Fabrication and Applications of Pentaerythritol Tetrakis(3-Mercaptopropionate) Addition to N-Phenylacrylamide Based on Thiol-Ene Click Reaction

Hongda Ding¹ and xiande shen¹

¹Changchun Sci-Tech University

March 14, 2024

Abstract

Thiol/ene free-radical reactions are highly effective when compared with complicated synthesis methods and precise sequence control. Investigation of mercapto-olefins for N-phenylacrylamide (NPA) by thiol/ene free-radical mechanism has not been reported so far. Herein, we report the thiol/ene free-radical reaction of N-phenylacrylamide (NPA)/pentaerythritol tetra(3-mercaptopropionate) (PETMP) by ultraviolet irradiation to give the final product (abbreviation: NPP). The preliminary applications of the NPP were also explored including photoluminescence, adhesive, and thermoresponsive. The adhesion of the NPP has been validated in various substrates. Moreover, it has a strong ability to stick to glass surfaces, even when submerged in water for an extended time. The better adhesion may be attributed to functional groups forming dynamic crosslinks based on hydrogen bonding, van der Waals interactions, and π-π interactions and high hydrophobicity of the phenyl group. This strategy opens an avenue for NPA by thiol-ene click reaction.

1. INTRODUCTION

Acrylamides are well-known for their ability to undergo thiol-ene reactions, whose mechanisms include nucleophilic addition and free-radical reactions [1-3]. Thiol/ene free-radical reactions are light-activated in the presence of a photoinitiator, the reaction is also called the thiol-ene click reaction [2-7]. The click reaction has become a popular method for synthesis and modification in organic chemistry due to its high selectivity and efficiency. It has several advantages such as the absence of side products, mild reaction conditions, and insensitivity to oxygen, aligning with the concept of atom economy [2]. Compared with the traditional thermal curing reaction, the UV-cured reaction of thiol-ene has several advantages such as delayed gel point, less consumption of energy, and simpler curing equipment [6].

NPA is one of the acrylamide derivatives containing functional groups of phenyl, vinyl, and amide, which has been used in some functional materials such as thermoresponsive poly(N-acryloyl glycinamide)-stat-poly(N-phenylacrylamide) brushes that exhibit Upper Critical Solution Temperature (UCST)-type behavior [8]. Additionally, a thermo-reversible coacervate of copolymer of N, N-dimethylacrylamide (DMAA) with N-phenylacrylamide (NPA) is also created. An increase in the content of NPA in the copolymer leads to an abrupt decrease in its cloud point (Lower Critical Solution Temperature, LCST) due to an increase in hydrophobicity [9]. The hydrophobicity of the phenyl group is also responsible for the enhancement of underwater cohesion strength [10]. The addition of a phenyl group in the compatibilizing agent resulted in both deoxidizing and compatibilizing effects. This adhesive film can be effectively used for electronic devices that require both deoxidization and adhesion [11]. Microfibrillar adhesives made from phenyl-containing polydimethylsiloxane (p-PDMS) elastomers have been proposed, which exhibit superior low-temperature reversible adhesion [12].
Pentaerythritol tetra(3-mercaptopropionate) (PETMP) has been researched as a thiol monomer for the fabrication of water/acetone vapor-responsive hierarchical films through one-step thiol-ene click reaction [3]. PETMP is also selected as the hardener for epoxy coatings due to its polyfunctionality, which is crucial for achieving desirable mechanical and physical properties of the coating [13].

However, there has been no report of a reaction of N-phenylacrylamide (NPA) and thiol based on radical mechanism so far. To expand its study, we synthesized NPP and examined its potential applications in terms of illumination, adhesion, and thermoresponsiveness.

Figure 1. Schematic diagram of the fabrication for the PETMP addition to NPA.

2. Materials and methods
2.1. Materials

Materials: N-phenylacrylamide (NPA), pentaerythritol tetra(3-mercaptopropionate) (PETMP), 2-hydroxy-2-methylpropioophenone (1173), ethanol, acetone, and deuterated chloroform (CDCl₃) were obtained from Energy Chemical (Anhui, China). The NPA and PETMP serve as vinyl and thiol monomers, respectively. 1173 was used as a photoinitiator. All materials were analytical purity and used as received unless stated otherwise.

2.2. Instruments of characterization

¹H NMR (Nuclear Magnetic Resonance) spectra were recorded by Bruker Avance III HD 500 instrument. Transmittance and absorbance measurements were taken using a Jasco V-770 UV-Vis spectrophotometer equipped with a temperature controller. The temperature was elevated at a rate of 2°C min⁻¹ when observed thermo responsiveness. Changes in transmittance with temperature were obtained under a wavelength of 500 nm.

2.3. Synthesis of the NPP

The NPP was prepared according to the following procedure, referring to the previous kinds of literature [2, 3, 7]. Photoinitiator (1173, 1% of total mass), the molar ratio of PETMP: NPA (thiol:ene) was 1:4, and the above mixture was dissolved in a mixed solvent of acetone and ethanol (volume ratio of 2:1) of 20 ml. Followed by it was illuminated by a 365 nm UV light lamp for 2 h. Besides, the reaction without PETMP was also conducted, which serves as a comparison and coded as NP.

