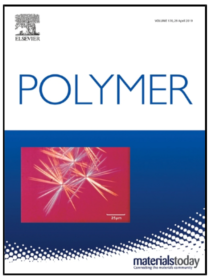

Synthesis of Novel Thioxanthone-Containing Macromolecular photosensitizer and Its Photocatalytic Property

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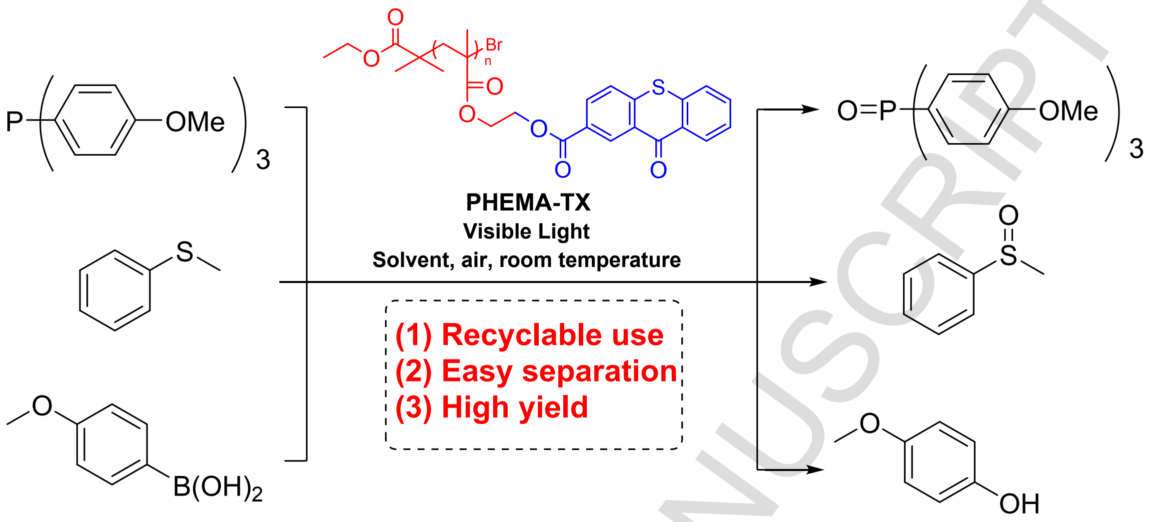
Graphical Abstract



Synthesis of Novel Thioxanthone-Containing Macromolecular photosensitizer and Its Photocatalytic Property

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ABSTRACT

Aiming to overcome the disadvantages of small molecule photosensitizers, a novel macromolecular photosensitizer was designed and synthesized in this work. Firstly, the functional small molecule photosensitizer 9-oxo-9H-thioxanthene-2-carboxylic acid (TX-COOH) and precursor poly(2-hydroxyethyl methacrylate) (PHEMA) was individually synthesized. Then, the macromolecular photosensitizer PHEMA-TX was realized by an optimized reaction procedure between PHEMA and TX-COCl, which was previously prepared by acyl chlorination of TX-COOH. The modification efficiency was calculated as 64 %. Finally, the photocatalytic reaction using the as-synthesized PHEMA-TX was investigated based on three substrates of tris(4-methoxyphenyl)phosphane, methyl(phenyl)sulfane, (4-methoxyphenyl)boronic acid. The results showed that the photocatalyst PHEMA-TX can be easily separated, recovered by a simple precipitation, and reused 7 times without significant loss of the catalytic activity. The excellent photocatalytic property, easy separation, and recyclability of PHEMA-TX were comprehensively confirmed, which contributed great potential of this novel macromolecular photosensitizer in future application.

Keywords

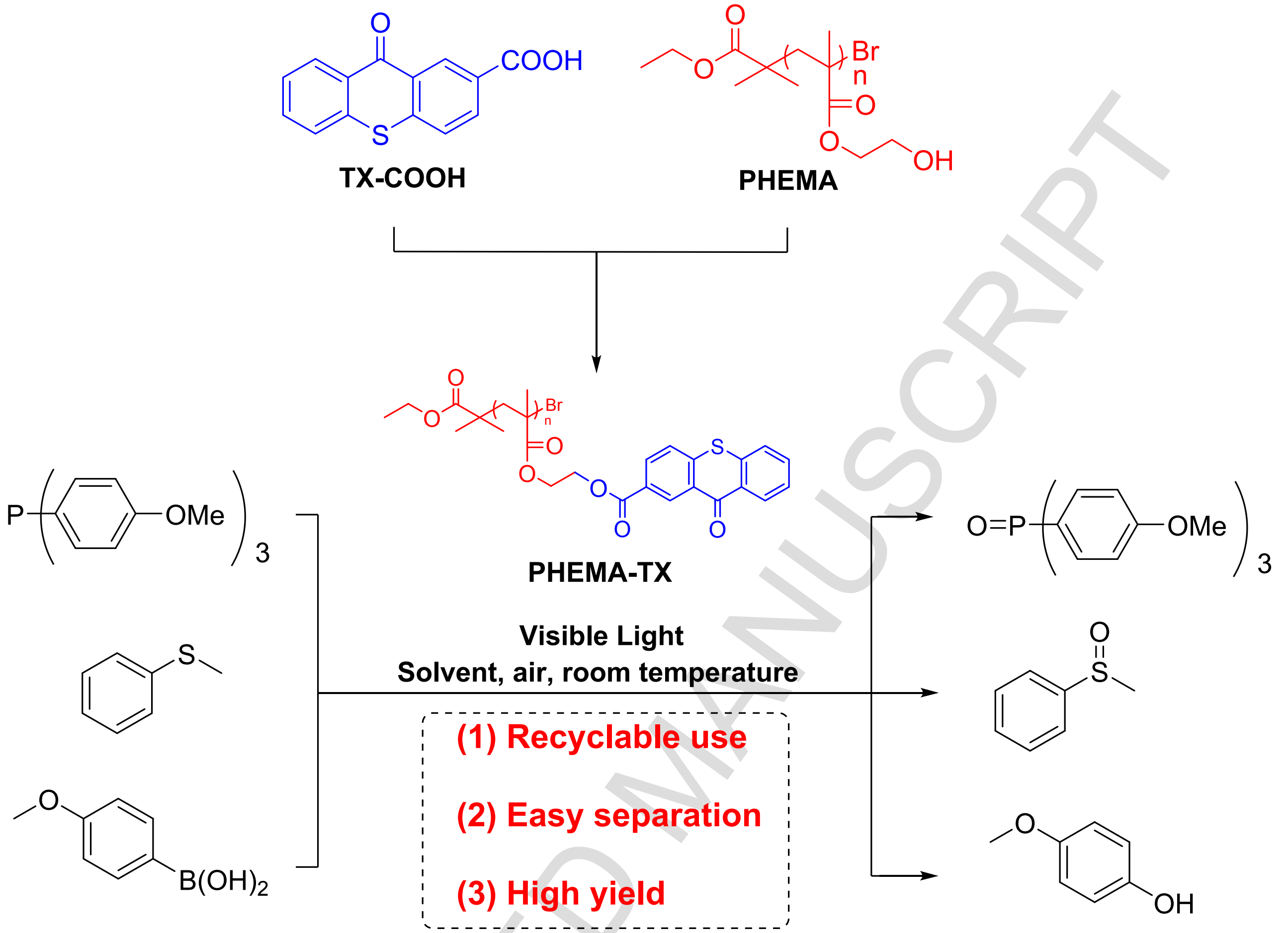
Thioxanthone, photosensitizer, recyclability, photooxidation, photocatalysis

