed to evaporate under reduced pressure. The product was purified by column chromatography using EtAc/ Hexane (1:10 (v/v)) as the eluent. Yield: 60%. ^{1}H NMR, 500 MHz, $CDCl_3$, δ (ppm): 2.1 (s, 6H), 2.76 (s, 2H) 2.77 (s, 3H), 5.6 (s, 1H), 6.3 (s, 1H), 6.58 (t, 1H), 6.84 (d, 1H), 6.9 (t, 1H), 7.02 (d, 1H), 7.09 (d, 1H), 7.23 (t, 1H), 7.58 (d, 1H), 7.65 (d, 1H), 7.69 (s, 1H).

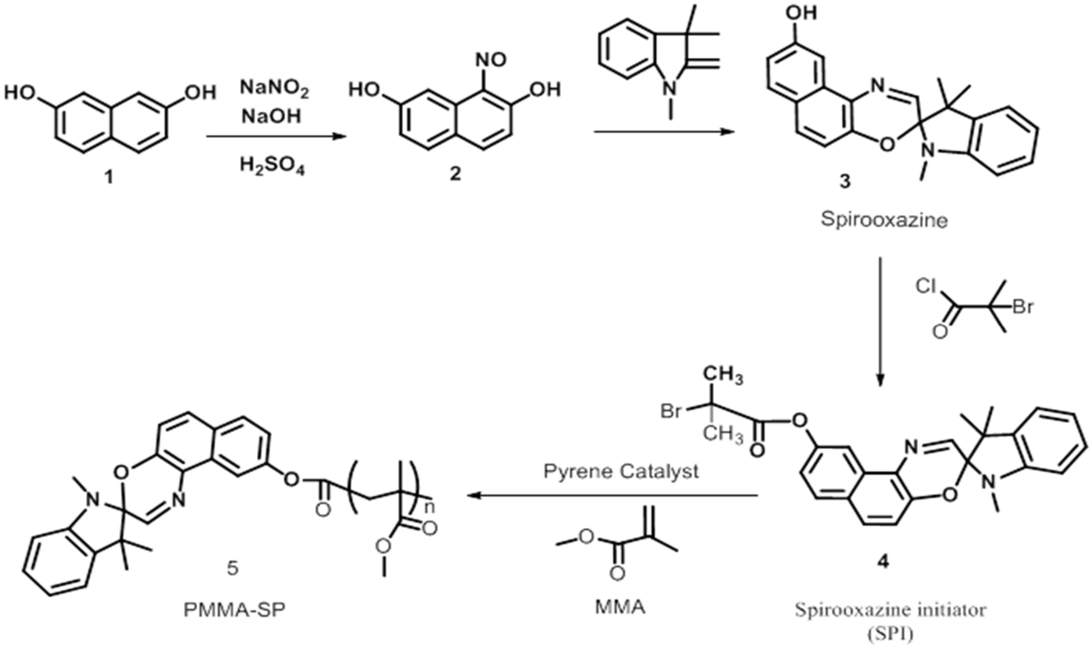
2.6. Synthesis of PMMA using pyrene as photo-catalyst with spirooxazine initiator

The polymerization reaction was performed in THF solvent with MMA(compound 9) as monomer, spirooxazine- as initior, pyrene as catalyst under nitrogen stream. To the solution of MMA (0,067 mL, 0.625 mmol) was added 1 mg of pyrene and spirooxazine (2.47 mg, 0.005 mmol) in 2 mL THF. Then the mixture was stirred to obtain a homogenous mixture. Next, the freeze-pump-thaw technique was adopted to rid the presence of oxygen of the reaction media (otherwise the reaction would not happen). The radical polymerization reaction was kept for 24h. The resulting mixture was precipitated in hexane and then the precipitate was centrifugally separated to obtain the solid product. Yield: 90%. ^{1}H NMR, 500 MHz, $CDCl_3$, δ (ppm): 0.7 – 2.1 (m, 11H), 2.67 (t, 3H), 3,6 (t, 3H), 6.5 – 8.5 (m, 9H).

