

Synthesis of novel organocatalysed phenoxazine for atom transfer radical polymerization of methyl methacrylate monomer

Thu Vo Hoang¹, Huong Thi Le¹, Nhung Thanh Thi Truong¹, Michal Michalak², Ha Tran Nguyen^{1,3*}

¹Vietnam National University, Ho Chi Minh city, Vietnam

²Centre of Polymer and Carbon Materials, Polish Academy of Sciences, Poland

³Faculty of Materials Technology, University of Technology, Vietnam National University, Ho Chi Minh city, Vietnam

Received 8 January 2020; accepted 11 March 2020

Abstract:

In this research, a novel organic photocatalyst of 10-(perylene-3-yl-10H-phenoxazine (PHP) has been successfully synthesized from perylene and phenoxazine via Buchwald-Hartwig C-N coupling. The chemical structure of catalyst was determined via FT-IR, proton nuclear magnetic resonance (¹H-NMR) spectrum and optical properties were investigated through UV-Vis spectroscopy. The PHP has been used as the reducing photoredox catalyst for organocatalyzed atom transfer radical polymerization (O-ATRP) under UV irradiation. The well controlled molecular weight of the methyl methacrylate polymers have been obtained nearly 80% with a low polydispersity index under 1.5.

Keywords: atom transfer radical polymerization, methacrylate monomer, organic photocatalyst, phenoxazine.

Classification number: 2.2

Introduction

The polymerization of synthetic polymers through metal catalysts by ATRP is considered the state-of-the-art in the polymer industry [1-3]. The use of transition metals during ATRP provides many advantages including effective control of the molecular weight and polydispersity as well as control of the end-groups of the obtained polymers. However, traces of transition metals always remains in the obtained polymeric products [4, 5]. The presence of metals has limited the subsequent use of polymer products in bio-medicine and opto-electronic applications. To overcome this issue, an organic photocatalyst (O-ATRP/metal-free ATRP) has been developed for synthesis of metal-free polymers via controlled radical polymerization, which will gradually replace the traditional ATRP-based transition metal catalysts [6-8]. There have been many studies of O-ATRP polymerization using organic photocatalysts [9, 10]. Pintauer, et al. [11] have used phenoxazine and phenothiazine as organic photocatalysts for the controlled polymerization of acrylonitrile. Dadashi-Silab, et al. [12]

used organic catalysts (perylene, diaryl dihydrophenazines) for ATRP of the MMA monomer under visible light. Further, Corrigan, et al. [13] used fluorescein as an organic catalyst to control the polymerization of MMA. In addition, metal-free ATRP has been applied to the modification/functionalization of polymer surfaces, which enhanced the reactivity of the polymer [14].

In this research, the novel organic photocatalyst PHP was synthesized and applied to the polymerization of an MMA monomer for the first time [15, 16]. The structure of PHP was characterized via FT-IR and ¹H-NMR spectroscopy. In addition, the optical properties of the PHP catalyst were evaluated via UV-Vis spectroscopy. We also investigated the efficiency of the PHP organic photocatalyst for the O-ATRP process.

Experimental

Materials

Perylene (99%), phenoxazine (99%), Pd(OAc)₂ (99%) were purchased by Sigma Aldrich. NBS (99%), P(t-Bu)₃

*Corresponding author: Email: nguyentranha@hcmut.edu.vn

(98%), NaOt-Bu (97%), and MMA (99%) were purchased by Merck. Phenyl 2-bromo-2-methylpropanoate ($C_{10}H_{11}BrO_2$) was synthesized at our lab. All the solvents were purchased from Fisher Chemicals.

Characterization

1H -NMR spectra were recorded in deuterated chloroform ($CDCl_3$), with tetramethylsilane as the internal reference, on a Bruker Avance 500 MHz. The UV-Vis spectrum of the polymer samples was recorded at the Key Laboratory, Faculty of Materials Technology, University of Technology, Vietnam National University, Ho Chi Minh city on a Shimadzu UV-Vis 2450 from Shimadzu Scientific at room temperature ($25^\circ C$) over the range of 300 nm to 800 nm and scanning speed of 200 nm/min. The spectra from gel permeation chromatography (GPC) were recorded at the Key Laboratory, Faculty of Materials Technology, University of Technology, Vietnam National University, Ho Chi Minh city on a Polymer PL-GPC 50.