1. Introduction

Visible light, as an economical green energy, has received much attention from researchers. [1-6] In most cases, small molecule compounds are used as photosensitizers.[7, 8] Although the small molecule photosensitizers have good catalytic property in the reaction, they always have some disadvantages, such as difficult separation from the reactants, hard recycling or increasing of cost, *etc*. In order to solve these problems, some alternative methods had been developed. For example, in recent years, the macromolecular photosensitizers were designed and synthesized by linking photosensitive groups onto polymeric chains.[9, 10] Comparing with the small molecule photosensitizers, macromolecular photosensitizers have an especial advantage. That is, the macromolecular photosensitizers can be easily separated from the reactant and recycling used, which greatly decreased the cost and simplify the producing technology. Thus, the macromolecular photosensitizers had attracted much attentions from the researchers and had been widely used in medical, biological and hydrogel fields.[11-15]

Up to now, a library of small molecule photosensitizers had been developed and used in photocatalytic reactions. The examples included the typical organic dyes of methylene blue, riboflavin and related aza heterocycles, fluorescein, Eosin Y, Eosin B, and rose red (RB),[16-22] as well as the infrequently used phenoxazines (such as Nile Red) and phenothiazine scaffolds,[23] larger aromatic systems (such as hydrazine or perylene and boron dipyrromethene derivatives),[24-26] transition metal ligands (such as CuI-phenanthroline derivatives).[27] In recent years, some novel photocatalysts, such as Ru(II) or Ir(III) polypyridyl complexes, aryl aldehyde ketones,[28] thioxanthone[29-31] and its derivatives were developed and found potential application in many fields. Among all the above photosensitizers, the thioxanthone and its derivatives are especially attracting more and more attentions due to its excellent photocatalytic property.[32] Besides of its function as catalyst for small molecules compounds, the thioxanthone and its derivatives can also be used as photosensitizers in free radical polymerization.[33-36] However, the study on macromolecular photosensitizeds with thioxanthone is still rather limited. On one hand, the functionalization of thioxanthone is always difficult. On the other hand, the introduced functional group might affect the photocatalytic property.[37, 38]

Considering the excellent properties of thioxanthone and the current limitation on macromolecular thioxanthone, a novel methodology was developed in this work to immobilize the TX groups on macromolecules (**Scheme 1**). Firstly, a thioxanthone derivative of 9-oxo-9H-thioxanthene-2-carboxylic acid (TX-COOH) containing a carboxyl group was synthesized, and precursor poly(2-hydroxyethyl methacrylate) (PHEMA) was obtained by an electron transfer atom transfer radical polymerization (AGET ATRP) procedure. Subsequently, the TX groups were attached onto PHEMA to give PHEMA-TX by an optimized synthetic procedure. The photocatalytic property of PHEMA-TX was finally studied by using three characteristic substrates. Furthermore, the recyclability and separation ability of this novel photocatalyst were also investigated.



Scheme 1. The synthetic procedure of macromolecular photosensitizer and its photocatalytic reaction.

2. Materials and methods

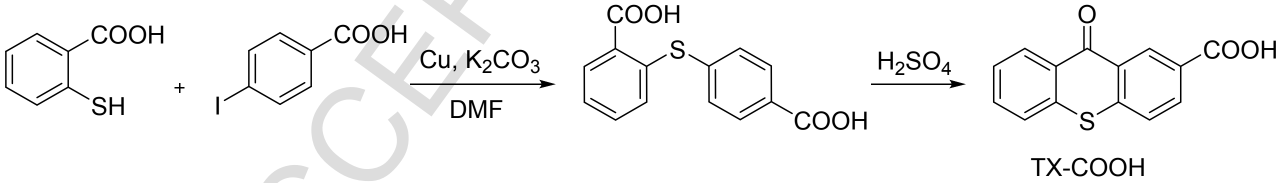
2.1 Materials

2-Hydroxyethyl methacrylate (HEMA, 97 %, Energy chemical) was passed over a column of basic alumina to remove inhibitor prior to use. 2-Mercaptobenzoic acid (97 %, Energy chemical), 4-iodobenzoic acid (97 %, Energy chemical), copper (99 %, Energy chemical), anhydrous potassium carbonate (K_2CO_3, 99%, Sinopharm Chemical Reagent Co., Ltd.), ethyl 2-bromoisobutyrate (EBiB, 98%, Energy chemical), cupric bromide ($Cu^{II}Br_2$, 99 %, Aldrich), 2,2'-bipyridine (Bpy, 98 %, Energy chemical), stannous octoate ($Sn(Oct)_2$, 97%, Energy chemical), thionyl chloride ($SOCl_2$, 99 %, Sinopharm Chemical Reagent Co., Ltd.), 4-dimethylaminopyridine (DMAP, 98 %, Energy chemical), dicyclohexylcarbodiimide (DCC, 98 %, Energy chemical), concentrated sulfuric acid (95 %, Sinopharm Chemical Reagent Co., Ltd.), tris(4-methoxyphenyl)phosphane (97 %, Energy chemical), methyl(phenyl)sulfane (97 %, Energy chemical), (4-methoxyphenyl)boronic acid (97 %, Energy chemical), N,N-diisopropylethylamine (*i*-Pr_2Net, 99 %, Energy chemical), methanol (AR), 2-butanolne (AR), triethylamine (Et_3N, AR), N,N-dimethylformamide (DMF, AR), dimethyl carbonate (AR) were used as recieved. All other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. And used as received unless otherwise specified.

2.2 Synthesis of 9-oxo-9H-thioxanthene-2-carboxylic acid (TX-COOH)

According to the literature,[39] the diphenylsulfide-2,4'-dicarboxylic acid was firstly prepared (**Scheme 2**). Into a 250 mL round-bottomed flask, thiosalicylic acid (4.622 g, 29.9 mmol) was firstly added and dissolved in DMF (100 mL). Then, the 4-iodobenzoic acid (7.443 g, 30.0 mol), K_2CO_3 (12.494 g, 90.4 mmol) and Cu powder (384 mg, 6.0 mmol) was sequentially added. After the mixture was refluxed for 36 h, water (300 mL) was added and the mixture was filtered to remove the Cu powder. The filtrate was carefully acidified with concentrated HCl (37 %) to pH < 1 and the product was precipitated. After the washing of the precipitate with water, the product was dried at 100 ^{o}C to give the white powder of diphenylsulfide-2,4'-dicarboxylic acid (6.995 g, 85%).