3. Result and Discussion

First, 2,7-Dihydroxynaphthalene (1) was nitrosated by $NaNO_2$ in presence of NaOH and H_2SO_4 to obtain 1-nitrosonaphthalene-2,7-diol (2, scheme 1). Then, 1-

nitrosonaphthalene-2,7-diol reacted with 1,3,3-trimethyl-2-methyleneindoline to form spirooxazine-hydroxyl (3, Scheme 1), which subsequently reacted with 2-bromo-2-methylpropionyl bromide to give spirooxazine initiator (SPI) (4, scheme 1). The synthesis of poly(methyl methacrylate) using SPI was described as scheme 1.



***Scheme 1.** Synthesis of spirooxazine initiator (SPI) and poly(methyl methacrylate) (PMMA)*

The ^{1}H NMR spectrum of spirooxazine - hydroxyl (compound 3) 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 sprirooxazine – hydroxyl moieties. Figure 1 showed all characteristic peaks of sprirooxazine – hydroxyl compound and spirooxazine - initiator.

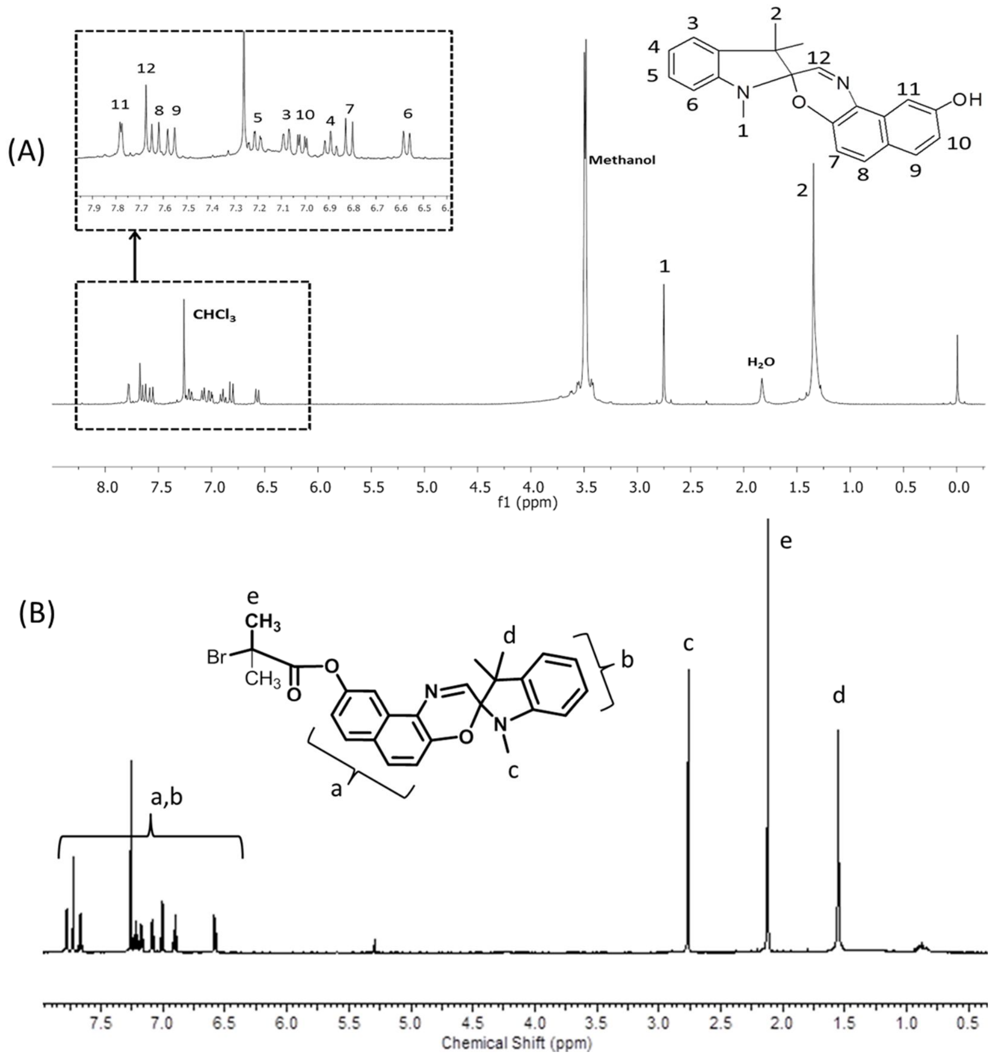


Figure 1. *^{1}H NMR spectrum of sprirooxazine – hydroxyl (A) and spirooxazine – initiator (B)*