Synthesis of 1-bromoperylene

Perylene (500 mg, 1.98 mmol) and anhydrous dimethyl formamide (DMF) (6 ml) were added to a 100 ml 3-necked flask at $0^\circ C$. Aluminium foil was thoroughly wrapped around to cover the reaction vial and block out light. In the dark, *N*-bromosuccinimide (NBS) (388 mg, 2.18 mmol) in 4 ml of anhydrous DMF was slowly added to this solution using a dropping funnel. It was stirred for 1 h at $0^\circ C$ and for 23 h at room temperature. Then, the reaction was terminated with 2 M HCl, extracted with $CHCl_3$, and dried with anhydrous Na_2SO_4 . The product was a brown yellow solid with a yield = 95%.

Synthesis of PHP [17, 18]

A procedure from the literature was adapted for this synthesis. A 50 ml storage flask was fit with magnetic stirring bar, flamed under vacuum, and back-filled with nitrogen three times. The flask was then charged with phenoxazine (183.21 mg), NaOtBu (144.15 mg), $Pd(OAc)_2$ catalyst (4.49 mg), $P(tBu)_3$ (8.09 mg), and dry toluene (45 ml). The flask was evacuated and back-filled three times with nitrogen before 1-bromoperylene (331.21 mg) was added. The flask was then placed in an oil bath at $110^\circ C$ while stirring for 24 h. The flask was then cooled to room temperature, diluted with $CHCl_3$, washed with water and brine, dried with K_2CO_3 , and purified using column chromatography (3.3% EtOAc/hexane). The product was dried under reduced pressure to yield 78% of a red-orange solid.

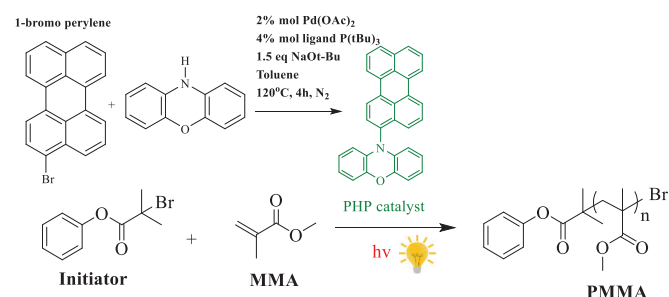
Synthesis of polymers [6, 19]

The polymerization of PMA was performed by O-ATRP using PhBMP as the initiator and PHP as the photocatalyst.

To start, a 25 ml storage flask was fit with a magnetic stir bar, flamed under vacuum, and backfilled with nitrogen three times. The MMA monomer (0.25 ml, 2.35 mmol) was dissolved in 0.5 ml of THF and placed in a flask. Then, 5.71 mg (23.5 μmol) of PhBMP initiator and PHP (1.02 mg, 2.35 μmol) were added separately. The mixture was stirred for 15 min. Then, three freeze-pump-thaw cycles were performed to remove the gas in the mixture. The mixture of the reaction solution was stirred until homogeneous. After that, the reaction solution was placed in a UV-box and irradiated with a wavelength of 365 nm for 24 h at room temperature. After the reaction process, the flask was removed from the UV-box and placed in the dark to stabilize. Finally, the polymer product was collected by precipitating the solution after reaction in cold methanol. Then it was dried and vacuumed to provide the cleaned polymer products.

Results and discussion

The PHP organic photocatalyst was successfully synthesized via Buchwald-Hartwig C-N coupling. Scheme 1 shows the synthesis process of the PHP organic photocatalyst. To synthesize 1-bromo perylene, the bromination of the electrophilic substitution was performed. The reaction took place in the presence of *N*-bromosuccinimide (NBS) in dimethylformamide (DMF) solvent. The yield of the reaction was 95% and the Buchwald-Hartwig C-N coupling reaction between 1-bromo perylene and phenoxazine was carried out. $Pd(OAc)_2$ and $P(t-Bu)_3$ as the catalyst and ligand, respectively, were used for this reaction process. The yield of the reaction was 78%.



