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Research Article

SYNTHESIS OF PMMA THROUGH PHOTO-INDUCED ATOM TRANSFER RADICAL POLYMERIZATION USING NOVEL PERYLENE-PHENOXAZINE-BASED ORGANO-CATALYST

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ABSTRACT

Poly(methyl methacrylate) (PMMA) is synthesized using a novel organo-catalyst derived from 10-(perylen-yl)-10H-phenoxazine (PHP) under UV irradiation at an ambient temperature. The study aims to demonstrate the capability of PHP in synthesizing PMMA via photo-induced ATRP and suggests a proper molar ratio of reactants engaged in the synthesis process to obtain outcome PMMA in terms of molecular weight and low polydispersity. In the O-ATRP process, the influence of the reaction conditions, including the molar ratios of catalyst and monomer, the initiator content, solvents, and the reaction time on the polymerization of PMMA were studied. The obtained PMMA was characterized using gel permeation chromatography (GPC) measurements to reveal the effect of the individual reaction condition on the outcome polymer. The experiment result shows a high monomer conversion of MMA with the novel PHP organo-photocatalyst (~75%). Among the investigated parameters, the concentration of PHP photocatalyst and polymerization time strongly affect the conversion and polydispersity of the obtained PMMA. Meanwhile, the concentration of the initiator is found to not significantly impact the outcomes of the O-ATRP. Furthermore, the characteristics of PMMA considerably depend on the polarity of the solvent. The higher conversion resulting in a higher molecular weight could be achieved with the solvent having lower polarity. With the increase in conversion, the PHP photocatalyst-based O-ATRP was demonstrated to produce well-controlled PMMA, which has polydispersity lower than 1.5. The optimized reacting system with a molar ratio of [Monomer]:[Initiator]:[PHP] = [100]:[1]:[0.05] under the UV irradiating period of 8 hours produced PMMA with Mn = 28,360 and polydispersity Đ = 1.25, respectively.

Keywords: ATRP; catalyst; perylene; phenoxazine; PMMA; polymerization

1. Introduction

Atom transfer radical polymerization (ATRP) is considered one of the powerful approaches to synthesizing a variety of polymers applied in numerous technical fields such as biomaterials, photo, and electronic materials (Matyjaszewski et al., 2012). Although the

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transition metal-mediated ATRP is commonly exploited to successfully produce polymers, possessing well-defined polymers with various desired structures, molecular weight, and narrow polydispersity, the trace of metal catalysts existing in the produced polymers is the limitation of the ATRP in such applications (Liu et al., 2016). Several efforts attempting to reduce and remove the metal catalysts from the final products have been conducted. However, a concern about difficulties in completely scavenging metals was reported. Therefore, several photoredox catalysts (PCs) derived from organic compounds such as pyrene, perylene, phenothiazines, and phenoxazines have been studied to alter the transition metal ones (Tran et al., 2019; Theriot et al., 2017). Such PCs have been demonstrated to mediate the ATRP with many advantages such as low catalyst loading in ppm, low energy consumption by using UV light, harmless for humans, and easy operation, which enables the metal-free ATRP to promisingly become environmentally friendly (Corbin et al., 2022).

Photocatalyst serves an important role in the activation of the ATRP process. Perylene was used to mediate an organo-ATRP (O-ATRP) of MMA through visible light. PMMA was produced with a small amount of perylene (< 1000 ppm). However, the low initiator efficiency (Ieff) of the process in a range of 0.01 to 0.049 leads to a large fluctuation in the polydispersity index (PDI) (Miyake et al., 2014). Matyjaszewski et al. successfully synthesized PMMA by O-ATRP under 380 nm light irradiance via light emitting diode (LED) using phenothiazine (PTH) with a loading of 1000 ppm. The resulting polymer has a PDI of 1.4 but the monomer conversion is relatively low (16%) (Pan et al., 2016). Phenoxazines have received considerable studies for O-ATRP because of their strong reducing property and high capability of visible light absorption (Pearson et al., 2016). Moreover, an extension of conjugation units on the phenoxazine core could alter the catalyst's absorption to be red-shifted and improve the visible light absorption of the catalyst (Pearson et al., 2016; Theriot et al. 2016; Swisher et al., 2021). In our previous study, the 10- (Perylene-3-yl-10H-Phenoxazine (PHP) photocatalyst was prepared with two components of perylene and phenoxazine (Vo et al., 2020). The PHP catalyst was found to enhance the visible light absorption via the combination of perylene and phenoxazine core, and thus it is proper to mediate the O-ATRP of vinyl monomers.

