

# Amino-yne Click Reaction for Facile Polymer-Polymer Conjugation and Post-Polymerization Modification

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## Summary

Electron-deficient alkynes, connected to electron-withdrawing groups like carbonyls, readily react with nucleophiles, particularly primary or secondary amines, in the amino-yne click reaction [1]. This catalyst-free, room-temperature reaction yields dynamic enamines efficiently, without requiring heat or prolonged times. While well-explored in polymer science, its use for polymer-polymer conjugation and modification of amine-functional commercial polymers is recent. This study pioneers the synthesis of block copolymers using the amino-yne click reaction, conjugating an alkyne end-functional methoxy poly(ethylene glycol) with amine end-functional polystyrene or poly(N-isopropylacrylamide) at room temperature, forming block copolymers. Additionally, hyperbranched poly(ethylene imine) and an aminoethylaminopropylmethylsiloxane-dimethylsiloxane copolymer were modified using electron-deficient alkynes in just two minutes [2]. This approach enables facile, greener, and energy-efficient polymer modification and block copolymer synthesis without metal catalysts or heat.

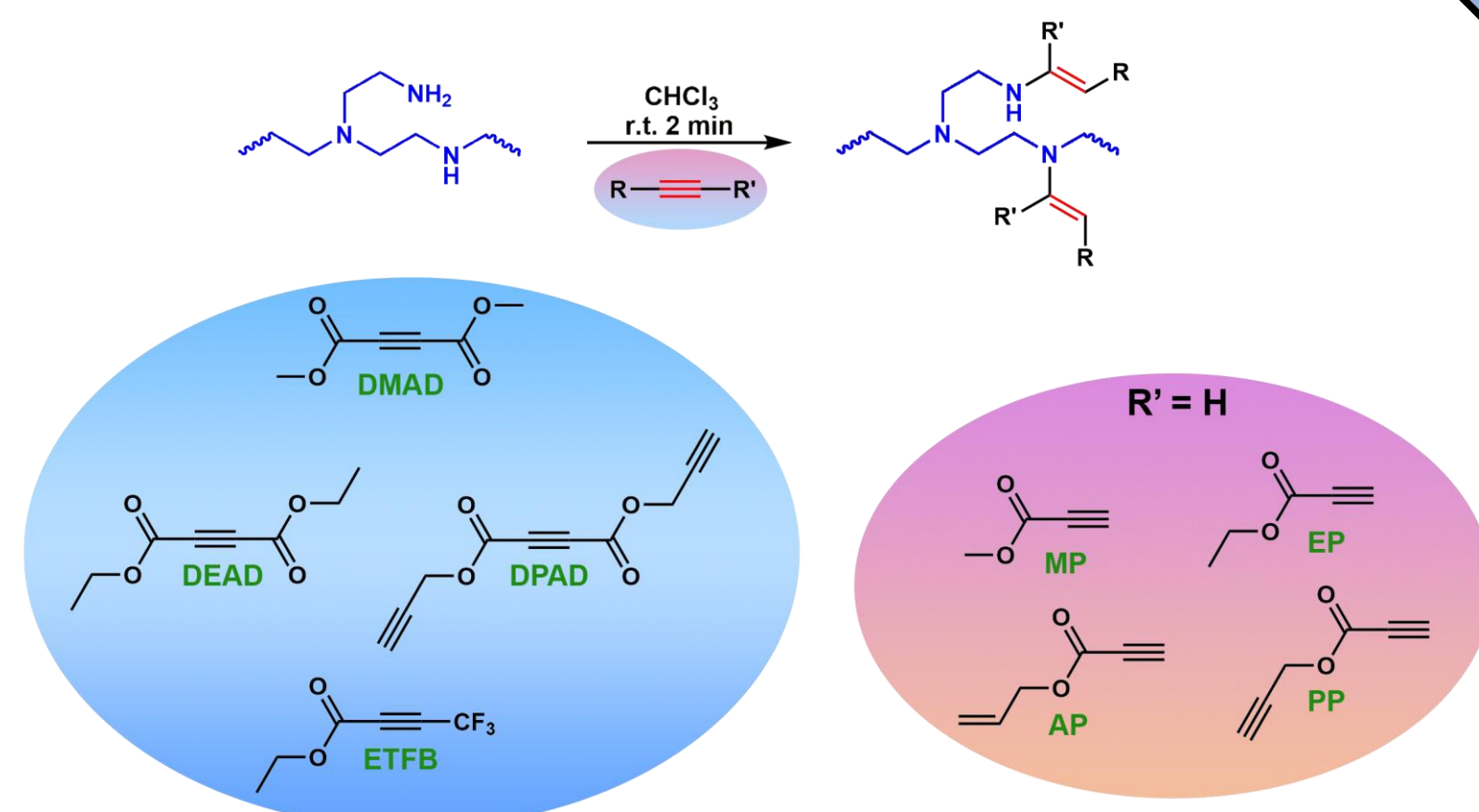


Figure 4: General scheme for PEI modification via amino-yne click reaction.