Scheme 1. Synthesis of the PHP organic photocatalyst and general O-ATRP of methyl methacrylate monomer.

After purification by silica column chromatography and vacuum for 24 hours, PHP predictive product was analyzed FT-IR to identify functional groups (Fig. 1). FT-IR results showed that the product had no fluctuations of N-H bond in phenoxazine at 3500 cm^{-1} . Specially, obtained product had the absorption peak at 3051 cm^{-1} , 1589 cm^{-1} , 1272 cm^{-1} , 1044 cm^{-1} that corresponds to Ar-H, C=C, C-N and C-O bond. This indicates that the predictive product PHP has specific links appropriate to its structure.

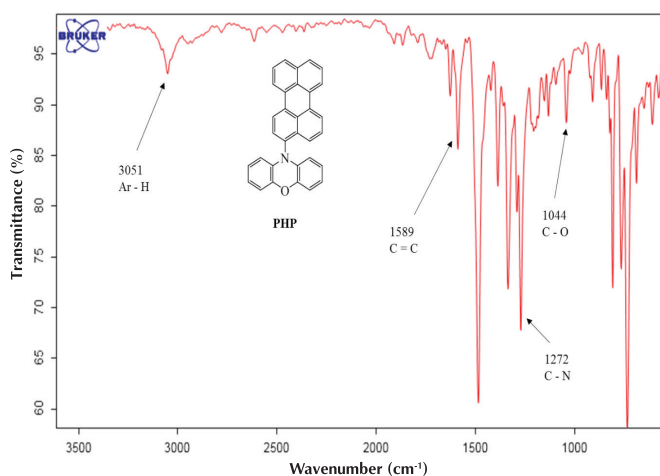


Fig. 1. Result of the FT-IR spectrum of the PHP product.

The chemical structure of PHP was analyzed via $^1\text{H-NMR}$ spectrum in Fig. 2 and the $^1\text{H-NMR}$ spectrum of phenoxazine showed in the Fig. 3. Comparing the $^1\text{H-NMR}$ spectrum of the phenoxazine precursor, the $^1\text{H-NMR}$ spectrum of the obtained product disappeared the peak at 4 ppm correspond to the proton of N-H bond in phenoxazine. The data in Fig. 2 showed that $^1\text{H-NMR}$ spectrum of PHP exhibited fully characteristic peaks of PHP including peaks of phenoxazine and perylene. The peaks from 7.48 ppm to 8.34 ppm corresponded to the protons of perylene. The peaks from 5.89 ppm to 6.73 ppm which assigned to the protons of phenoxazine ring. Based on the characteristics peaks, the reasonable their integration and the disappearance of N-H bonds in $^1\text{H-NMR}$ spectrum of PHP, the obtained product has been concluded that PHP catalyst was synthesized successfully.

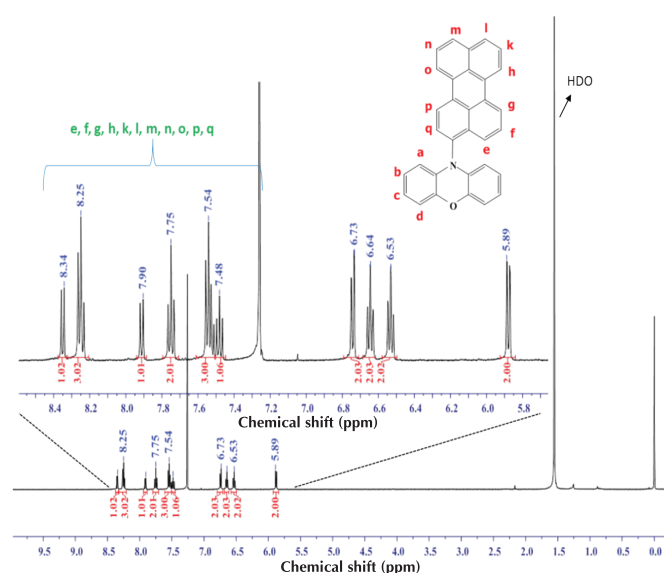


Fig. 2. The $^1\text{H-NMR}$ of PHP catalyst.