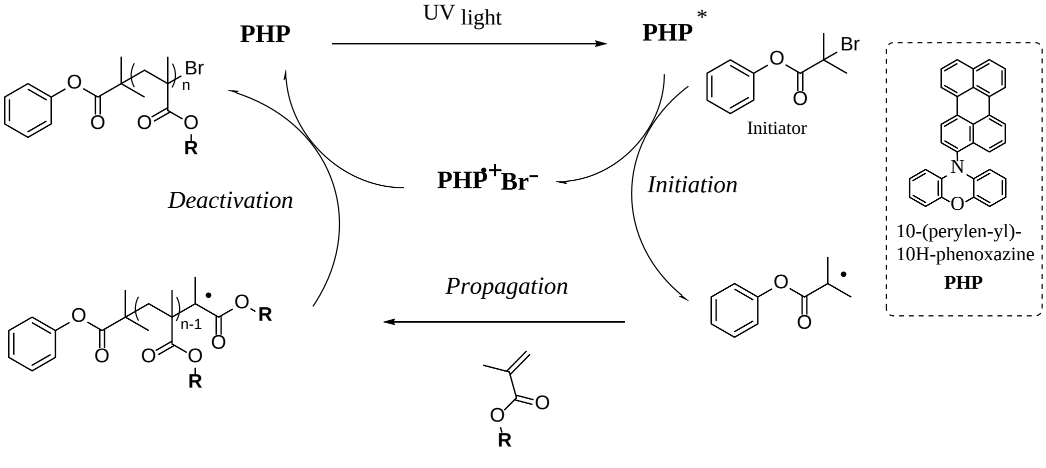

Figure 1. *Conceptual mechanism of the O-ATRP for MMA using PHP as the photocatalyst*

The polymerization of MMA is based on O-ATRP using PHP as the photocatalyst (Fig. 1). The photoexcitation of ground-state PHP to excited-state PHP* is triggered under UV irradiation. The PHP* directly reduces the PhBMP initiators to active radicals leading to the propagation of the polymer and producing a complex of deactivator $PHP^{\bullet+}Br^{-}$. Then, the relative complex deactivator oxidizes the active radicals to reversibly deactivate polymerization and regenerate the initiator. The controlled polymerization cycle depends on the established balance between activation and deactivation rates, in which the inherent property of monomer, monomer/initiator molar ratio, the reactant concentrations, and the ATRP efficiency of the catalyst as well as initiator strongly affect the activation and deactivation (Matyjaszewski et al., 2006). Consequently, the components involved in the synthesis system are crucial to define the characteristics, in terms of molecular weight, PDI, and structure of the synthesized polymer.

In this work, we synthesize PMMA via O-ATRP using PHP as the photocatalyst under UV light. The effects of synthesis conditions of the polymerization, including PHP content, reaction time, MMA concentration, solvents with different polarity, and initiator concentration on the molecular weight and PDI of the achieved PMMA are systematically investigated. Accordingly, we attempt to prove the ability of PHP catalyst in O-ATRP for preparing PMMA and appropriately select the proper molar ratio of synthesis components for the well control of PMMA via O-ATRP.

2. Experimentation

2.1. Materials

Perylene (99%), Phenoxazine (99%), and Palladium acetate (Pd(OAc)2) (99%) were provided from Sigma Aldrich (USA). N-Bromosuccinimide (NBS) (99%), tri-tertbutyl phosphine ($P(t\text{-}Bu)_3$) (98%), sodium tertbutoxide (NaOt-Bu) (97%), and methyl methacrylate (MMA) were obtained from Merck (Germany). Phenyl 2-bromo-2-methylpropanoate ($C_{10}H_{11}BrO_2$) was prepared at our lab. All the solvents used in the study were purchased from Fisher Chemicals.

2.2. Characterization

The monomer conversion, number average molecular weight (M_n), and polydispersity Đ (M_w/M_n) of the polymers were measured with a calibration based on polystyrene standard, using a gel permeation chromatography (GPC) equipped with a refractive index detector (PL-GPC 50, Agilent). Tetrahydrofuran (THF) was used as an eluent with a flow rate of 1 $mL\times min^{-1}$ at 25^{o}C. The presence of the chemical functional groups in the resulting polymers was determined by an FT-IR (Bruker Tensor 27).

The polymerization yield or monomer conversion is defined as an equation (1). Where, m is the weight of PMMA; m_I, m_{PHP}, and m_M are the weight of initiator, PHP catalyst, and monomer, respectively.

$$Conversion\ (\%) = \frac{m - m_I - m_{PHP}}{m_M} \tag{1}$$

The polydispersity index (PDI) is calculated by equation (2). Where $M_{n,GPC}$ and $M_{w,GPC}$ are the number average molecular weight and mass molecular weight of the PMMA, respectively which are determined by GPC measurements.

$$PDI = \frac{M_{n,GPC}}{M_{w,GPC}} \tag{2}$$

The initiator efficiency (I_{eff}) is defined as the fraction of the radicals produced upon decomposition of the initiator that should initiate propagating chains, the calculation is presented in equation (3).

$$I_{eff} = \frac{M_{n,theory}}{M_{n,GPC}} \tag{3}$$

Where, $M_{n,\ theory}$ is the theoretical number average molecular weight of the PMMA.