Subsequently, the as-synthesized diphenylsulfide-2,4'-dicarboxylic acid (4.002 g, 14.6 mmol) and concentrated sulfuric acid (76 mL) were charged into a 250 mL dry three-necked flask. After the reaction was stirred at room temperature for 33 h, 90 mL of boiling water was added and the reaction was continued for another 1 h at 100 ^{o}C. The mixture was then cooled down to room temperature and the crude product 9-oxo-9H-thioxanthene-2-carboxylic acid was precipitated from the mixture. The precipitate was filtrated and washed with water for three times. The 9-oxo-9H-thioxanthene-2-carboxylic acid was obtained with the yield of 48 % (1.792 g). ^{1}H NMR (400 MHz, DMSO) δ 13.37 (s, 1H), 8.96 (s, 1H), 8.46 (d, J = 6.4 Hz, 1H), 8.19 (d, J = 6.0 Hz, 1H), 8.02 – 7.73 (m, 3H), 7.61 (s, 1H).

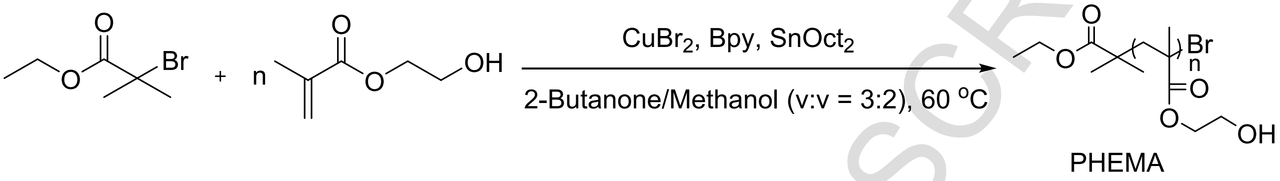


Scheme 2. The synthetic procedure for TX-COOH.

2.3 Synthesis of precursor poly(2-hydroxyethyl methacrylate) (PHEMA)

According to our previous work[40] and literatures,[41-43] the precursor PHEMA was synthesized by an electron transfer atom transfer radical polymerization (AGET ATRP) procedure (**Scheme 3**). Typically, the monomer HEMA (40.0 mL, 330 mmol), initiator EBiB (0.1602 g, 0.8 mmol), catalytic complex of $Cu^{II}Br_2$ (0.1862 g, 0.8 mmol) and Bpy (0.2587 g, 1.6 mmol), mixture solvent of 2-butanone

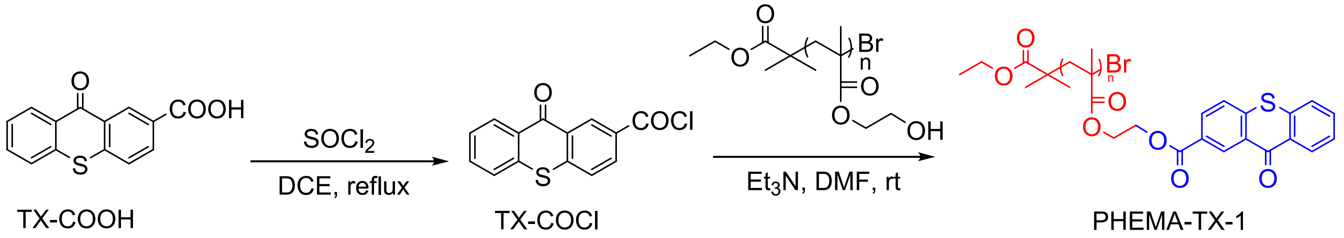
(58 mL) and methanol (38 mL) were sequentially added into a 250 mL Schlenk flask. After the flask was purged with argon for 30 min, the reducing agent of $SnOct_2$ (0.2844 g, 0.7 mmol) dissolved in a mixture solvent of 2-butanone (2.0 mL) and methanol (2.0 mL) was charged into the flask to trigger the polymerization. After the mixture was stirred at 60 °C for 40 h, the crude product was precipitated into a large amount of water. The obtained PHEMA was further dried under vacuum to a constant weight at 60 °C. ^1H NMR (400 MHz, DMSO, δ, ppm, TMS): 0.78 (m, $-CH_2C(C\boldsymbol{H}_3)-$), 1.23-2.13 (m, $-C\boldsymbol{H}_2C(CH_3)-$), 3.42-4.05 (m, $HOC\boldsymbol{H}_2C\boldsymbol{H}_2-$). $M_{n,\mathrm{GPC}} = 27,800$, $M_w/M_n = 1.55$.



Scheme 3. The synthetic procedure for PHEMA.

2.4 Synthesis of PHEMA-TX-1 hanging with TX groups (Route A)

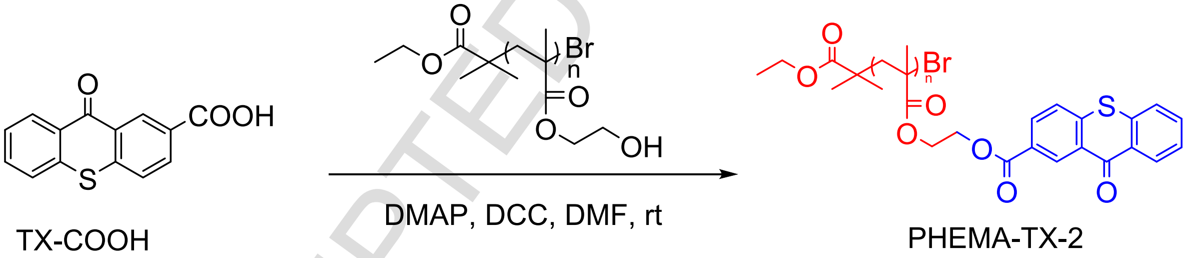
The PHEMA-TX-1 hanging with TX groups was prepared by reaction between PHEMA and TX-COCl (**Scheme 4**). Firstly, the TX-COOH was transformed into TX-COCl as the following procedure. In a dry 100 mL Schlenk flask, under argon atmosphere, TX-COOH (0.343 g, 1.34 mmol) was refluxed with $SOCl_2$ (0.3 mL) in anhydrous dichloroethane (10 mL). After 4 h, the mixture was concentrated under vacuo and the residue was stripped twice with anhydrous dichloroethane (10 mL). Subsequently, the residue was dissolved in 5 mL anhydrous DMF and transferred into another dry 100 mL Schlenk flask containing precursor PHEMA (0.3487 g) which was previously dried by azeotropic distillation procedure with 30 mL toluene. Anhydrous Et_3N (2.0 mL) was syringed into the flask and used as acid-binding agent. The system was set into an ice bath (0 °C) and allowed to warm to room temperature, the reaction was continued for 60 h. The product was precipitated into a mixture of water and methanol (water: methanol = 2:1) with three times. The obtained PHEMA-TX-1 was further dried under vacuum to a constant weight at 60 °C. ^1H NMR (400 MHz, DMSO, δ, ppm, TMS): 0.78 (m, $-CH_2C(C\boldsymbol{H}_3)-$), 1.23-2.13 (m, $-C\boldsymbol{H}_2C(CH_3)-$), 3.47-4.16 (m, $TXOC\boldsymbol{H}_2C\boldsymbol{H}_2-$), 7.58-9.01 (m, Ar-$\boldsymbol{H}$). $M_{n,\mathrm{GPC}} = 84,800$, $M_w/M_n = 1.47$.