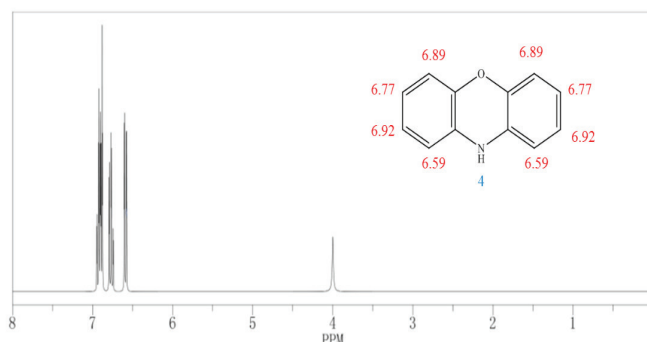


Fig. 3. The $^1\text{H-NMR}$ of phenoxazine.

From the results of FT-IR and $^1\text{H-NMR}$ analyzed above, it could be said that PHP catalyst has been successfully synthesized. Next, PHP and perylene were analyzed by UV-Vis to compare the spectral absorption in soluble form in THF solvent (Fig. 4). Perylene and PHP were dissolved in THF at different concentrations of 50, 40, 30, 20, 10 (μM) as measured by Shimadzu UV-Vis 2450 at room temperature range of 200 nm to 800 nm, 50 nm/min. Based on the UV-Vis spectrum of PHP catalyst, we recognized that the PHP absorbs the wavelength from 200-500 nm while the pyrene absorbs the wavelength from 200-450 nm. The UV-Vis spectrum of PHP curves exhibited two distinct absorption peaks at 250 and 450 nm which corresponding to the absorption of phenoxazine moieties and perylene, respectively. Moreover, the spectra showed a linear correlation between concentration and absorbance, and the molar extinction coefficient was determined through the Lambert - Beer law. In addition, the PHP exhibited the high intensity UV absorption at wavelength $\lambda_{\text{max}1}=441$ nm, $\lambda_{\text{max}2}=417$ nm with coefficient is $\epsilon_1=40870$ ($\text{M}^{-1}\cdot\text{cm}^{-1}$), $\epsilon_2=36980$ ($\text{M}^{-1}\cdot\text{cm}^{-1}$). This results confirmed that the PHP catalyst can activate in UV light.

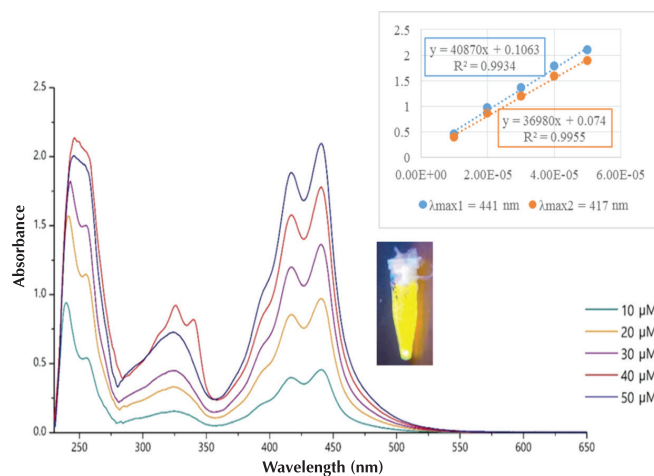


Fig. 4. The UV-Vis spectrum of PHP.

For a clearer picture, we consider the same concentration of the perylene precursor and PHP at 50 μM , shown in Fig. 5.