2.3. Synthesis of 3-bromoperylene

3-bromoperylene was prepared by allylic bromination (Vo et al., 2020; Quasdorf et al., 2022). For this, perylene (600 mg, 2.378 mmol) was added into 10 ml DMF in a two-necked reaction flask covered by aluminum foil to prevent light exposure. The flask was cooled to 0^o C before slowly adding the solution of NBS (423.25 mg, 2.378 mmol) in 5 ml DMF through a dropping funnel. The reaction was carried out under stirring conditions for 4 hr and then 20 hr at ambient temperature. Finally, an HCl solution of 2 M was added to the flask to terminate the reaction. Next, the obtained solution was extracted with 100 ml $CHCl_3$ before drying with anhydrous K_2SO_4. Finally, yellow powder of 3-bromoperylene was obtained through precipitation with cold n-hexane before drying under a vacuum ambient.

^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 8.23 (d, 1H), 8.20 (d, 1H), 8.15 (d, 1H), 8.07 (d, 1H), 7.99 (d, 1H), 7.76 (d, 1H), 7.71 (d, 2H), 7.58 (t, 1H), 7.49 (t, 2H).

2.4. Synthesis of phenyl 2-bromo-2-2methylpropanoate (PhBMP) initiator

PhBMP initiator was synthesized by the reaction esterification between benzyl alcohol and 2-bromo-2-methylpropanoyl chloride. For this, the dry reaction flask was flamed under vacuum conditions and purged three times by N_2 gas. Then, phenol (10 mg) was added into the flask containing 10 ml anhydrous THF solution at 0^o C under N_2 condition. The solution of 2-bromo-2-methylpropanoyl chloride (21.45 mg) and THF (10 ml) was dropwise added into the flask at 0^o C and then continuously stirred for 4 hr at ambient temperature. After that, 10 ml of distilled water was introduced into the reaction mixture before extracting with CH_2Cl_2. The organic component was dried over anhydrous K_2CO_3 after washing with 10 % $Na_2S_2O_3$ and 10 % KOH solutions, respectively. Finally, the obtained PhBMP was purified via column chromatography using EtOAc/henxane (50/50 wt%) eluent (yield 97%, R_f 0.7).

^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.31 (t, 3H), 7.520 (d, 2H), 1.98 (d, 6H).

2.5. Synthesis of 10-(perylen-yl)-10H-phenoxazine (PHP)

The preparation of the photocatalyst PHP was based on our previous study (Vo et al., 2020). Briefly, after flaming a dry reaction flask under vacuum pressure and back-filling with N_2 three times, phenoxazine (183.21 mg), NaOtBu (144.15 mg), $Pd(OAc)_2$ (4.49 mg), $P(tBu)_3$ (8.09 mg) and anhydrous toluene (45 ml) were added. 3-bromoperylene (331.21 mg) was then added after evacuating the flask under the N_2 atmosphere three times. Next, the C-N coupling reaction took place under stirring for 24 hr at the temperature of 110° C. The flask was then cooled to room temperature before diluting the solution in the flask with $CHCl_3$. The flask was subsequently washed with water and brine, dried with K_2CO_3, and purified by column chromatography (3.3 % EtOAc/hexane). Finally, the red-orange solid of PHP photocatalyst was obtained with a yield of 78% by vacuum drying.

^1H NMR (500 MHz, CDCl3), δ (ppm): 8.34 – 7.48 (m, 11H), 6.73 (d, 2H), 6.64 (t, 2H), 6.53 (t, 2H), 5.89 (d, 2H).

2.6. General procedure for photoinduced ATRP

The synthesis of PMMA was conducted via metal-free ATRP under UV light using PhBMP and PHP as the initiator and photocatalyst, respectively. In a reaction flask, PhBMP (11.43 mg, 47 µmol) and degassed THF (1 ml) were added and stirred to become homogenous. After that, MMA (0.5 ml, 4.7 mmol) was added before the addition of PHP (2.1 mg, 4.7 µmol). The flask was then degassed through a freeze-pump-thaw process with three cycles. After continuously stirring to obtain a homogenous solution, the flask was placed in a UV reactor emitting light having a wavelength of 365 nm for 24 hr at an ambient temperature. The reaction mixture was collected, and the polymer product was isolated by precipitation in cold methanol, followed by drying under reduced pressure.