3. Results and discussion

3.1. Synthesis of the NPP

The NPP was fabricated by thiol-ene click reaction. NPA is the ene, PETMP is the thiol, and 1173 is a photoinitiator. The schematic diagram is given in Figure 1. Herein, a 1:4 molar ratio of thiol to ene was utilized to enable the full reaction of NPA.

3.2. Characterization of the NPP

UV illumination and UV-Vis spectra were employed to observe changes in the precursor of PETMP addition to NPA and the final product-NPP. Figures 2a and b show color changes in the precursor of PETMP addition to NPA with and without UV irradiation, it is a blue color under UV irradiation, whereas as we can see the
NPP under UV irradiation (Figure 2c) is green. Figures 2d and e are comparisons of the NPP (left) after concentrating at fume hood and precursor (right) with and without UV irradiation, the concentrated NPP is yellow without UV irradiation and green under UV, green is more apparent when the glass coated NPP under UV irradiation (Figure 2f), to confirm successful synthesis of NPP, absorbances and wavelengths of the NPP (UVA) and precursor (UVB) were obtained (Figure 2g). It is seen that the wavelength more wider and absorbance more intense after UV irradiation, indicating synthesis of NPP was achieved.

![Figure 3](image)

Figure 3. $^1$H NMR spectra of NPA, PETMP, and NPP in CDCl$_3$ (500 MHz).

To further confirm that the observed product corresponded to the expected thiol-addition adduct, NMR experiments were performed. $^1$H NMR spectra of NPA, PETMP, and the resultant product in CDCl$_3$ (500 MHz) were gained to further prove the successful fabrication of NPP. The peaks of the double bond in NPA at 5.93 and 6.36 ppm and thiol in PETMP at 1.68 ppm disappeared as presented in Figure 3, respectively. In addition, the peak of the methylene in the resultant product at 2.8 ppm appeared, further proving the molecular structure and successful preparation of NPP [2]. $^1$H NMR spectra of NPA reactions with and without PETMP in CDCl$_3$ (500 MHz) were used as a reference to demonstrate the route of thiol-ene click reaction is effective. It was shown in Figure 3, as we expected that the peaks of the double bond in NP were retained, and there was no formation of the peak of the methylene.
3.3. Practical applications

The preliminary evaluation of the application of NPP as an adhesive was also explored. The as-synthesized NPP exhibits superior adhesion on various material surfaces, including glass, tinfoil, natural rubber, and pan paper (Figure 5 a1-a4). Moreover, the NPP proved to retain better adhesion strength for the glass for a long time even in water and would thus be suitable for practical applications underwater. The better adhesion may be attributed to functional groups forming dynamic crosslinks based on hydrogen bonding [14], Van der Waals interactions existing among the adhesive molecules and the adhesive/substrate interface [15],
and intermolecular π-π interactions of phenyl of NPA [10]. The high hydrophobicity of the phenyl group is responsible for the enhancement of cohesion strength underwater. Figures 5 c1-c4 show changes in the NPP in water within 12 hours, compared with NP in water within 72 hours (Figure 5 d1-d4). It is an intuitive phenomenon that NPP is an oily liquid, whereas NP is a solid precipitation, both are insoluble in water.

![Figure 6. (a and b) Plots of temperature versus transmittance for NPP and NP.](image7.emf)

NPA has been used as a thermoresponsive component due to its functional group of amides [8, 9], so we conducted the thermosensitive tests. Figures 6 a and b show plots of temperature versus transmittance for NPP and NP. NPP has a similar phenomenon compared with thermoresponsive materials with a LCST, whose transmittance declines regularly as the temperature rises [16, 17], however, NP has an irregular tendency. Inserts are changes in solubility of NPP with temperature rise in the CDCl3 in Figure 6 a, which is consistent with the LCST compound.

### Hosted file


### 3.4. The mechanism of thiol-ene click reaction for NPP

The thiol-ene click reaction proceeds in three steps, as illustrated in Figure 7. Step I involves photoinitiation, which generates free radicals to facilitate subsequent steps. In the first step, a photoinitiator 1173 was utilized to generate thiol radicals. The thiol free radical works as a nucleophilic reagent, while the vinyl acts as an electrophilic reagent. When both mercapto radical and vinyl exist together, they react swiftly to produce an intermediate that contains an active carbon-centered radical (RC·). This carbon-centered free radicals intermediate, being an exceptionally strong base, can dehydrogenate another thiol to renew the thiolate free radicals (steps II and III) [6], which corresponds to chain transfer and termination, more importantly, both are beneficial to the formation of NPP.

### 4. Conclusions

In this work, we synthesized NPP by a facile thiol/ene free radical reaction under ultraviolet irradiation, investigations of NMR and UV were utilized to further confirm the successful developed of the NPP. In addition, it can be utilized as promising candidates involving optical anti-counterfeiting, adhesive, and thermoresponsive materials. This study provides an idea for research and applications of NPA.

### Research Data Policy and Data Availability Statements

The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

### Credit authorship contribution statement
Hongda Ding: Investigation, Conceptualization, Writing-original draft, Validation, Data curation. Xiande Shen: Resources, Writing-review & editing, Supervision.

Declaration of Competing Interest
The authors declare that there are no related interests that influence the submitted work.

REFERENCES