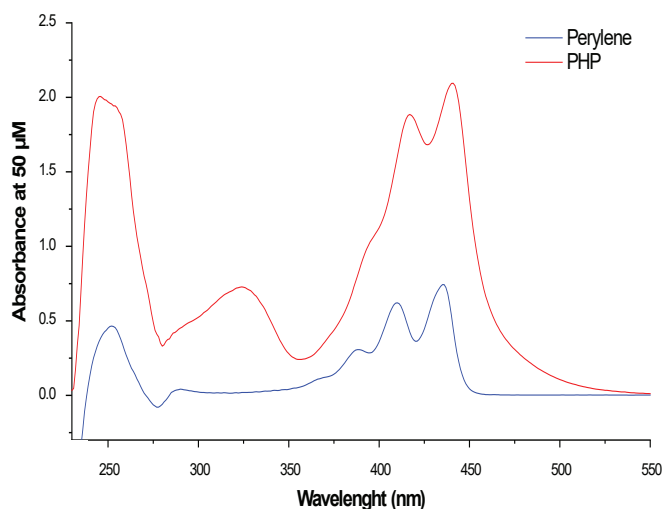


Fig. 5. The UV-Vis spectrum of PHP and perylene at 50 μM .

The spectrum shows that PHP has a higher absorbance than perylene at any wavelength. For example, at a wavelength of $\lambda=440$ nm, the absorbance of perylene was 0.536 while that of PHP was 2.093 (4 times higher). It can be said that PHP has a superior absorption capacity when compared to the commercial catalyst perylene.

According to the studies of Hawker, Matyjaszewski, and Miyake, PHP was used as the organic photocatalyst for O-ATRP of an MMA monomer. The O-ATRP of the MMA monomer involves photoexcitation of the PHP catalyst to an excited state, PHP^* , when under UV irradiation. This PHP^* was capable of reducing the PhBMP initiator to generate an active radical for polymerization propagation. Efficient deactivation was considered to be the most important aspect of the production of a controlled polymer. Deactivation of the propagating radical regenerates the alkyl bromide and the ground state PHP. Here, we report PHP as a novel class of photocatalysts for O-ATRP and thus we surveyed several molar ratios of the PHP catalyst to the initiator and monomers to consider the effects of PHP toward polymerization.

The polymerization process was performed in the presence of the PHP catalyst following the O-ATRP procedure. The content of the catalyst at 0.5, 0.1, 0.05, and 0.02 were investigated for the polymerization of methyl methacrylate. The reactions were carried out in a THF solvent under 365 nm UV irradiation for 24 h. The results of O-ATRP for MMA polymerization using the PHP catalyst are presented in Table 1.

Table 1. Macromolecular Characteristic Features of PMMA Synthesized by O-ATRP Using PHP Catalyst.

[MMA]:[I]:[PHP]	Conv(%)	M_n (g mol^{-1})	M_w (g mol^{-1})	Dispersity (\mathcal{D})
[100]:[1]:[0.5]	62.69	21670	31160	1.44
[100]:[1]:[0.1]	60	17969	25742	1.43
[100]:[1]:[0.05]*	77.61	30457	38880	1.28
[100]:[1]:[0.02]	56.42	24913	33677	1.35

The results show that about 5% molar ratio of PHP to initiator has the highest monomer conversion of 77.61%. On the other hand, the conversion of monomers during the polymerization decreased when the amount of PHP catalyst increased. It should be noted that the resulting polymethyl methacrylate (PMMA) exhibited a M_n of 30457 g mol^{-1} , with a polydispersity index (\mathcal{D}) of 1.28, which is reasonable for controlled polymerization (normally \mathcal{D} is required to be below 1.5). This result demonstrated that the MMA monomer has been successfully polymerized via O-ATRP using PHP as an organic photocatalyst. Furthermore, it should be noted that 365 nm UV light was used for polymerization of the MMA monomer. Fig. 4 showed the lowest absorption range of PHP to be around 360-365 nm wavelength, but the efficiency of polymerization was over 50% at different catalytic concentrations. To promote the polymerization reaction, higher absorbance wavelengths should be used for monomer polymerization with the appropriate catalyst content. In addition, PHP can be used as a solar-driven photocatalyst for the ATRP process because of its ability to absorb photons over the corresponding wavelength range.