Scheme 4. The synthetic procedure for PHEMA-TX-1.

2.5 Synthesis of PHEMA-TX-2 hanging with TX groups (Route B)

Alternatively, using DMAP and DCC as catalyst, the direct esterification between PHEMA and TX-COOH was performed for PHEMA-TX-2. The detailed procedure was shown in (**Scheme 5**). The PHEMA (0.3490 g) dried by azeotropic distillation with 50 mL toluene, TX-COOH (0.343 g, 1.34 mmol), DMAP (0.033 g, 0.27 mmol), and DCC (1.117 g, 5.36 mmol) were sequentially added into the flask and dissolved in 20 mL DMF. The mixture was stirred under room temperature for 36 h. The crude product was concentrated in vacuo and precipitated into a large amount of mixture solvent of water and methanol (water: methanol = 2:1) with three times. The obtained PHEMA-TX-2 was further dried under vacuum to a constant weight at 60 ^{o}C. ^{1}H NMR (400 MHz, DMSO, δ, ppm, TMS): 0.78 (m, -$CH_2C(C\boldsymbol{H}_3)$-), 1.23-2.13 (m, -$C\boldsymbol{H}_2C(CH_3)$-), 3.47-4.16 (m, TXO$C\boldsymbol{H}_2C\boldsymbol{H}_2$-), 7.58-9.01 (m, Ar-***H***). $M_{n,\mathrm{GPC}}$ = 63,100, M_w/M_n = 1.52.

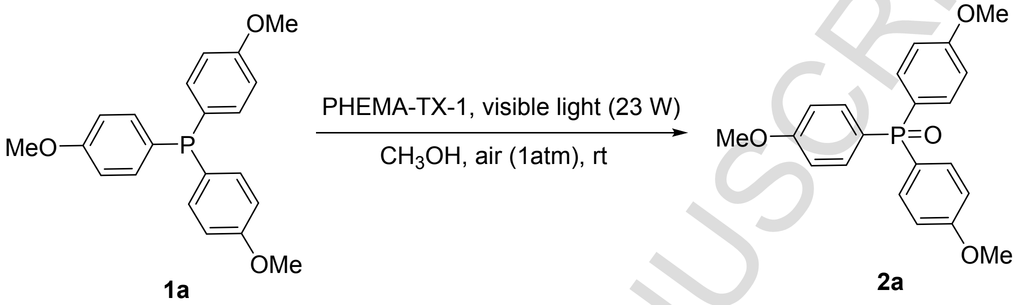


Scheme 5. The synthetic procedure for PHEMA-TX-2.

2.6 Photocatalytic reaction of tris(4-methoxyphenyl)phosphane

Using PHEMA-TX-1 as catalyst, the tris(4-methoxyphenyl)phosphane (**1a**) was transformed into tris(4-methoxyphenyl)phosphine oxide (**2a**) (**Scheme 6**). Typically, **1a** (352 mg, 1.0 mmol), PHEMA-TX-1 (0.52 mg, 0.001 mmol, 19 μL stock solution prepared by dissolving 56 mg PHEMA-TX-1 in 2.0 mL of DMF), CH_3OH (30 mL) were added into to a 100 mL round bottom flask equipped with a magnetic stirrer. The reaction was triggered by irradiation of a 23 W household lamp at room temperature under air atmosphere. The photocatalytic reaction was monitored by TLC (eluent:

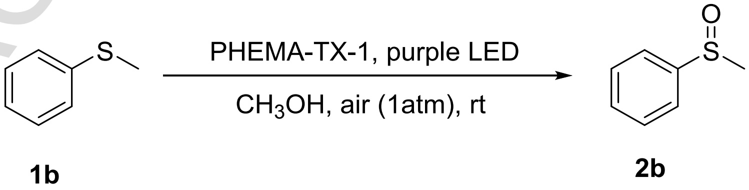
petroleum ether/ethyl acetate = 20/1) and finished after 8 h. The solution was concentrated under vacuo and the mixture was again dissolved in 5 mL of ethyl acetate (EA). The PHEMA-TX-1 was precipitated in EA and recovered for the second cycle of photocatalytic reaction. The NMR yield of **2a** in the first cycle was 99 % as determined by ^{1}H NMR analysis of the crude reaction mixture using dibromomethane as internal standard. Subsequently, using the recovered PHEMA-TX-1 as catalyst, the following cycles of reactions were performed using the same procedure as above. The result was shown in **Scheme 6**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, J = 9.4, 9.4 Hz, 6H), 6.95 (d, J = 8.0 Hz, 6H), 3.83 (s, 9H).



Scheme 6. The photocatalytic reaction of **1a**.

2.7 Photocatalytic reaction of methyl(phenyl)sulfane

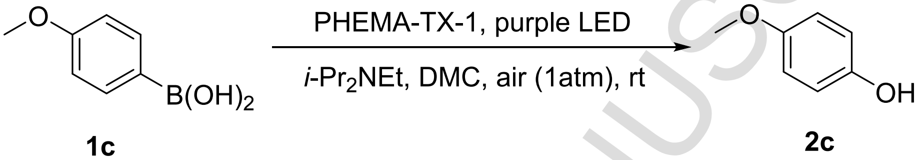
Using PHEMA-TX-1 as catalyst, the methyl(phenyl)sulfane (**1b**) was transformed into methyl(phenyl)sulfoxide (**2b**) (**Scheme 7**). Typically, **1b** (0.12 mL, 1.0 mmol), PHEMA-TX-1 (0.52 mg, 0.001mmol, 19 μL, prepare a solution of 56 mg of PHEMA-TX-1 with 2 mL of DMF), CH_3OH (5 mL) were added into a 25 mL round bottom flask equipped with a magnetic stirrer. The reaction was triggered by irradiation of a purple LED lamp at room temperature under air atmosphere. The monitoring procedure and the final purification operation were similar as those for the above **2a**. The NMR yield of **2b** in the first cycle was 99 % as determined by ^{1}H NMR analysis of the crude reaction mixture using dibromomethane (1 mmol) as internal standard. The result was shown in **Scheme 7**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 5.6 Hz, 2H), 7.52 (d, J = 5.6 Hz, 3H), 2.72 (s, 3H).