Potential organic photocatalysts were examined in the polymerization of methyl methacrylate (MMA) using SPI as the alkyl bromide initiator. Excitingly, pyrene showed promise to mediate radical polymerization through an oxidative quenching pathway. Pyrene is the simplest dye, one of the oldest classifications of pigments. Pyrene dyes are well-established, stable colorants that have gained increasing attention in organic photovoltaics, are known to be strong reductants in their photoexcited state, and have found use as photoinitiators for polymerization.

Irradiation of a THF solution of MMA, SPI and pyrene ([MMA]:[SPI:[Pyrene] = 100:10:1) with a blue LED for 24 h afforded poly(methylmethacrylate)) in 87.8% yield with a weight-average molecular weight (M_n) of 13200 g/mol and relatively low dispersity

(PDI) of 1.27. The experimentally measured molecular weight (M_w) is much greater than the theoretical M_n (considering [MMA]:[SPI]). Control experiments revealed that omission of any single component (pyrene, SPI, or light source) resulted in no polymeric product, even after 72 h. Changing the light source to an orange LED also resulted in no polymerization, eliminating the possibility of a thermally initiated polymerization. The polymerization does not proceed in the presence of oxygen but can be run neat. Investigating the effects of solvent on polymerization provided the observation that, in general, less polar solvents increased the polymer yield. For example, when methanol was used as the solvent, the resulting polymer was isolated in a low 17.8% yield, with a low M_n of 2100 g/mol kDa. When the polymerization was performed in ethyl acetate, the polymer product was isolated in 20% yield with an average M_n of 4300 g/mol. In the other hand, When we performed the polymerization in toluene, the yield of reaction was obtained the yield of 80.4% (M_n = 14600 g/mol, unfortunately, this was accompanied by a large increase in PDI to 1.8. Especially, the polymerization was controlled in the best manner in THF solvent, with the yield of 90-92%, and M_n = 13200 g/mol with low polydispersity (PDI < 1.5). Table 1 present the effect of different solvent to the polymerization of MMA.

Table 1. *Results of the Polymerization of MMA Using Pyrene as the Photocatalyst in different solvents*

Run no	[MMA]:[SPI:[Pyrene]	Solvent	M_n (g/mol)	PDI
PMMA-1	100:10:1	Methanol	2100	1.41
PMMA-2	100:10:1	THF	13200	1.27
PMMA-3	100:10:1	Ethyl acetate	4300	1.56
PMMA-4	100:10:1	Toluene	14600	1.8

The resulted polymers were characterized via GPC to determine the M_n of polymer. Figure 2 exhibited the GPC traces of PMMA. It is clear that the conversion of monomer was increase gradually with time reaction that would be referred to the chain growth polymerization mechanism. As seen in Figure 2, the molecular weight of PMMA was accelerated at the beginning stage of polymerization (6h), and the polymerization reaches to the consummation of MMA monomer in 24h.

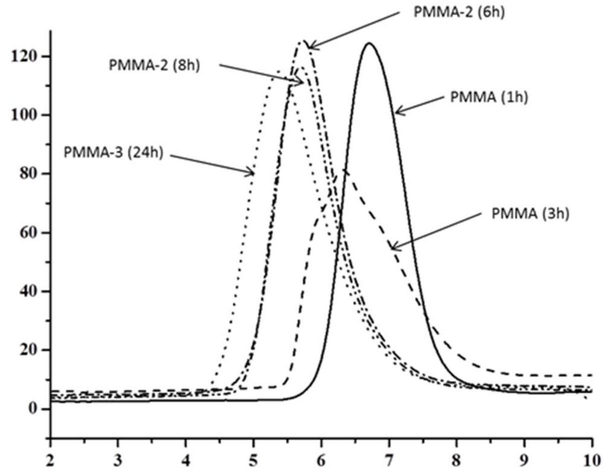


Figure 2. *GPC trace of synthesized PMMA following time reaction*

The obtained PMMA was characterized via ^{1}H NMR spectrum, as seen in Figure 3. The characteristic peaks of PMMA including spirooxazine inhibitor were fully observed in the ^{1}H NMR spectrum. The peaks in range of 6.5 – 8.5 ppm which corresponding to the spirooxazine proton, and peaks in range of 0.7 – 2.1 ppm that exhibited for MMA moieties. The peaks at 3.6 ppm (peak h, Figure 3) which is corresponding to the proton of methyl group in MMA units. It is also clear that the polymerization was initiated form spirooxazine as efficient inhibitor.