Several experiments of the $[\text{MMA}]:[\text{I}]:[\text{PHP}]^*$ system were also performed to investigate the change of the monomer with respect to reaction time.

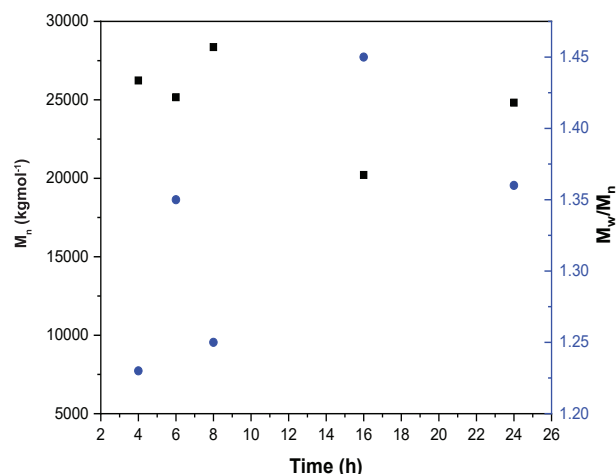


Fig. 6. Results for the polymerization of MMA using the PHP vs. time.

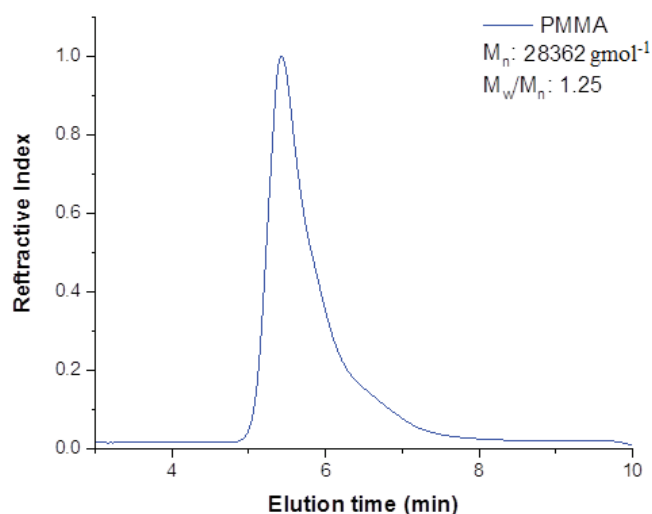


Fig. 7. The GPC of MMA polymer after an 8 hours reaction.

From these experimental results, it was shown that the MMA polymer with M_n molecular mass between 20000-30000 (gmol^{-1}) had a low \bar{D} , under 1.5, when using PHP as a catalyst for the O-ATRP process (shown in Figs. 6 & 7). Clearly, the MMA polymer has a high $M_n=28362$ (gmol^{-1}) and low $\bar{D}=1.25$ after 8 h of reaction time. This result shows that the obtained MMA polymer has a well-controlled molecular weight and a low \bar{D} with short reaction time compared to other catalysts.

Conclusions

The PHP catalyst has been successfully synthesized based on phenoxazine and has been shown to be an effective non-metallic catalyst for O-ATRP. We have also demonstrated the successful metal-free organocatalyzed atom transfer radical polymerization using PHP as a photoredox catalyst. PHP leads to a controlled, photo-mediated process that bears many characteristics including accurate control over molecular weight, low polydispersity, and high retention of chain end groups. Specifically, PHP was used to produce polymethacrylate with a controlled molecular weight of 28362 gmol^{-1} as well as a narrow polydispersity of 1.25 after 8 h reaction with the MMA monomer. The organic photocatalyst PHP has shown its advantages over previous catalyst generations in ATRP. Further, this research enables a synthesis procedure for potential bio/electronic applications that required metal-free polymeric materials.

ACKNOWLEDGEMENTS

This research is funded by Vietnam National University, Ho Chi Minh city under grant number NV2019-20-03.

The authors declare that there is no conflict of interest regarding the publication of this article.