Scheme 7. The photocatalytic reaction of **1b**.

2.8 Photocatalytic reaction of (4-methoxyphenyl)boronic acid

Using PHEMA-TX-1 as catalyst, the (4-methoxyphenyl)boronic acid (**1c**) was transformed into 4-methoxyphenol (**2c**) (**Scheme 8**). Typically, **1c** (152 mg, 1.0 mmol), PHEMA-TX-1 (5.16 mg, 0.01 mmol, 214 μL, prepare a solution of 56 mg of PHEMA-TX-1 with 2 mL of DMF), *i*-Pr_2NEt (330 μL, 2 mmol), and dimethyl carbonate (5 mL) were added into a 25 mL round bottom flask equipped with a magnetic stirrer. The reaction was also triggered by irradiation of a purple LED lamp at room temperature under air atmosphere. The monitoring procedure and the final purification operations were similar as that for the above **2a**. The NMR yield of **2c** in the first cycle was 99 % as determined by ^{1}H NMR analysis of the crude reaction mixture using dibromomethane (1 mmol) as internal standard. The result was shown in **Scheme 8**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81-6.73 (m, 4 H), 5.44 (br s, 1H), 3.76 (s, 3H).



1c

2c

Scheme 8. The photocatalytic reaction of **1c**.

2.5 Characterization

The apparent molecular weight (MW) and molecular weight distribution (M_w/M_n) of polymers was analyzed by size exclusion chromatography (SEC) measurement, which was performed in LiBr-added N,N-dimethylformamide (DMF) ([LiBr] = 14 mM) at 55 °C with an elution rate of 1.0 mL/min on an Agilent 1260 equipped with a G1310B pump, a G1362A refractive index detector, and a G1314F variable wavelength detector. Two 5 μm LP gel columns (500 Å, molecular range 500 - 1.2×10^5 Da and 200 - 1.0×10^6 Da) were calibrated using poly(methyl methacrylate) (PMMA) standards. ^{1}H Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker (400 MHz) spectrometer in CD_3Cl_3 or DMSO-*d*6 at 298 K.

3. Results and discussion

3.1 Synthesis and characterization of PHEMA-TX

According to the literature,[38] the TX-COOH was prepared from thiosalicylic acid and 4-iodobenzoic acid. The structure of TX-COOH was confirmed by ^{1}H NMR spectrum as shown in **Figure 1.** The characteristic resonance signal on phenyl can be clearly attributed at 6.96-9.10 ppm. According to our previous work[39] and literatures,[40-42] the precursor PHEMA was synthesized by AGET

ATRP of HEMA monomer using $Cu^{II}Br_2$ / Bpy as catalyst system and $Sn(Oct)_2$ as reducing agent. The apparent molecular weight of PHEMA was calibrated as 27,800 g/mol by SEC instrument using PMMA as calibration (**Figure 2**). From **Figure 1** for ^1H NMR spectrum of PHEMA, the characteristic resonance signals for methylene protons ($HOC\boldsymbol{H}_2C\boldsymbol{H}_2$-) can be clearly discriminated at 3.42-4.05 ppm, and signal for methyl protons ($-CH_2C(C\boldsymbol{H}_3)$-) can be observed at 0.78 ppm.

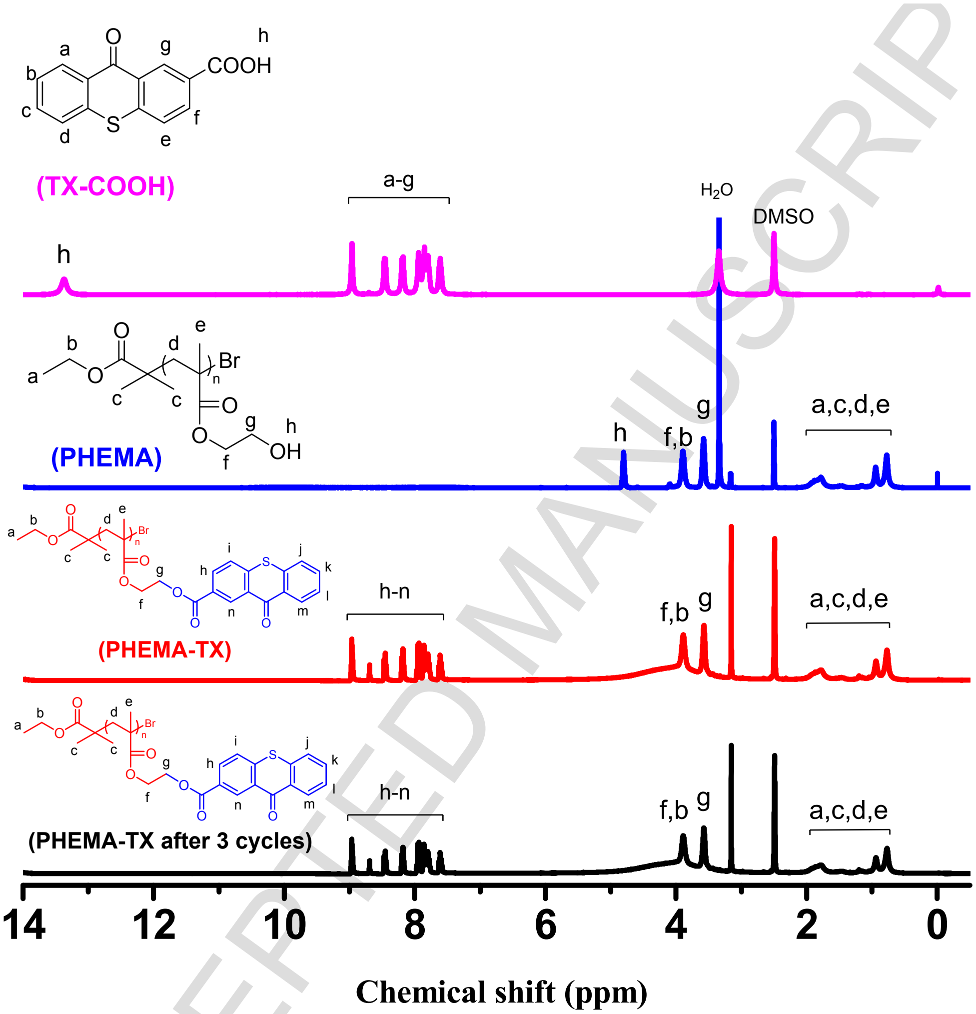


Figure 1. ^1H NMR spectra for TX-COOH, PHEMA and PHEMA-TX in DMSO-*d*6.

