



A New Strategy of Post-Polymerization Modification to Prepare Functionalized Poly(disubstituted acetylenes)

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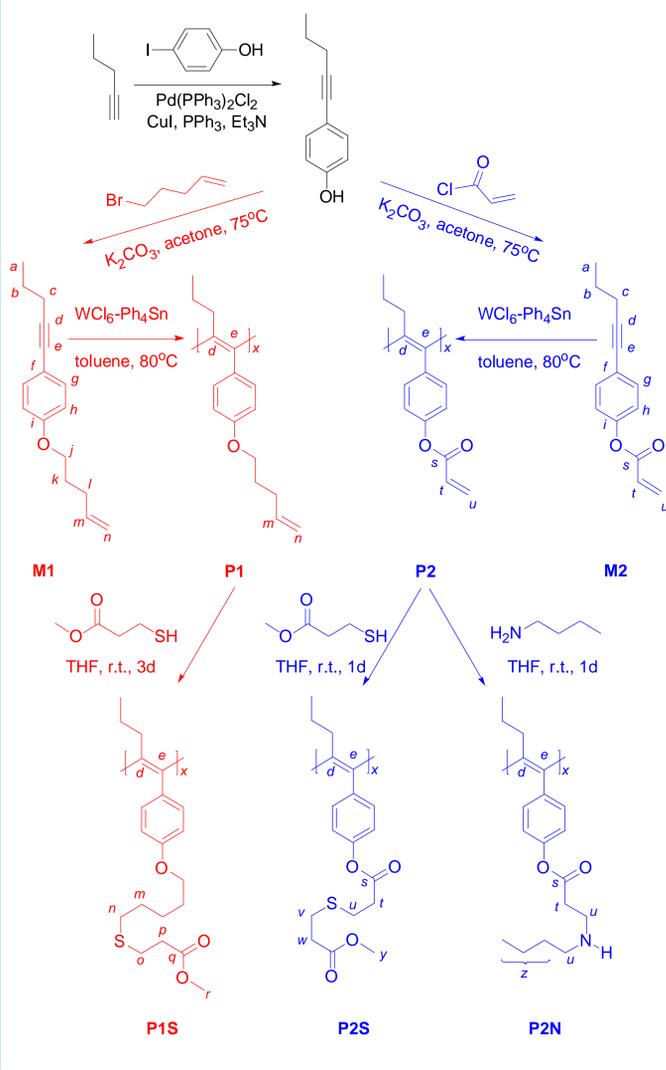
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INTRODUCTION

Poly(disubstituted acetylenes) (PDSAs) prepared from the polymerization of disubstituted acetylene monomers possess greatly enhanced fluorescent emitting property in comparison to their counterparts of mono-substituted polyacetylenes.^[1] Due to the fact that the catalysts for the preparation of PDSAs are intolerant to the polar functional groups, the species of functional PDSAs are rare and the exploration of proper synthetic routes is of fundamentally significant. Post-polymerization modification is a powerful tool that has been widely used in the production of functional polymers.^[2] Till now, activated ester strategy^[3] and CuAAC reaction^[4] have been successfully used in synthesis of functional PDSAs. In this work, we demonstrate our attempt to use thiol-ene click chemistry and Michael addition reaction for the preparation of post-functionalized PDSAs.

RESULTS AND DISCUSSION

Synthetic Routes



Scheme 1. Synthesis of poly(disubstituted acetylene) with reactive end-vinyl groups (**P1**, **P2**) and their derivatives (**P1S**, **P2S**, **P2N**) after thiol-ene reaction and Michael addition reaction.

CONCLUSIONS

PDSAs (**P1** and **P2**) with reactive vinyl groups at their side chains have been synthesized, and their derivatives **P1S** and **P2S** was obtained by using the thiol-ene click reaction, **P2N** was obtained through Michael addition. All of the derived polymers were fluorescent. From this work, the thiol-ene click reaction and Michael addition reaction have been demonstrated to be accessible paths to new functional PDSAs.