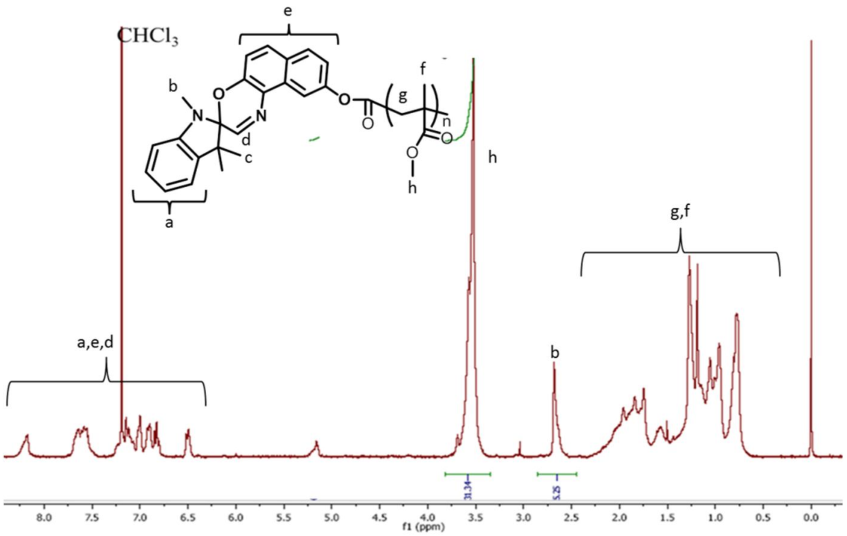


Figure 3. *^{1}H NMR of PMMA-SP*

The solution of PMMA-SP in THF (0.16 mM) was prepared to check the absorption of PMMA-SP after and before irradiation. Before irradiation process, the solution of PMMA-SP has a colorless. PMMA-SP solution was irradiated under 365 nm of UV light, the colorless solution immediately changes to light blue and come back the colorless if removing of UV-irradiation. The Figure 4 exhibited the color exchange of PMMA-SP under UV-irradiation.

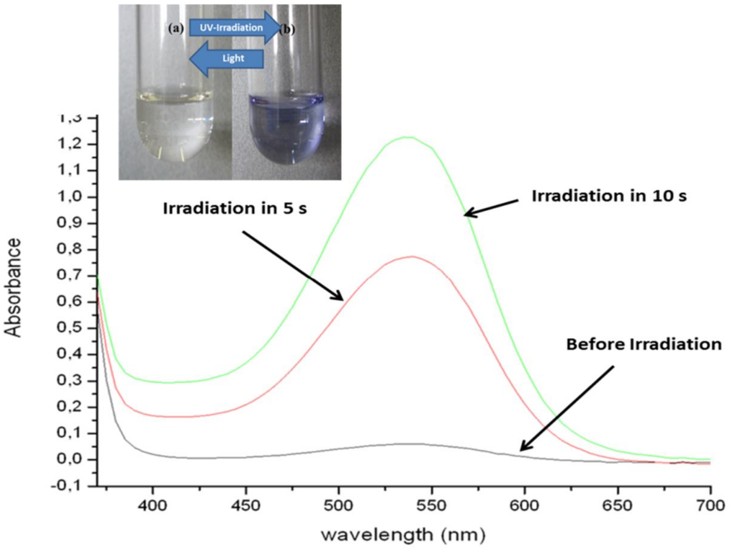


Figure 4. *UV-Vis of PMMA-SP under UV-irradiation*

4. Conclusion

In conclusion, we have successful synthesized the PMMA using pyrene as oganic photo-catalyst with SPI as initiator. Spirooxazine initiator was synthesized via three steps including of nitrosation, imination and esterification. The obtained PMMA-SP) structure was confirmed by ^{1}H NMR spectrum and its molecular weight was analysized via GPC traces. The polymerization of MMA exhibited was investigated in different solvents. The PMMA-SP exhibited the exchange color properties under UV-irradiation which would be reasonable for photoresponsive polymer film using in optical data recording application.