Subsequently, the TX-COOH was attached onto PHEMA. Two synthetic routes were adopted to optimize the methodology. In route A, the PHEMA-TX-1 was prepared by reaction between PHEMA and TX-COCl, which was previously prepared from TX-COOH and $SOCl_2$. The high activity of TX-COCl to hydroxyl groups guaranteed the high modification efficiency of TX onto PHEMA. Comparing with the GPC curves of precursor PHEMA, one can observe that the GPC curve of PHEMA-TX-1 obviously shift to the higher molecular weight region (84,800 g/mol) (**Figure 2**). By comparing the integral areas at aromatic region (8.18-8.22 ppm) and peak at 3.58 ppm (peak g), the modification efficiency can be calculated as 64 %.

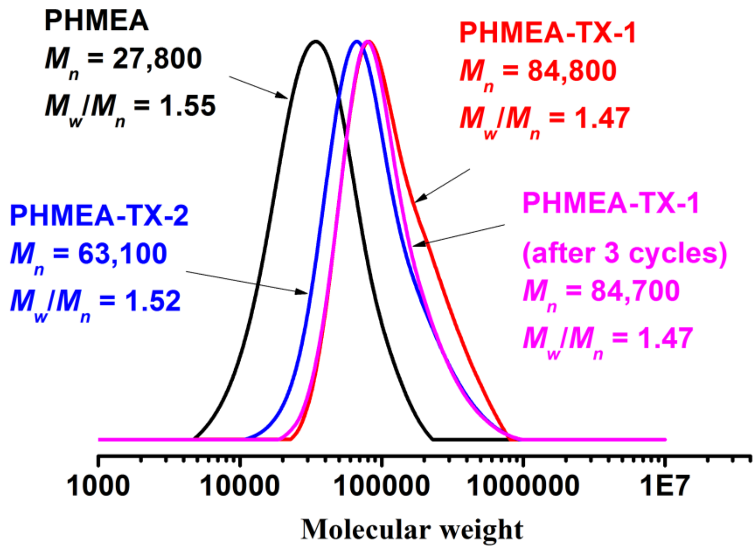


Figure 2. The GPC traces of PHEMA and PHEMA-TX.

Because the preparation of TX-COCl was always complicated and should be carefully operated, an alternative route B was adopted using DMAP and DCC as catalyst and PHEMA-TX-2 was obtained. Although the SEC curve of PEHMA-TX-2 shift to the higher molecular weight region (63,100 g/mol), the low modification efficiency of 18.5% was obtained. The reason can be reasonably attributed to the bulky substituent group of TX and low activity of carboxyl group. Thus, in the following photocatalytic reactions, the PHEMA-TX-1 was used.

3.2 Study on PHEMA-TX based photocatalytic reaction

Using PHEMA-TX-1 as catalyst, the photocatalytic reaction and its recycling ability was systematically studied. Three typical substrates of tris(4-methoxyphenyl)phosphane, methyl(phenyl)sulfane, (4-methoxyphenyl)boronic acid were selected. The yield was determined by ^{1}H NMR analysis of the crude reaction mixture using dibromomethane as internal standard, respectively.

For the reactant of tris(4-methoxyphenyl)phosphane (**1a**), it can be completely consumed in 8 h and the NMR yield of the corresponding product tris(4-methoxyphenyl)phosphine oxide (**2a**) was 99 % in the first cycle of photocatalytic reaction. From ^{1}H NMR spectrum for **1a**, the resonance signal of protons on phenyl group can be attributed at 6.90 ppm and 7.32 ppm. After the photocatalytic reaction, from ^{1}H NMR spectrum for **2a**, the resonance signal of protons shift to 6.95 ppm and 7.57 ppm, respectively. The ^{1}H NMR results clearly confirmed that **1a** was completely converted into **2a** (**Figure 3**). After the first cycle, the catalyst PHEMA-TX-1 can be recovered by simple precipitation in EA and directly used for the second cycle. The following cycles of reactions were performed using the same procedure. It could be reused seven times without significant loss of the catalytic activity. From the seventh cycle, a slightly yield decreasement was observed (**Figure 4**).

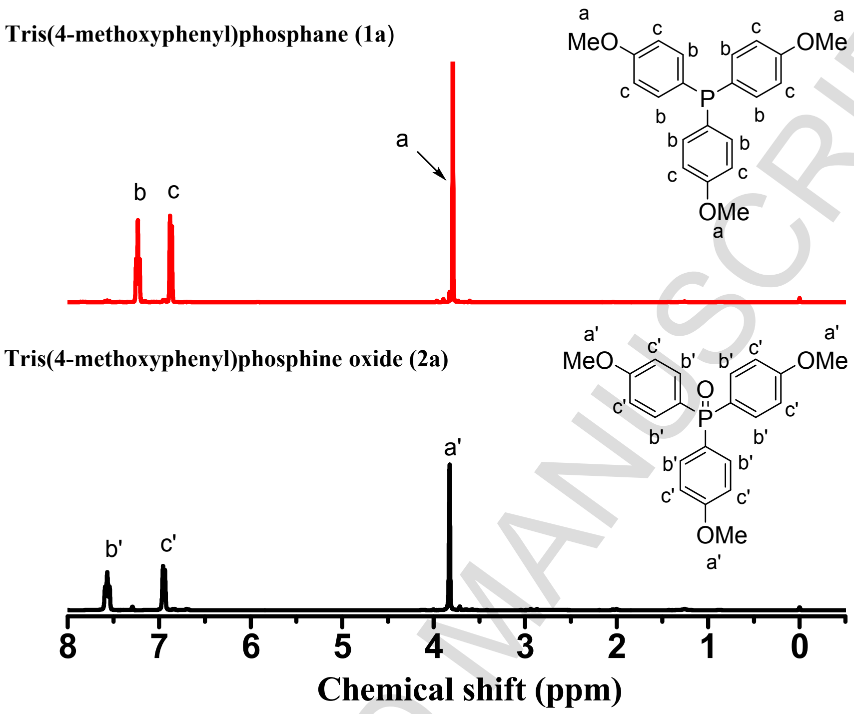


Figure 3. ^{1}H NMR spectra of **1a** and **2a** in $CDCl_3$.