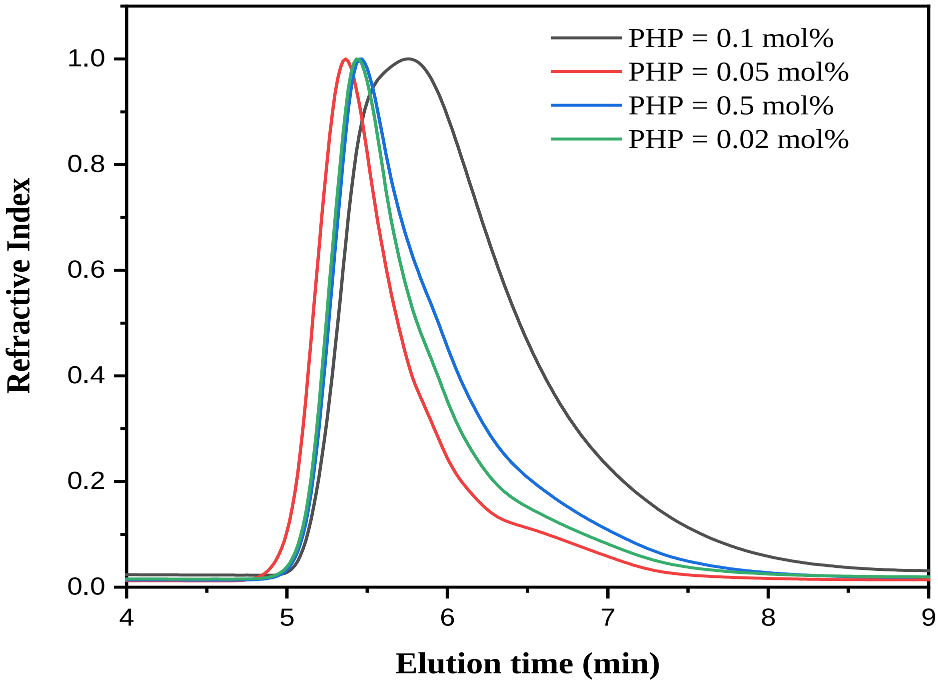

Figure 2. *GPC curves of PMMA via O-ATRP with different catalyst content*

3. Results and discussion

3.1. Effect of organic photocatalyst content

To understand the effect of the photocatalyst content on the polymerization of MMA by O-ATRP, the PHP content is varied in a range of 0.02 to 0.5 molar ratio. The reaction was carried out in the two-necked flask, previously scavenged oxygen through a three-time freeze-pump-thaw cycle. The O-ATRP was activated by UV irradiation of 365 nm with an intensity of 2.2 mW×cm^{-1} in 24 hr. The GPC curves of PMMA synthesized with various PHP photocatalyst content are presented in Figure 2. It shows that PMMA prepared by the PHP photocatalyst of 0.05 molar ratio has not only the lowest elution time but also the narrowest peak width, implying that the obtained PMMA possesses both the highest molecular weight and the lowest PDI. Moreover, the photocatalyst content lower or higher than 0.05 molar ratio results in a decline in the monomer conversion and an increase in PDI, which is unfavorable for the O-ATRP. The PHP content of 0.05 molar ratio provides the relative polymer with the lowest PDI of 1.28. Table 1 shows the characteristics of the synthesized PMMA depending on the amount of PHP photocatalyst in O-ATRP. It is revealed that the conversion of MMA increases and decreases around the peak at nearly 75 %, which is relevant to the PHP content of 0.05 molar ratio. Moreover, the prepared PMMA has a molar molecular weight (M_n) higher than 18×10^3 g×mol^{-1}, differing from the theoretical M_n design, while the PDI fluctuates around 1.28 to 1.44.

Table 1. *Effect of the amount of PHP photocatalyst on the O-ATRP of MMA*

[MMA]:[I]:[PHP] molar ratio	Conversion (%)	$M_{n,theory}$ (g×mol^{-1})	$M_{n,GPC}$ (g×mol^{-1})	$M_{w,GPC}$ (g×mol^{-1})	I_{eff}	DPI
[100]:[1]:[0.02]	56.42	5,642	24,910	33,677	0.23	1.35
[100]:[1]:[0.05]	77.61	7,761	30,450	38,880	0.25	1.28
[100]:[1]:[0.1]	60.00	6,000	17,970	25,742	0.33	1.43
[100]:[1]:[0.5]	62.69	6,269	21,670	31,160	0.29	1.44

Regardless of the GPC and characteristic results in Figure 2 and Table 1, the PDI is lower than 1.44 indicating a well-control of O-ATRP using PHP photocatalyst. Meanwhile, the experimental M_n is larger than the theoretical Mn, which could be due to the coupling or combination between the two propagating radicals to form an irreversible C-C bond during the O-ATRP (Swisher et al., 2021; Truong et al., 2021). This is correlated with the insignificant change of I_{eff}, which is in a range of 0.23 to 0.33, even though the molar ratio of PHP content considerably increases. Particularly, the O-ATRP using merely PHP content of 500 molar ratio (500 ppm) could produce PMMA owning an M_n bigger than 30,000 g×mol^{-1} with a low PDI of 1.28, implying a well-defined polymer. Based on the results, the PHP photocatalyst is suggested to remain at 0.05 molar ratio for the O-ATRP.

