Synthesis and Characterization of Phthalocyanine Polymer Towards Nonlinear Optical Applications

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Abstract. In the present study, linear poly(methyl methacrylate-co-phthalonitrile) (P(MMA-co-CPMA)) polymer was prepared by reversible addition-fragmentation chain transfer (RAFT) polymerization. Then the P(MMA-co-CPMA) polymer followed by macrocyclization reaction to form poly(methyl methacrylate-co-zinc phthalocyanine) (P(MMA-co-ZnPc)) polymer. The P(MMA-co-ZnPc) polymer was characterized by fourier transform infrared, nuclear magnetic resonance, ultraviolet-visible absorption. The nonlinear optical properties of the P(MMA-co-ZnPc) polymer were investigated by using the Z-scan technique at 532 nm with 7 ns laser pulses. The results revealed that the P(MMA-co-ZnPc) polymer exhibited excellent reverse saturable absorption (RSA) performance.

1. Introduction
Among many nonlinear optical (NLO) materials, organic dyes with long π-conjugated structures had garnered more attention [1-3]. Metallophthalocyanines (MPcs) with the highly delocalized aromatic 18 π-electron system revealed characteristic reverse saturable absorption (RSA) properties in NLO field [4-6]. For improvement RSA properties and solubility, MPcs was introduced into polymer. And the polymer containing MPcs could be better protection of human eyes and optical sensors from the exposure to severe laser beams through RSA properties [7-9]. In this work, for improvement of the RSA properties and solubility, polymers containing ZnPc molecules were prepared. The results revealed that P(MMA-co-ZnPc) polymer had satisfactory RSA properties and good solubility.

2. Experimental Section

2.1. Materials
Methyl methacrylate (MMA) was distilled at reduced pressure. 4-Hydroxyphthalonitrile, methacryloyl chloride, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 4-nitrophthalonitrile, benzyl alcohol and zinc acetate were purchased from Aladdin Reagent Company and used as received. And ultrapure water was used for all the experiments.

2.2. Instruments
Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer Frontier spectrometer. ¹H NMR spectra were recorded on a Bruker AVANCE II 500 MHz NMR spectrometers. UV-Vis absorption spectra were recorded on a Shimadzu UV-2600 UV-Vis spectrophotometer. Molecular weight (Mn) and the polymer dispersity index (PDI) were determined using gel permeation chromatography (GPC) with RID detector. The Z-scan measuring instrument was performed with a...
532 nm laser with a repetition rate of 10 Hz.

2.3. Route of 3,4-Dicyanophenyl Methacrylate (CPMA)
The synthetic routes were as the reference [10]. 4-Hydroxyphthalonitrile (1.44 g, 10 mmol) and pyridine (0.8 mL, 10 mmol) were added into tetrahydrofuran solution at 0 °C ice-water bath. Methacryloyl chloride (1.03 mL, 10.5 mmol) in CH$_2$Cl$_2$ solution was added into reaction flask. The mixture solution was synthesized for 12 h. Following, the solution was extracted with ethyl acetate, and the ethyl acetate organic phase was abstersive with brine. The purified product was obtained by silica gel chromatography on (ethyl acetate: petroleum ether (v: v) =1: 4) to obtain the purified white powder 1419 mg. $^1$H NMR (DMSO-d$_6$, δ, ppm): 8.26(d, 1H$_{3}$), 8.15(d, 1H$_{2}$), 7.86(dd, 1H$_{4}$), 6.35 (s, 1H$_{5}$), 6.01(s, 1H$_{1}$), 2.01(s, 3H$_{6}$). FT-IR ($\nu_{\text{max.}}$, cm$^{-1}$): 3114, 3056, 2235, 1735, 1636, 1603, 1572, 1485, 1246.

2.4. Route of Poly(Methyl Methacrylate$_{161}$-co-Phthalonitrile$_{1,5}$) (P(MMA$_{161}$-co-CPMA$_{1,5}$): R1) Polymer
The procedures were as the reference [11]. AIBN (3.2 mg, 0.02 mmol), MMA (0.95 mL, 9 mmol), CPMA (0.02 g, 0.08 mmol), chain transfer agent (0.04 g, 0.1 mmol) and 1,4-dioxane (6 mL) were added to a dried flask. The flask content was filled with argon. The reaction solution was heated at 70 °C for 8 h and following the 1,4-dioxane was evaporated. The mixture was dissolved in 4 mL tetrahydrofuran and then the mixture solution was precipitated in cold hexane for four times. White power was obtained drying at ambient temperature under vacuum.