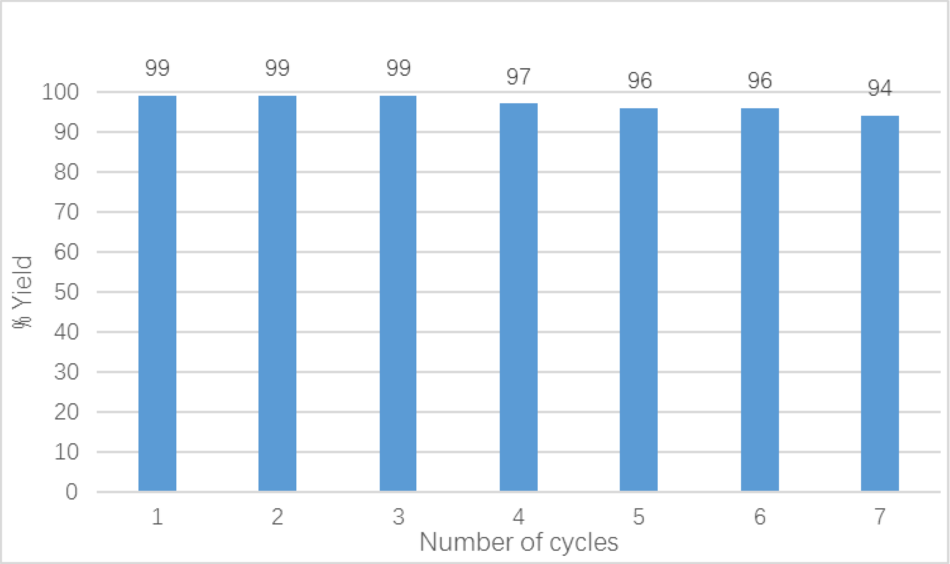


Figure 4. Recycling experiments of the photocatalytic reaction of **1a**.

For the reactant of methyl(phenyl)sulfane (**1b**), the first cycle of photocatalytic reaction was finished in 12 h and the NMR yield of the corresponding product methyl(phenyl)sulfoxide (**2b**) was 99 %. From **Figure 5**, the high conversion of **1b** can be confirmed by the complete shift of resonance signal of methyl groups (-C$\boldsymbol{H}_3$) from 2.40 ppm (before the photocatalytic reaction) to 2.72 ppm (after the photocatalytic reaction). Additionally, the protons on phenyl group completely shift from 7.25-7.35 ppm to 7.52-7.65 ppm. Similarly, after the first cycle, the catalyst PHEMA-TX-1 can be recovered by simple precipitation in EA and was directly used for the second cycle. The following cycles of reactions were performed using the same procedure. ^{1}H NMR (Figure 1) and GPC (Figure 2) of PHEMA-TX-1 were still identical to the freshly prepared ones after 3 cycles. The catalyst could be reused seven times without significant loss of the catalytic activity. From the seventh cycle, a slightly yield decreasement was observed (**Figure 6**).

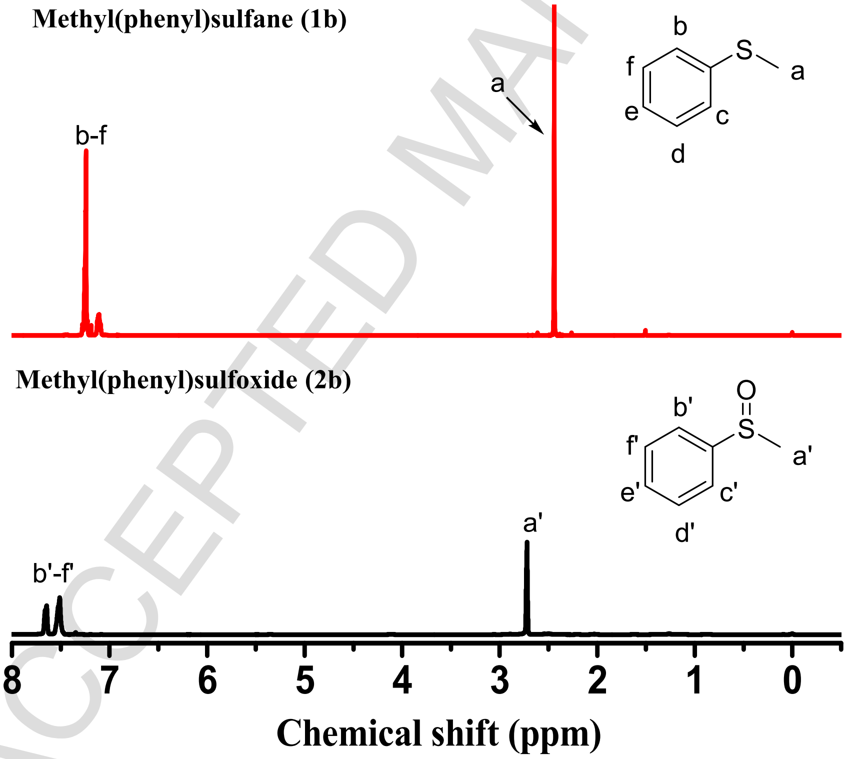


Figure 5. ^{1}H NMR spectra of **1b** and **2b** in $CDCl_3$.

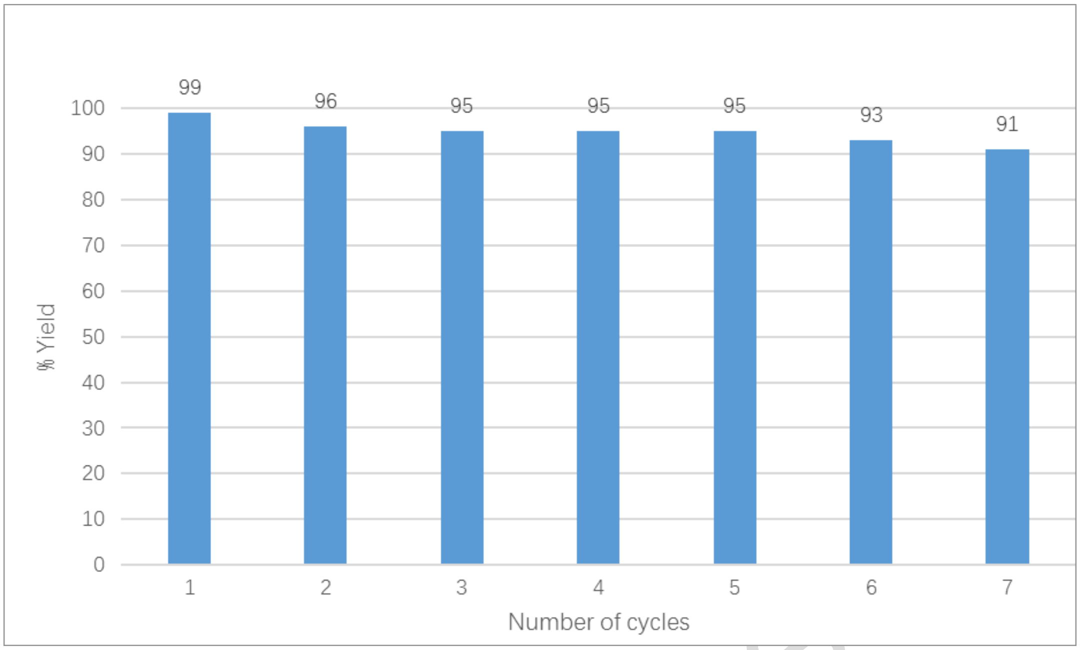


Figure 6. Recycling experiments of the photocatalytic reaction of **1b**.