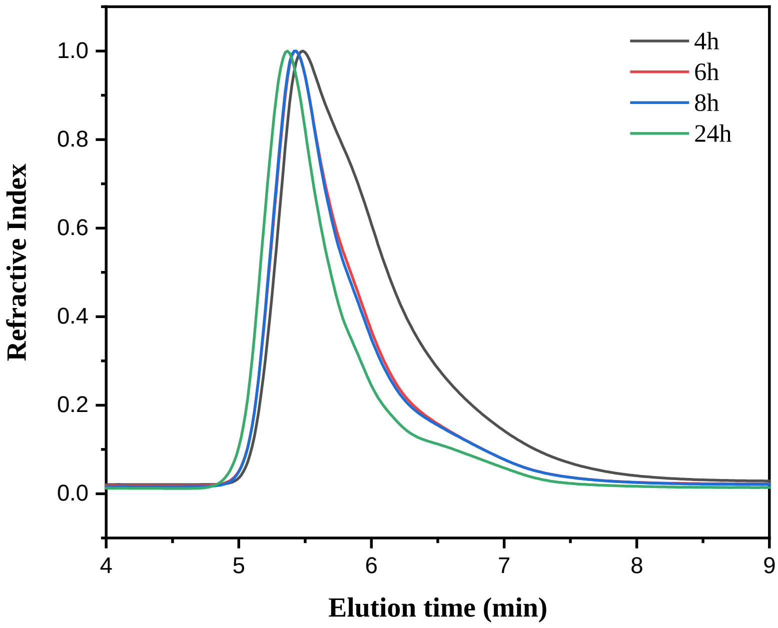

Figure 3. *GPC curves of PMMA via O-ATRP with various polymerization time*

3.2. Effect of polymerization time

GPC curves of PMMA via O-ATRP with various polymerization times illustrated in Figure 3 show that increasing reaction time to 8 hr benefits both the molecular weight and the PDI for the obtained PMMA. The PDI reduces from 1.45 to the lowest value of 1.25 when increasing reaction time from 4 to 8 hr. However, the polymerization time longer than 8 hr is found to not only insignificantly increase the conversion but also slightly enlarge the PDI of the relative polymer. According to the GPC results in Figure 3, the width of the peak is narrowed, while the shifting of the peak is negligible during the period of reaction time from 4 to 24 hr. The effect of polymerization time on the characteristics of the obtained PMMA is shown in Table 2. Prolonging reaction time increases the conversion of MMA, and accordingly the M_n of the relative polymer. Furthermore, the I_{eff} is observed to grow from 0.17 to the highest value of 0.26 in the range of the reaction time from 4 to 8 hr and remaining in further period of the polymerization. It reveals that the increase in I_{eff} contributes to the growth of the PMMA.

Table 2. *Effect of the reaction time on the O-ATRP of MMA*

Reaction time (hr)	**Conversion (%)**	**$M_{n,theory}$ (g×mol^{-1})**	**$M_{n,GPC}$ (g×mol^{-1})**	**$M_{w,GPC}$ (g×mol^{-1})**	**I_{eff}**	**PDI**
4	33.18	3,318	20,210	29,305	0.17	1.45
6	54.60	5,460	25,160	33,866	0.22	1.35
8	74.70	7,470	28,360	35,423	0.26	1.25
24	77.61	7,761	30,450	38,880	0.25	1.28

The observation indicates that the O-ATRP occurs in a short time and reaches a high conversion of about 75% in 8 hr (Table 2). Moreover, the synthesis of PMMA longer than 8 hr is unfavorable for the O-ATRP since the increase in viscosity of the reacting solution could impede the diffusion of radicals for the propagation of the polymer (Corbin et al., 2022; Vieira et al., 2016). Notably, rising polymerization time inconsiderably affects the M_n of the obtained PMMA, but significantly suppresses the PDI. This indicates a profound impact of reaction time on the uniform chain length of the relative polymer synthesized by O-ATRP using a PHP photocatalyst. Consequently, the polymerization time of 8 hr is suggested for the O-ATRP process.