2.5. Route of Poly(Methyl Methacrylate$_{167}$-co-Zinc Phthalocyanine$_{1,1}$) (P(MMA$_{167}$-co-ZnPc$_{1,1}$): R2) Polymer
The synthetic procedures were as the reference [12]. R1 (0.25 g), 4-nitrophthalonitrile (0.03 g), zinc acetate (0.02 g), DBU (8 μL) and benzyl alcohol (35 mL) were added to a dried flask. The flask content was filled with argon. The reaction solution was heated at 155 °C for 2 days. Then the solution was dialyzed with dimethylformamide for 4 days and deionized water for 5 days. After filtration, the greenish product was obtained 214 mg drying at ambient temperature under vacuum.

3. Results and Discussion

3.1. Synthesis and Characterization
The characteristic of R1 and R2 polymers was confirmed by FT-IR and $^1$H NMR in figure 1 and figure 2. From the FT-IR spectrum in figure 1, the C≡N stretching vibration absorption disappeared at 2238 cm$^{-1}$, and the typical -NO$_2$ stretching vibration absorption of ZnPc molecule appeared at 1527 cm$^{-1}$ after macrocyclization reaction of R1. From the $^1$H NMR spectrum in figure 2, after macrocyclization of R1, the characteristic chemical shifts of CPMA molecule disappeared at 7.73 ppm, 7.64 ppm, 7.55 ppm, and new feature peaks of the ZnPc molecule appeared at 7.62 ppm, 7.47 ppm, 7.36 ppm in figure 2 (b). The polymers molecular weight ($M_n$, $M_w$) and polymer dispersity index (PDI) were obtained by GPC, and the detail results of R1 and R2 polymers were summarized in table 1.
Figure 1. The FT-IR spectra of R1: P(MMA$_{161}$-co-CPMA$_{1.5}$) and R2: P(MMA$_{167}$-co-ZnPc$_{1.1}$).

![FT-IR spectra](image)

Figure 2. The $^1$H NMR spectra of (a) R1: P(MMA$_{161}$-co-CPMA$_{1.5}$) and (b) R2: P(MMA$_{167}$-co-ZnPc$_{1.1}$).

![NMR spectra](image)

Table 1. Characterization data of polymers.

| Polymer | $M_n$ | $M_n$,GPC | $M_w$,GPC | PDI |
|---------|-------|-----------|-----------|-----|
| R1      | 16500 | 17800     | 30500     | 1.71|
| R2      | 17500 | 15000     | 26200     | 1.42|

$^a$ Determined by $^1$H NMR.

$^b$ Determined by GPC with RID detector

3.2. Optical Properties

The UV-Vis absorption spectra of the R1 and R2 were researched in DMF solution. As presented in figure 3, R1 showed the absorption pink at 309 nm that could be assigned to the typical absorption pink of CPMA molecule. After macrocyclization of R1, new characteristic absorption pinks showed at 351 nm and 702 nm in UV-Vis absorption spectra of R2, which were put down to the B-band and Q-band of ZnPc molecule.
Figure 3. The UV-Vis spectra of R1: P(MMA\textsubscript{161}-co-CPMA\textsubscript{1.5}) and R2: P(MMA\textsubscript{167}-co-ZnPc\textsubscript{1.1}) in DMF (5×10\textsuperscript{-5} mol/L).

3.3. *Reverse Saturable Absorption Properties*

Figure 4 showed the open aperture RSA tests of the R1 and R2 in DMF solution. The results revealed that R1 has no change in the transmittance when the position changed in the RSA test. However, the transmittance of R2 showed a valley with the position changing. This evolution process of the transmittance of R2 could be contributed to the RSA properties. And the nonlinear absorption coefficients of R2 was 13×10\textsuperscript{-11} m/W. The consequences suggested that the efficient ZnPc units played important role in the RSA properties of R2 polymer.

Figure 4. The Open aperture Z-scan tests of R1: P(MMA\textsubscript{161}-co-CPMA\textsubscript{1.5}) and R2: P(MMA\textsubscript{167}-co-ZnPc\textsubscript{1.1}) in DMF (3×10\textsuperscript{-4} mol/L).

4. *Conclusions*

In this research, R1 polymer including phthalonitrile was synthesized by RAFT polymerization, and following R1 polymer was used to prepare R2 polymer containing ZnPc by the macrocyclization reaction. The P(MMA\textsubscript{167}-co-ZnPc\textsubscript{1.1}) polymer containing ZnPc showed good solubility in organic solution. With introduction ZnPc units in R2 polymer, R2 polymer obtained satisfactory RSA properties.
5. Acknowledgements
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