For the reactant of (4-methoxyphenyl)boronic acid (**1c**), in the first cycle of photocatalytic reaction, the reaction time for the complete conversion was 8.5 h and the NMR yield was 99 %. Again, the high conversion of substrate was confirmed by ^{1}H NMR spectrum. Before the photocatalytic reaction, the resonance signal of protons on phenyl groups can be observed at 7.0 ppm and 8.20 ppm. Notably, after the photocatalytic reaction, one can observed that the signal completely shift to 6.78 ppm (**Figure 7**). After the first cycle, the catalyst PHEMA-TX-1 can be recovered by simple precipitation in EA and directly used for the second cycle. The following cycles of reactions were performed using the same procedure. It could be reused seven times without significant loss of the catalytic activity. From the seventh cycle, a slightly yield decreasement was observed (**Figure 8**).

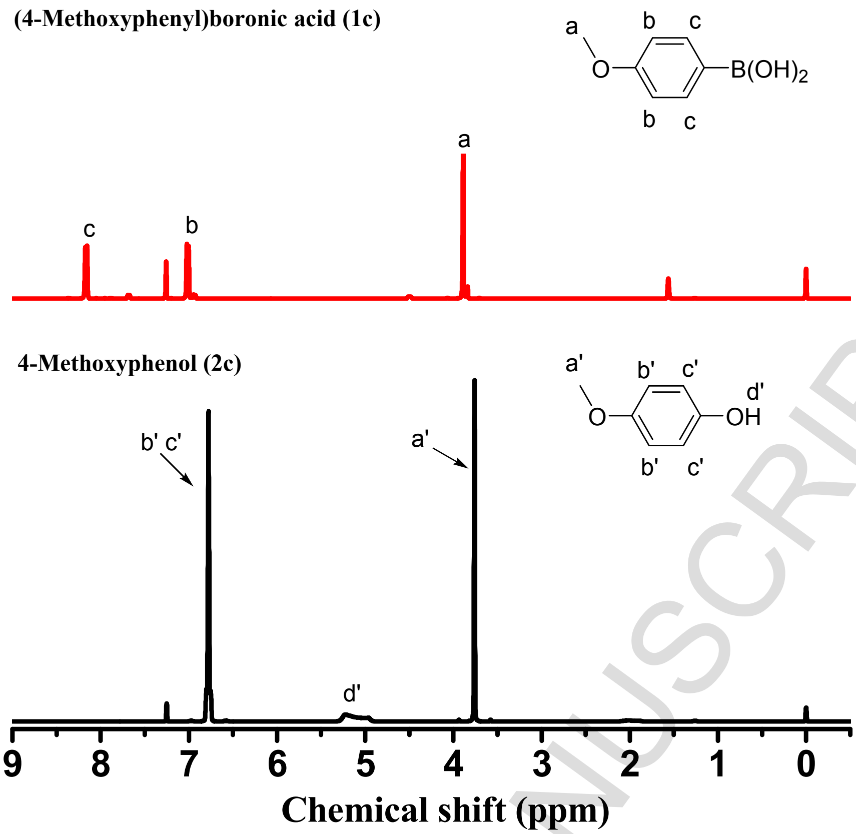


Figure 7. ^{1}H NMR spectra of **1c** and **2c** in $CDCl_3$.

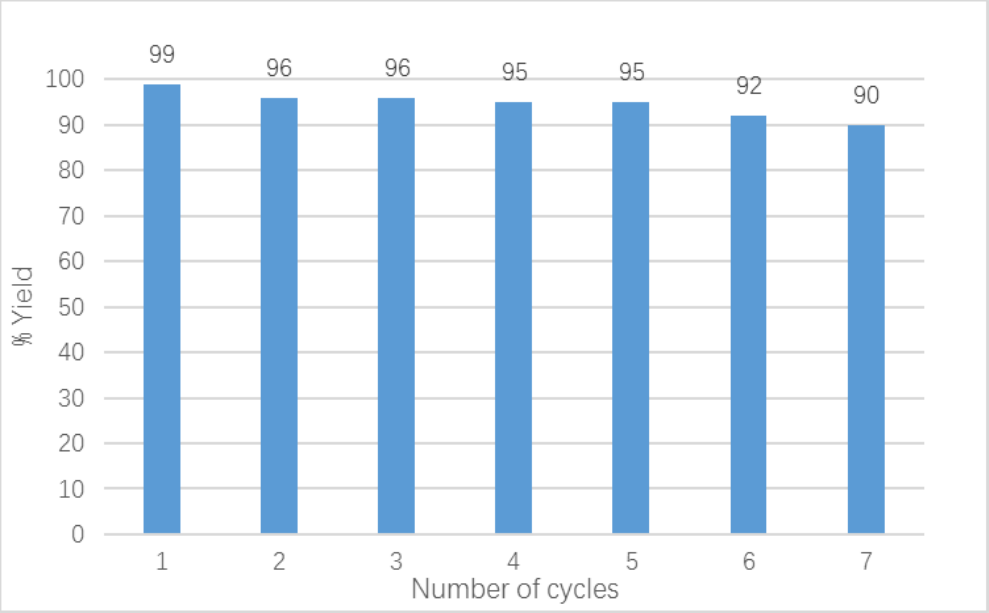


Figure 8. Recycling experiments of the photocatalytic reaction of **1c**.

From the above three photocatalytic reactions, we can draw a conclusion that the designed photocatalyst PHEMA-TX in this work has an excellent photocatalytic property and recyclability. The slight loss of the catalytic activity from the seventh cycle, might be attributed to the loss of PHEMA-TX during the recover procedure and the possible side reaction on the functional group of TX.

4. Conclusion

In summary, the functional TX groups were immobilized on precursor PHEMA and the novel macromolecular photosensitizer PHEMA-TX was prepared. In order to introduce high content of TX groups onto PHEMA, two modification routes was attempted. When TX-COCl was used, a relatively high modification efficiency of 64 % can be reached. However, when an alternative route using DMAP and DCC as catalyst, the modification efficiency was rather low (18.5 %). The reason can be attributed to the bulky substituent TX group was used, which limited the modification efficiency. Subsequently, the as-synthesized PHEMA-TX was used as photocatalyst for three substrates. The results showed that the photocatalyst PHEMA-TX could be easily recovered from the reaction mixture by a simple precipitation and reused for at least seven times. The excellent photocatalytic property, easy separation, and recyclability are actually acting solid evidences for the potential of PHEMA-TX developed in this work.

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Highlights

1) A novel synthetic method of thioxanthone-containing macromolecular photosensitizer was developed.

2) This PHEMA-TX showed very nice photocatalytic activity in photo oxidation of tris(4-methoxyphenyl)phosphane, methyl(phenyl)sulfane, (4-methoxyphenyl)boronic acid.

3) This photocatalyst PHEMA-TX could be easily separated, recovered by a simple precipitation, and reused.