3.3. Effect of monomer concentration

Figure 4 illustrates the GPC curves of PMMA synthesized by O-ATRP using various monomer concentrations. It is observed that the elution time of the obtained PMMA decreases as monomer concentration increases, proving the propagation of the relative polymer. The significant decrease in the PDI from 1.40 to 1.25 with the monomer concentration of 100 molar ratios indicates the well-defined PMMA. However, the monomer concentration higher than the 200 molar ratio is insufficient for the synthesized PMMA due to the unimprovement of the PDI. The characteristics of the PMMA synthesized by O-ATRP with different monomer concentrations are shown in Table 3. Increasing monomer concentration has a profound effect on the polymerization yield. The conversion of MMA increases from 39% to 85% when the I_{eff} rises steeply and reaches the highest value of 1.35 when the MMA concentration increases from 50 to 500 molar ratio.

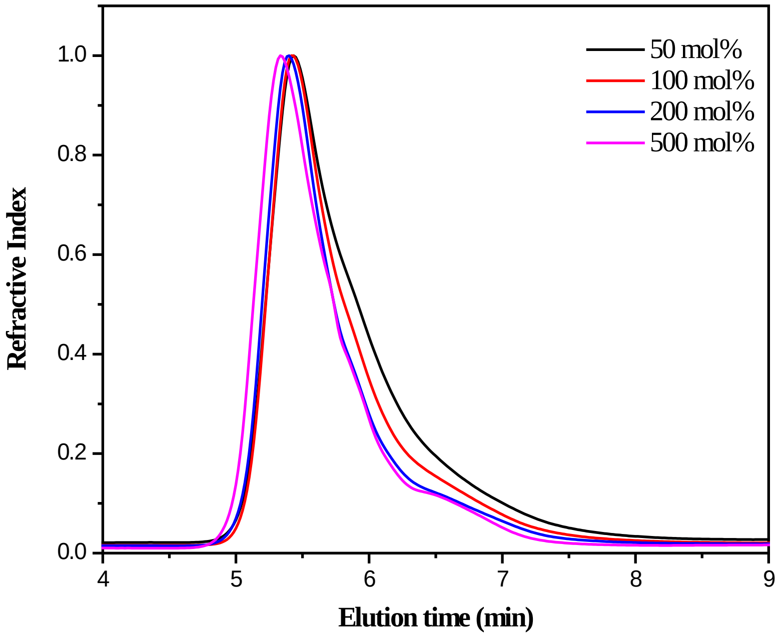

Figure 4. *GPC curves of PMMA via O-ATRP with different monomer concentrations*

The GPC and characteristic results in Figure 4 and Table 3, respectively demonstrate that the increment of monomer concentration is attributed to the increase in the I_{eff} leading to significant improvement in the conversion of MMA, and therefore the M_n of the synthesized PMMA. Furthermore, increasing monomer concentration could considerably lessen the PDI from 1.4 to 1.25, implying the beneficial role of monomer concentration on the well-controlled O-ATRP. Based on the findings, the monomer concentration of 100 molar ratios is suitable for the preparation of PMMA through O-ATRP using PHP organic photocatalyst.

Table 3. *Effect of the monomer concentration on the O-ATRP of MMA*

Monomer molar ratio	**Conversion (%)**	**$M_{n,theory}$ ($g \times mol^{-1}$)**	**$M_{n,GPC}$ ($g \times mol^{-1}$)**	**$M_{w,GPC}$ ($g \times mol^{-1}$)**	**I_{eff}**	**PDI**
50	39.03	1,952	23,520	32,990	0.08	1.40
100	74.70	7,470	28,360	35,423	0.26	1.25
200	84.94	16,988	28,380	36,817	0.60	1.29
500	85.06	42,530	31,435	39,552	1.35	1.26

3.4. Effect of solvent

The influence of the three solvents, including non-polar Toluene, polar THF, and DMAc on the characteristics of the PMMA is described in Table 4. Toluene is the worst solvent for synthesis of PMMA when presenting the lowest monomer conversion (15.5%) and the largest PDI. Despite having the highest polarity, DMAc shows a relatively low conversion, which is nearly two times higher than the Toluene counterpart. Meanwhile, PMMA prepared in the THF solvent exhibits the highest I_{eff} which facilitates the propagation of the synthesized polymer and thus enhances the polymerization yield accompanied by a well-defined PMMA, with a PDI of 1.25. Therefore, THF is chosen for the synthesis of PMMA via O-ATRP using the PHP photocatalyst.