REFERENCES

- [1] P.B. Zetterlund, Y. Kagawa, M. Okubo (2008), "Controlled/living radical polymerization in dispersed systems", *Chemical Reviews*, **108**(9), pp.3747-3794.
- [2] G. Moad, E. Rizzardo, S.H. Thang (2008), "Radical addition-fragmentation chemistry in polymer synthesis", *Polymer*, **49**(5), pp.1079-1131.
- [3] D.J. Keddie, et al. (2011), "Switchable reversible addition-fragmentation chain transfer (RAFT) polymerization in aqueous solution, N, N-dimethylacrylamide", *Macromolecules*, **44**(17), pp.6738-6745.
- [4] K. Matyjaszewski, J. Xia (2001), "Atom transfer radical polymerization", *Chemical Reviews*, **101**(9), pp.2921-2990.
- [5] K. Matyjaszewski (2012), "Atom transfer radical polymerization (ATRP): current status and future perspectives", *Macromolecules*, **45**(10), pp.4015-4039.
- [6] N.J. Treat, et al. (2014), "Metal-free atom transfer radical polymerization", *Journal of the American Chemical Society*, **136**(45), pp.16096-16101.
- [7] B. Mao, L. Gan, Y. Gan (2006), "Ultra high molar mass poly [2-(dimethylamino) ethyl methacrylate] via atom transfer radical polymerization", *Polymer*, **47**(9), pp.3017-3020.
- [8] K. Matyjaszewski (1996), "The importance of exchange reactions in controlled/living radical polymerization in the presence of alkoxyamines and transition metals", *Macromolecular Symposia*, **29**(24), pp.7661-7670.
- [9] G.M. Miyake, J.C. Theriot (2014), "Perylene as an organic photocatalyst for the radical polymerization of functionalized vinyl monomers through oxidative quenching with alkyl bromides and visible light", *Macromolecules*, **47**(23), pp.8255-8261.
- [10] J.C. Theriot, et al. (2016), "Organocatalyzed atom transfer radical polymerization driven by visible light", *Science*, **352**(6289), pp.1082-1086.
- [11] T. Pintauer, P. Zhou, K. Matyjaszewski (2002), "General method for determination of the activation, deactivation, and initiation rate constants in transition metal-catalyzed atom transfer radical processes", *Journal of the American Chemical Society*, **124**(28), pp.8196-8197.
- [12] S. Dadashi-Silab, X. Pan, K. Matyjaszewski (2017), "Phenyl benzo [b] phenothiazine as a visible light photoredox catalyst for metal-free atom transfer radical polymerization", *Chemistry-A European Journal*, **23**(25), pp.5972-5977.
- [13] N. Corrigan, et al. (2016), "Photocatalysis in organic and polymer synthesis", *Chemical Society Reviews*, **45**(22), pp.6165-6212.
- [14] K. Matyjaszewski, N.V. Tsarevsky (2009), "Nanostructured functional materials prepared by atom transfer radical polymerization", *Nature Chemistry*, **1**(4), pp.276-288.
- [15] R.M. Pearson, G.M. Miyake, et al. (2016), "Organocatalyzed atom transfer radical polymerization using N-aryl phenoxazines as photoredox catalysts", *Journal of the American Chemical Society*, **138**(35), pp.11399-11407.
- [16] B.G. McCarthy, et al. (2018), "Structure-property relationships for tailoring phenoxazines as reducing photoredox catalysts", *Journal of the American Chemical Society*, **140**(15), pp.5088-5101.
- [17] M.M. Heravi, et al. (2018), "Buchwald-Hartwig reaction: an overview", *Journal of Organometallic Chemistry*, **861**, pp.17-104.
- [18] C.H. Lim, M.D. Ryan, G.M. Miyake, et al. (2017), "Intramolecular charge transfer and ion pairing in N, N-diaryl dihydrophenazine photoredox catalysts for efficient organocatalyzed atom transfer radical polymerization", *Journal of the American Chemical Society*, **139**(1), pp.348-355.
- [19] J.C. Theriot, et al. (2017), "Organocatalyzed atom transfer radical polymerization: perspectives on catalyst design and performance", *Macromolecular Rapid Communications*, **38**(13), Doi: 10.1002/marc.201700040.