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REFERENCES

[1] Braunecker, W. A.; Matyjaszewski, K., “Controlled/living radical polymerization: Features, developments, and perspectives,” *Prog. Polym. Sci*., 32 (1), pp. 93−146, 2007.

[2] Matyjaszewski, K.; Xia, J. H., “Atom transfer radical polymerization,” *Chem. Rev*., 101 (9), pp. 2921−2990, 2001.

[3] Wang, J. S.; Matyjaszewski, K. “Controlled Living Radical Polymerization - Atom-Transfer Radical Polymerization in the Presence of Transition-Metal Complexes,” *J. Am. Chem. Soc*. 117 (20), pp. 5614−5615, 1995.

[4] Hawker, C. J.; Bosman, A. W.; Harth, E. “New polymer synthesis by nitroxide mediated living radical polymerizations,” *Chem. Rev*.,101 (12), pp. 3661−3688, 2001.

[5] Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. “Development of a universal alkoxyamine for "living" free radical polymerizations,” J. *Am. Chem. Soc*., 121 (16), pp. 3904−3920, 1999.

[6] Audran, G.; Bremond, P.; Marque, S. R. A. “Labile alkoxyamines: past, present, and future. Chem. Commun,” 50 (59), pp. 7921−7928, 2014.

[7] Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. “Living free-radical polymerization by reversible addition-fragmentation chain transfer: The RAFT process,” *Macromolecules*, 31 (16), pp. 5559−5562, 1998.

[8] Moad, G.; Rizzardo, E.; Thang, S. H. “Living radical polymerization by the RAFT process,” *Aust. J. Chem*, 58 (6), pp. 379−410, 2005.

[9] Matyjaszewski, K. “Atom Transfer Radical Polymerization (ATRP): Current Status and Future Perspectives,” *Macromolecules*, 45 (10), pp. 4015-4039, 2012.

[10] Guan, Z. B.; Smart, B. “A remarkable visible light effect on atomtransfer radical polymerization,” *Macromolecules*, 33 (18), pp. 6904−6906, 2000.

[11] Pan, X. C.; Malhotra, N.; Simakova, A.; Wang, Z. Y.; Konkolewicz, D.; Matyjaszewski, K. “Photoinduced Atom Transfer Radical Polymerization with ppm-Level Cu Catalyst by Visible Light in Aqueous Media,” *J. Am. Chem. Soc*., 137 (49), pp. 15430-15433, 2015..

[12] Wang, Y.; Zhang, Y. Z.; Parker, B.; Matyjaszewski, K. “ATRP of MMA with ppm Levels of Iron Catalyst,” *Macromolecules*, 44, 13, pp. 4022−4025, 2011.

[13] Nikolaou, V.; Anastasaki, A.; Alsubaie, F.; Simula, A.; Fox, D. J.; Haddleton, D. M. “Copper(II) gluconate (a non-toxic food supplement/dietary aid) as a precursor catalyst for effective photo-induced living radical polymerisation of acrylates,” *Polym. Chem*, 6 (19), 3581-3585. 2012, 45 (10), pp. 4015-4039, 2015.

[14] Miyake, G. M.; Theriot, J. C. "Perylene as an Organic Photocatalyst for the Radical Polymerization of Functionalized Vinyl Monomers through Oxidative Quenching with Alkyl Bromides and Visible Light," *Macromolecules*, 47, pp. 8255-8261, 2014.

[15] Theriot, J. C.; Lim, C.-H.; Yang, H.; Ryan, M. D.; Musgrave, C. B.; Miyake, G. M. "Organocatalyzed atom transfer radical polymerization driven by visible light," *Science*, 352, pp. 1082-1086, 2016.

[16] Liu, X.; Zhang, L.; Cheng, Z.; Zhu, X. "Metal-free photoinduced electron transfer−atom transfer radical polymerization (PET−ATRP) via a visible light organic photocatalyst," *Polym. Chem*, 7, pp. 689-700, 2016.