Table 4. *Effect of the solvent on the O-ATRP of MMA*

Solvent	**Polarity**	**Conversion (%)**	**$M_{n,theory}$ ($g \times mol^{-1}$)**	**$M_{n,GPC}$ ($g \times mol^{-1}$)**	**$M_{w,GPC}$ ($g \times mol^{-1}$)**	**I_{eff}**	**PDI**
Toluene	2.4	15.50	1,550	23,975	33,244	0.06	1.38
THF	4.0	74.70	7,470	28,360	35,423	0.26	1.25
DMAc	6.5	28.87	2,887	30,906	36,716	0.09	1.19

The results in Table 4 demonstrate that the choice of solvent could influence the synthesis system and the characteristics of the obtained PMMA. The non-polar toluene could adversely affect the control of polymerization by O-ATRP since its C-H bond in the aromatic ring could be broken to form radicals which act as a chain transfer agent to terminate the polymerization (McCathy et al., 2020). Furthermore, the polarity of the solvent plays an important role in the dissolution of the monomer and synthesis components, which determines the outcome polymer. The less polar THF providing better outcomes O-ATRP than the more DMAc for MMA conversion is also evident from previous studies (McCathy et al., 2020; Bhattacherjee et al., 2021). This is illuminated by the increasing lifetime of excited states of the organic photocatalyst in the lower polarity solvent, contributing to the improvement of the activation throughout the O-ATRP (McCathy et al., 2020; Bhattacherjee et al., 2021; Borrell et al., 2020).

3.5. Effect of the concentration of initiator

As can be seen from Figure 6 describing the GPC curves of PMMA synthesized by O-ATRP employing different initiator's concentration, the polymerization system having the initiator's concentration of 1.0 molar ratio produces the PMMA with the fastest elution time, indicating the highest molecular weight, while the difference in the elution time of the other initiator's concentration is negligible. Furthermore, the synthesized PMMA displays good control with the initiator's concentration of 1.0 and 2.0 molar ratio, which is relevant to the PDI of 1.25 and 1.23, respectively. However, the initiator's concentration of 1.0 exhibits a higher polymerization yield and molecular weight. Therefore, the O-ATRP system having the initiator concentration of 1.0 molar ratio is suitable for synthesizing PMMA. The dependency of the characteristics of the PMMA synthesized with different concentrations of the initiator by O-ATRP using PHP photocatalyst is presented in Table 5. The I_{eff} is observed to remain nearly unchanged with a varied concentration of initiator, except for the initiator concentration of 1.5 molar ratios, while the molecular weight of the relative polymer fluctuates from about 26,000 to 35,000 g×mol^{-1}. Nevertheless, the conversion of the MMA increases and decreases from the highest value of 74.7 % related to the initiator concentration of 1.0 molar ratio.

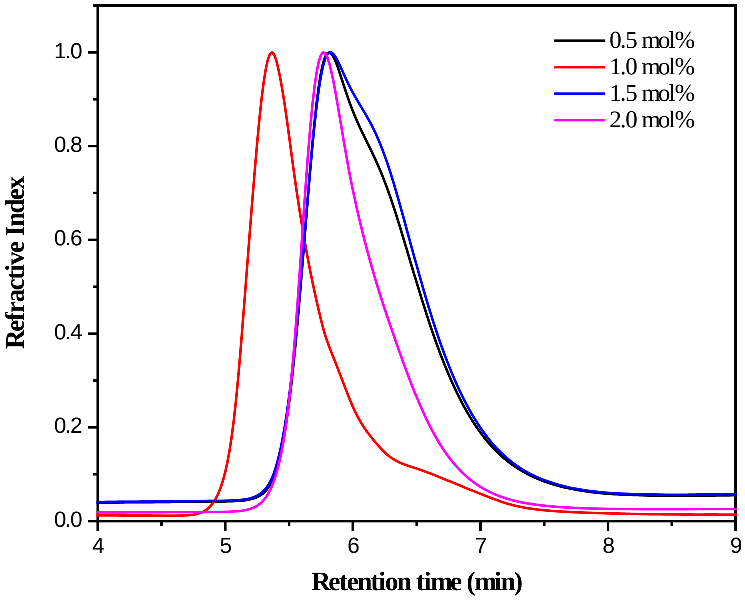

Figure 5. *GPC curves of PMMA via O-ATRP with different initiator concentration*

The GPC results in Figure 5 confirm that the concentration of initiator in a range of 0.5 to 1.0 molar ratio just affected the conversion of the MMA, and thus the propagation of the obtained polymer. On the other hand, the initiator's concentration higher than 1.0 molar ratio is detrimental to the polymerization control because the more initiator creates, the more radicals considerably promoting the propagation of the PMMA and reducing the deactivation rate of polymer radicals. Consequently, the combination of propagating radicals takes place to terminate the O-ATRP. The phenomenon is in accordance with the difference between theoretical M_n and experimental M_n as increasing initiator concentration (Table 5). Based on the results, the initiator concentration of 0.5 molar ratio is suggested to obtain a well-defined PMMA.