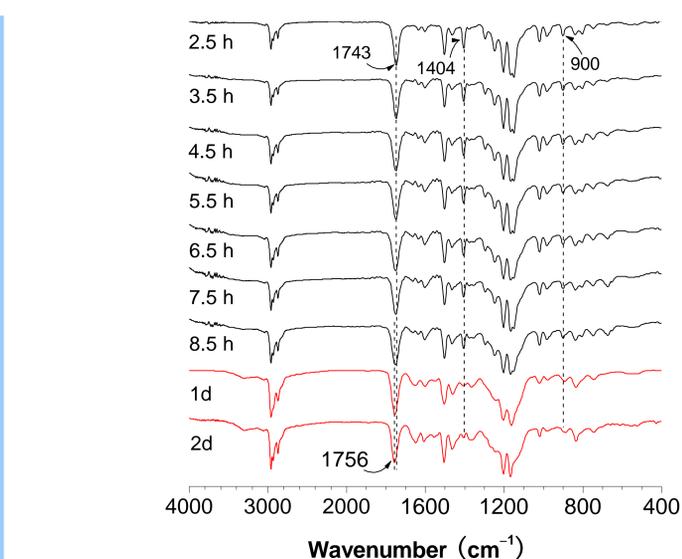
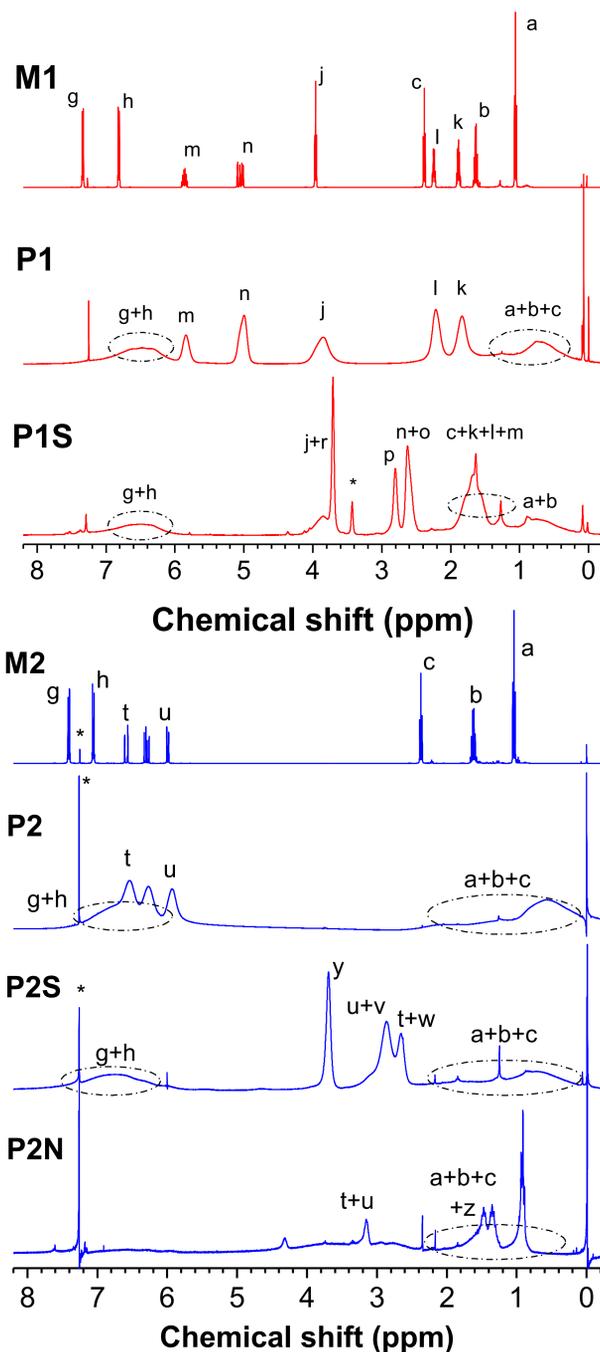


Figure 2. FTIR spectra of the reactant mixture of **P2** and *n*-butylamine. The characteristic bands for $-\text{CH}=\text{CH}_2$ and $\text{C}=\text{O}$ groups are labelled with wavenumbers.

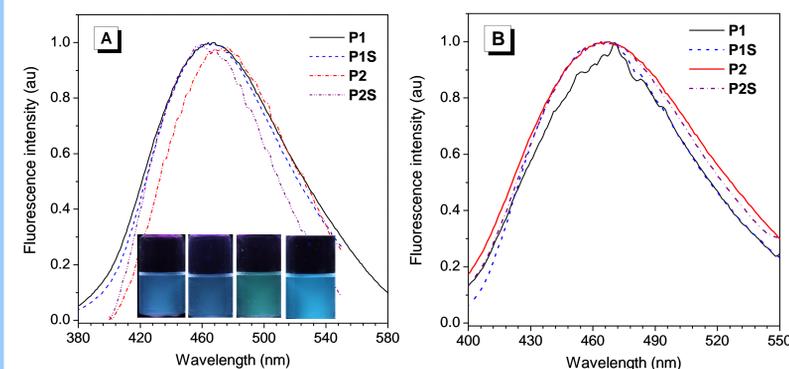


Figure 3. Fluorescence spectra of **P1**, **P1S**, **P2** and **P2S** in THF solution (A) and cast film (B). Inset of A shows the fluorescent images of the solutions, Polymer concentration: 10 μM , Excitation wavelength: 280 nm.

Figure 1. ^1H NMR spectra of the disubstituted acetylene monomer (**M1**, **M2**) and its polymers (**P1** and **P1S**, **P2**, **P2S** and **P2N**).

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