



A Versatile Approach to the Synthesis of Polyphosphazene Derivatives via the Thiol–Ene Reaction

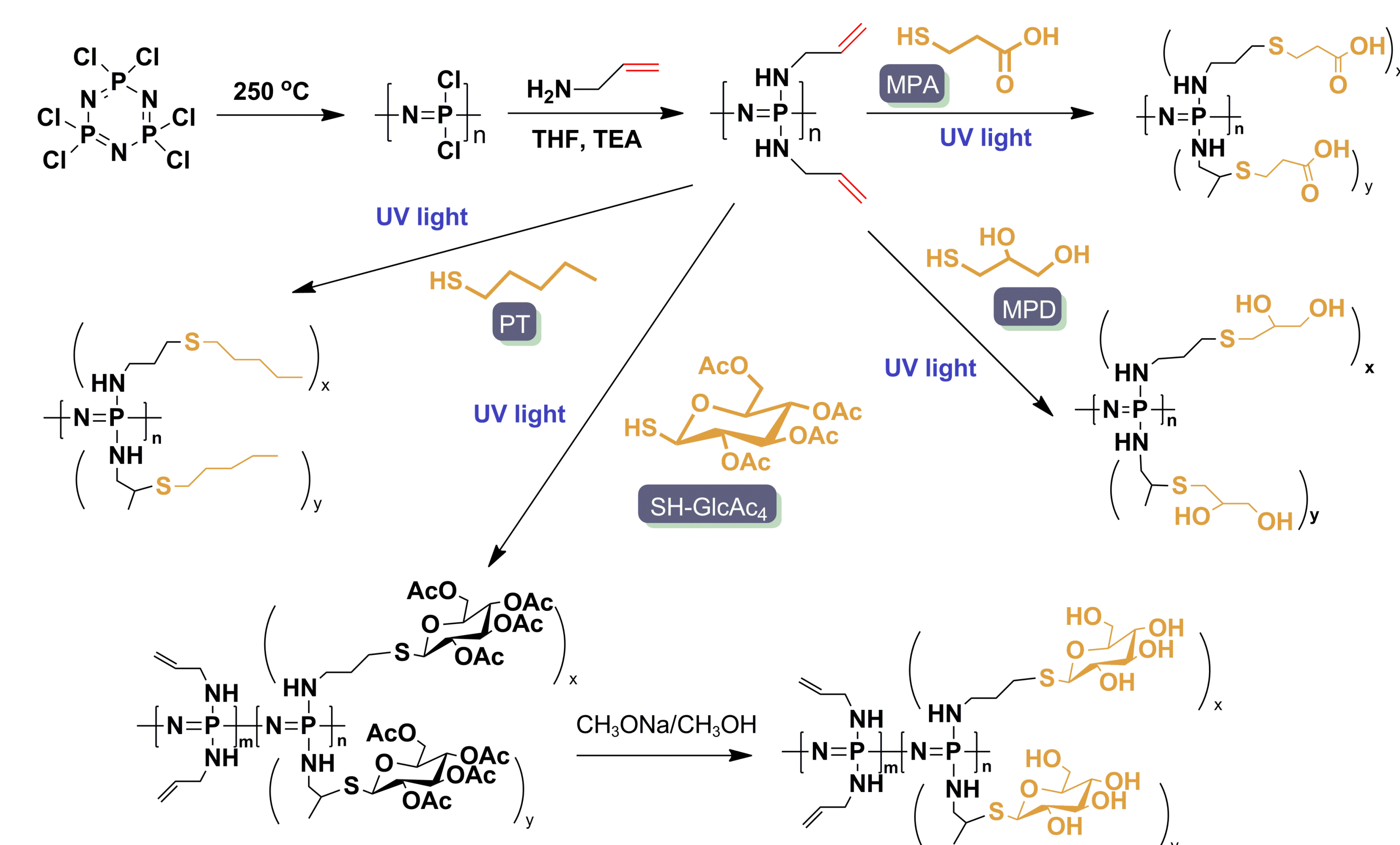


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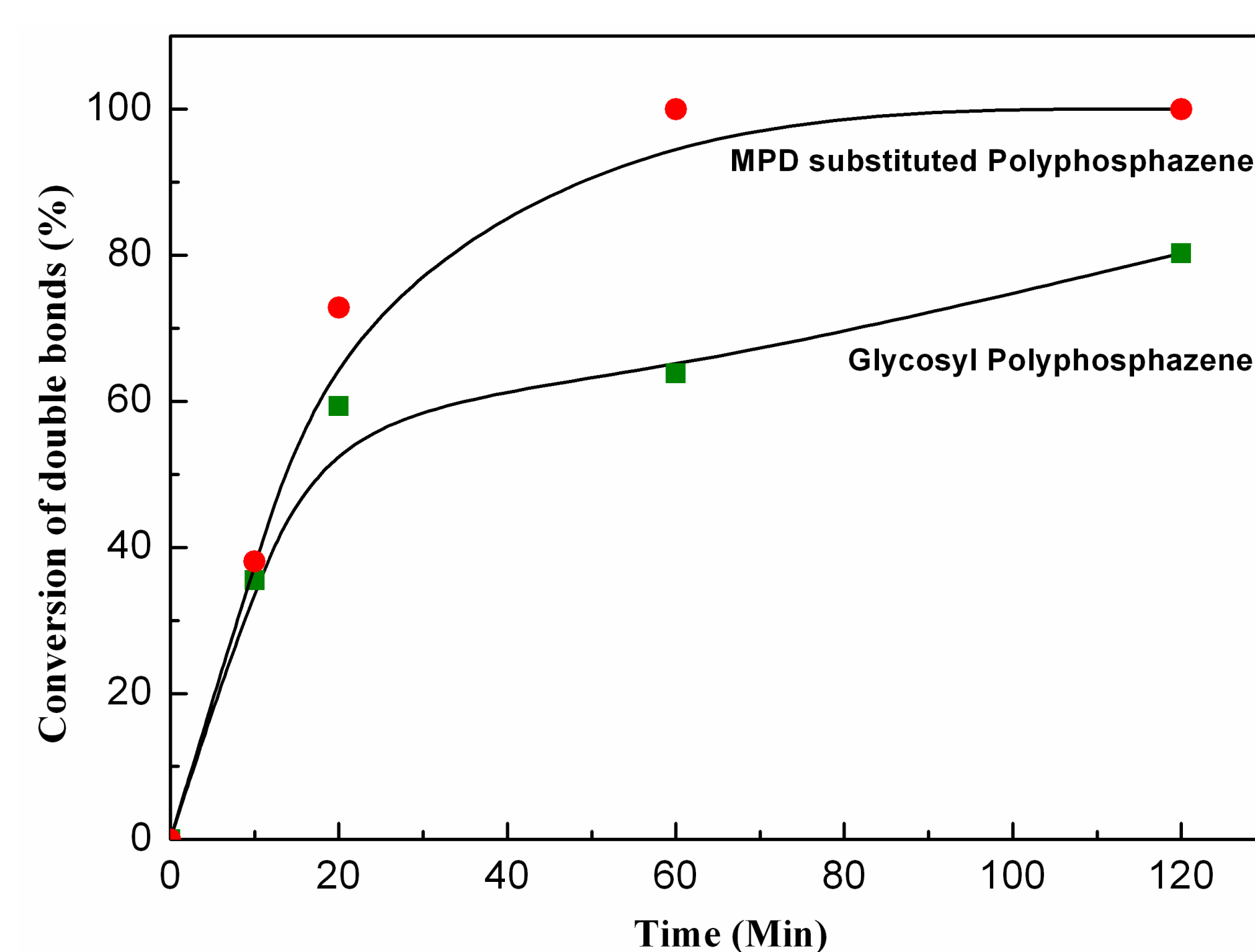
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Introduction

The thiol–ene radical addition reaction has been successfully used to synthesize polyphosphazene derivatives. Poly[bis(allylamino)phosphazene] with pendant allyl groups was reacted with different thiol reagents under UV irradiation. These thiol reagents include 1-pentan-3-thiol, 3-mercaptopropionic acid, 3-mercapto-1,2-propane- diol, and 2,3,4,6-tetra-*O*-acetyl-1-thio- β -D-glucopyranose. ^1H NMR analyses confirmed that the allyl polyphosphazene can be quantitatively modified by the mercaptans. 100% conversion of the allyl groups were reached in less than 60 min towards the first three mercaptans, while about 80% conversion of the allyl groups were reached after 120 min reaction towards the thioglucose. Using commercially available mercaptans, various functional groups were introduced into the polymer chain with ease, endowing polyphosphazene with different properties. Especially, trivial protection/deprotection procedures for traditional synthesis of polyphosphazene were not needed via this route.