Table 5. *Effect of the concentration of initiator on the O-ATRP of MMA*

Innitiator molar ratio	**Conversion (%)**	**$M_{n,theory}$ ($g\times mol^{-1}$)**	**$M_{n,GPC}$ ($g\times mol^{-1}$)**	**$M_{w,GPC}$ ($g\times mol^{-1}$)**	**I_{eff}**	**PDI**
0.5	51.21	10,242	19,408	26,123	0.53	1.35
1.0	74.70	7,470	28,360	35,423	0.26	1.25
1.5	72.25	4,817	19,420	25,934	0.25	1.34
2.0	65.48	3,274	24,596	30,195	0.13	1.23

4. Conclusion

PMMA is successfully synthesized via O-ATRP under UV light irradiation using PHP photocatalyst. The impact of the reaction conditions involved in the synthesis system, such as photocatalyst content, reaction time, monomer concentration, solvents, and initiator concentration are systematically studied. The findings show a sophisticated effect of the components in the O-ATRP on the characteristics, in terms of conversion and PDI of the obtained PMMA. The monomer conversion and PDI considerably depend on the PHP photocatalyst content and polymerization time, while the influence of the initiator concentration is insignificant. The polarity of the solvents plays a key role in both the monomer conversion and the PDI of the synthesized PMMA. The less polar solvent could favor not only the higher conversion but also the lower PDI. Furthermore, the PHP photocatalyst is observed to demonstrate its capability of activating a well-controlled ATRP via the PDI in a range of 1.25 – 1.45 and the high molecular weight of the synthesized PMMA, which is activated by UV light in a short reaction time. In this study, the optimized synthesis components including [MMA]:[Initiator]:[PHP] of [100]:[1]:[0.05] molar ratio, under UV light irradiation in 8 hr produces well-defined PMMA owning the M_n of approximately 28,360 $g\times mol^{-1}$ with the PDI of 1.25.

- ***Conflict of Interest:*** *Authors have no conflict of interest to declare.*

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TỔNG HỢP PMMA BẰNG PHƯƠNG PHÁP TRÙNG HỢP CHUYỂN ĐỔI GỐC TỰ DO NGUYÊN TỬ DƯỚI TÁC DỤNG CỦA ÁNH SÁNG SỬ DỤNG CHẤT XÚC TÁC HỮU CƠ MỚI DỰA TRÊN PERYLENE-PHENOXAZINE

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TÓM TẮT

Trong nghiên cứu này, Poly(methyl methacrylate) (PMMA) được tổng hợp bằng phương pháp O-ATRP sử dụng một chất xúc tác hữu cơ mới dựa trên 10-(perylen-yl)-10H-phenoxazine (PHP) dưới tác dụng của ánh sáng UV ở nhiệt độ phòng. Mục tiêu của nghiên cứu nhằm chứng minh khả năng của xúc tác PHP trong tổng hợp PMMA bằng phản ứng O-ATRP dưới tác dụng ánh sáng và đưa ra một tỉ lệ mol phù hợp giữa các tác chất tham gia quá trình phản ứng để đạt được PMMA có khối lượng phân tử phù hợp và độ đa phân tán thấp. Trong quá trình phản ứng O-ATRP, ảnh hưởng của các điều kiện phản ứng bao gồm tỉ lệ mol của hàm lượng monome, chất khơi mào, loại dung môi và thời gian phản ứng lên quá trình trùng hợp PMMA đã được nghiên cứu. Sản phẩm PMMA được phân tích bằng phương pháp đo sắc kí thẩm thấu gel (GPC) để đánh giá ảnh hưởng của từng điều kiện phản ứng lên polyme. Các kết quả thực nghiệm cho thấy hiệu suất chuyển hóa monome MMA cao khi dùng chất xúc tác quang hữu cơ mới PHP (~ 75%). Trong các điều kiện khảo sát, nồng độ chất xúc tác quang PHP và thời gian trùng hợp có ảnh hưởng mạnh lên độ chuyển hóa và độ đa phân tán của PMMA tạo thành. Ngược lại, nồng độ chất khơi mào không có ảnh hưởng lớn đến kết quả của quá trình phản ứng O-ATRP. Ngoài ra, các đặc tính của PMMA phụ thuộc lớn vào độ phân cực của dung môi hòa tan. Dung môi có độ phân cực càng thấp dẫn đến độ chuyển hóa càng cao và do đó khối lượng phân tử của polyme càng lớn. Với độ chuyển hóa được gia tăng, phản ứng O-ATRP dựa trên xúc tác quang PHP đã chứng minh có thể tạo ra PMMA với khả năng kiểm soát tốt, với độ đa phân tán nhỏ hơn 1.5. Với hệ phản ứng tối ưu với tỉ lệ mol giữa các tác chất [Monome]:[Chất khơi mào]:[Chất xúc tác PHP] = [100]:[1]:[0.05] dưới tác dụng của ánh sáng UV trong 8 giờ đã tạo ra PMMA có Mn = 28,360 và độ đa phân tán Đ = 1.25.

Từ khóa: ATRP; xúc tác; perylene,; phenoxazine; PMMA; trùng hợp