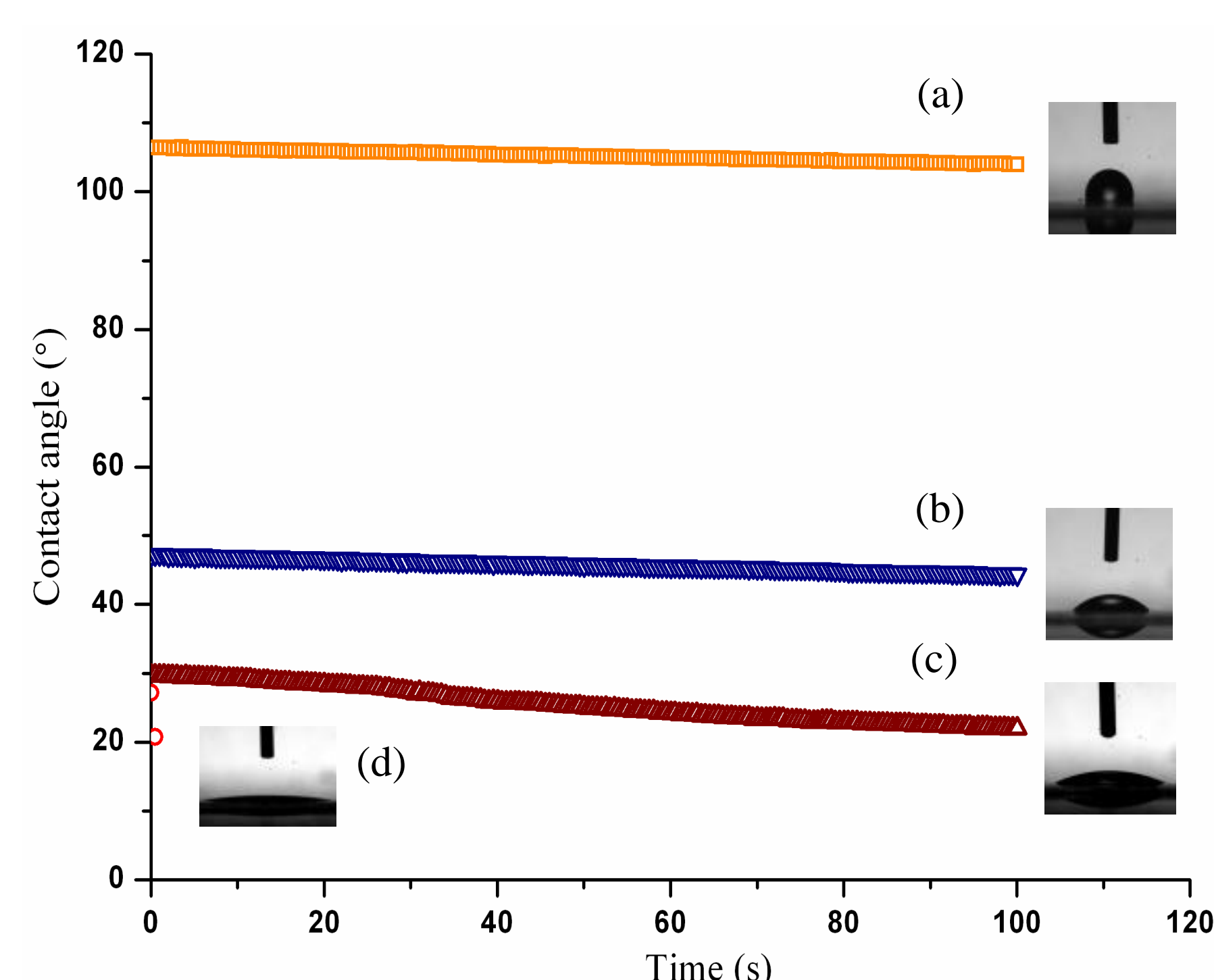


Schematic representation of the thiol–ene addition reaction between the allyl substituted polyphosphazene and the thiol reagents



Quantitatively functionalized polyphosphazene derivatives were synthesized via thiol-ene reaction without occurrence of side reaction such as cyclization between neighboring alkene groups as indicated by ^1H NMR.

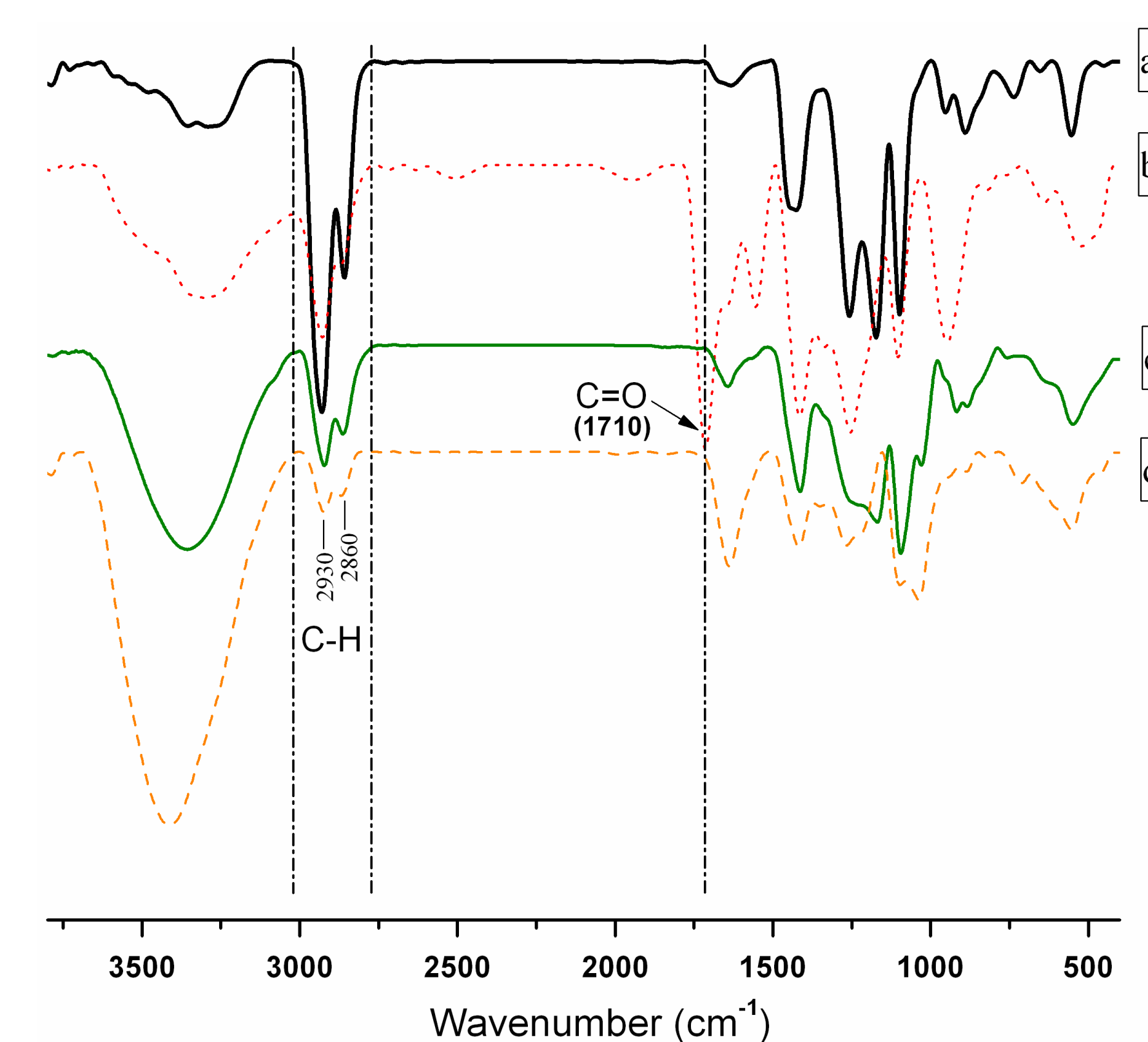
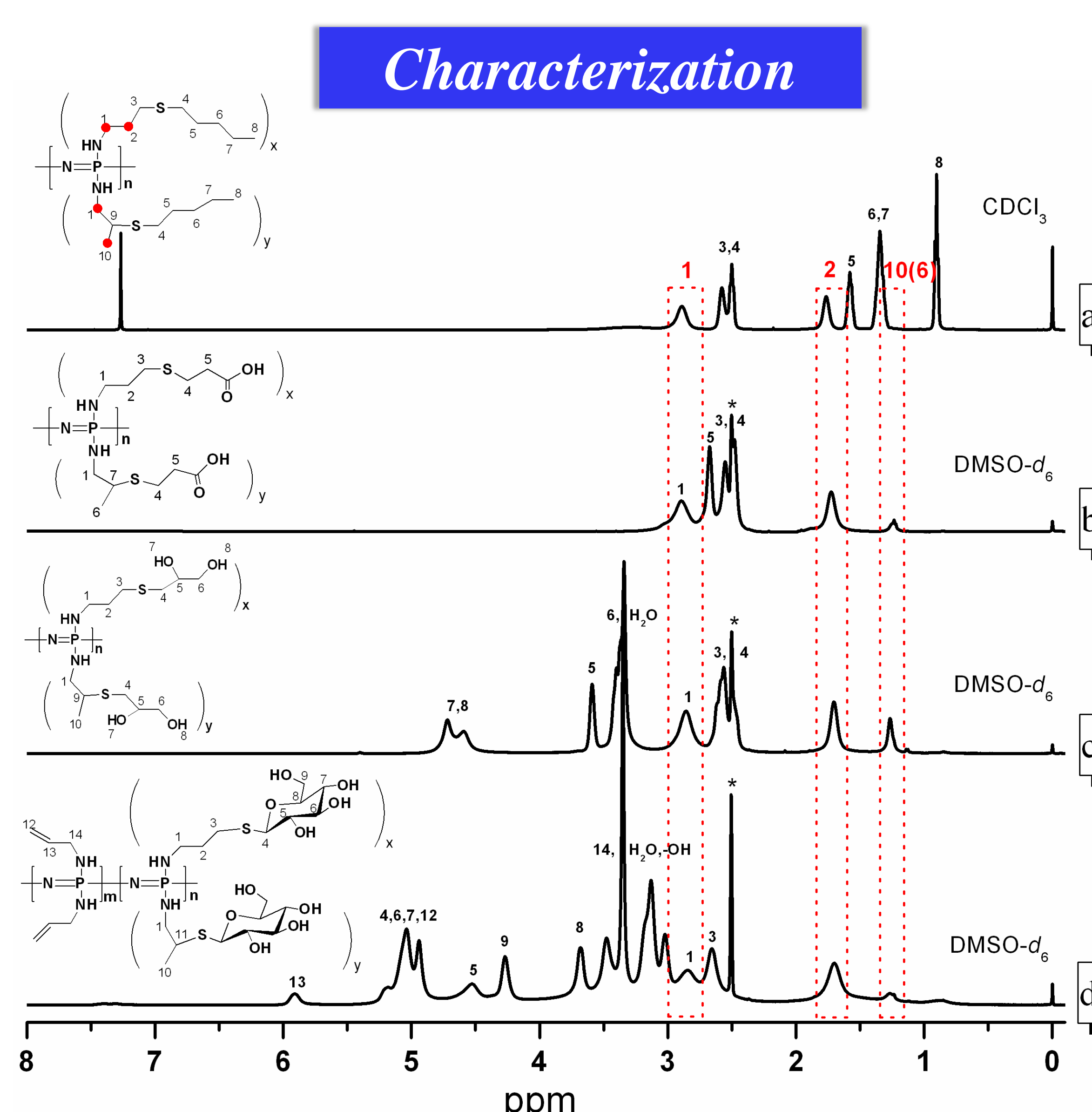
Besides, steric effects played an important role during the photochemical reaction of polymers with high local densities of alkene groups and thiols. A trace of the allyl group was still present in glucosyl polyphosphazene following 2 h of UV irradiation, whereas the conversion of the allyl group was complete in the MPD substituted polyphosphazene after only 1 h of reaction.



Water contact angle (left) of spin-coating films prepared from polyphosphazene derivatives with a) alkyl, b) glyceryl, c) carboxyl and d) glucosyl as pendant groups and SEM images (right) of platelet adsorption on these films.

Properties of spin-coating films prepared from polyphosphazene derivatives

Characterization



The behavior of platelet adsorption on these films was related with properties of side groups. Adsorption can not be observed on both the most hydrophobic or hydrophilic films with alkyl and glucosyl as pendant groups, respectively.

Conclusions

Quantitatively functionalized polyphosphazene derivatives were synthesized via thiol-ene reaction under UV irradiation. Spin-coating films prepared from polyphosphazene derivatives showed different hydrophilicity/hydrophobicity, furtherly affecting the behavior of platelet adsorption on these films.

Acknowledgement

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References

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