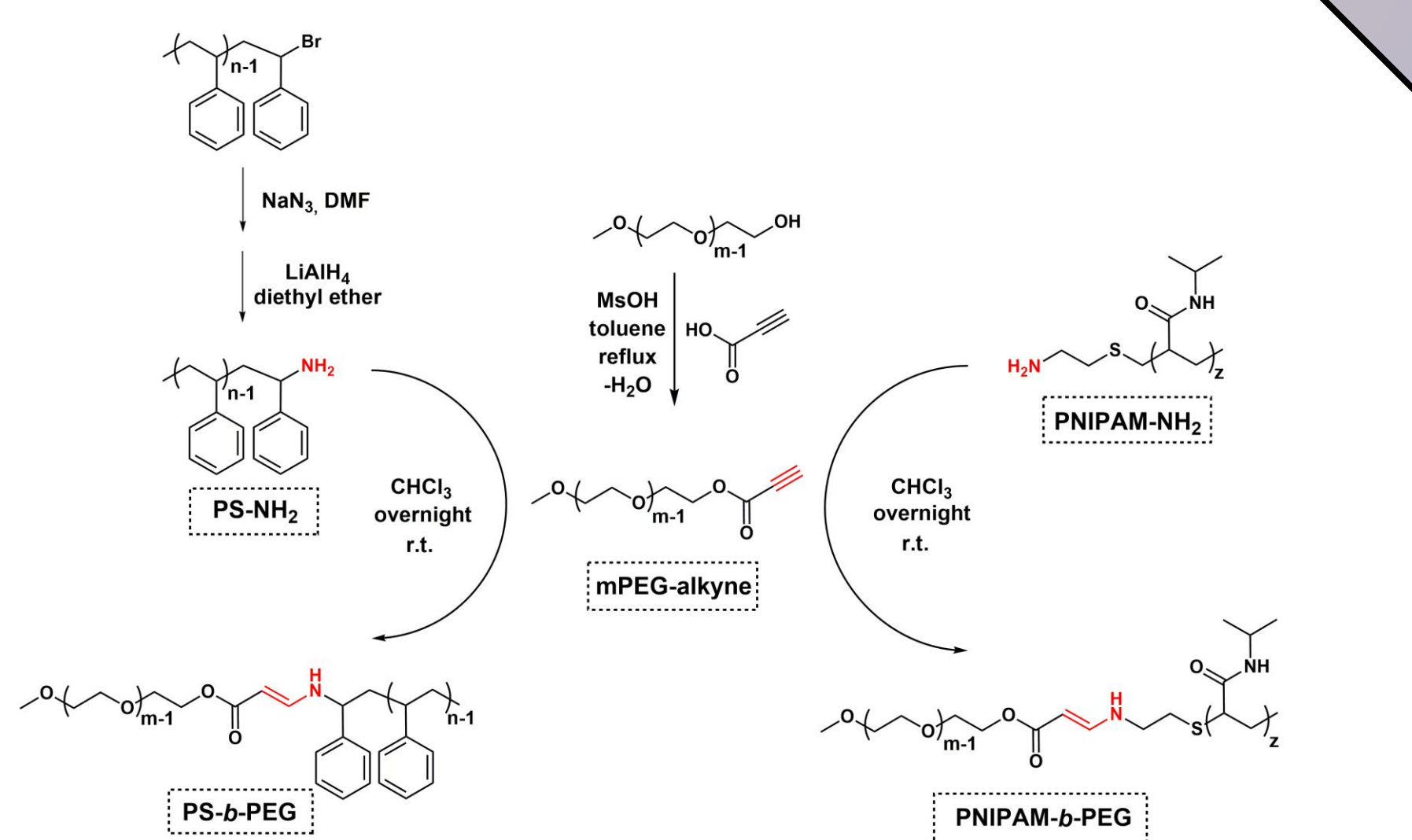


Figure 1: General scheme for polymer-polymer conjugation using amino-yne click reaction.

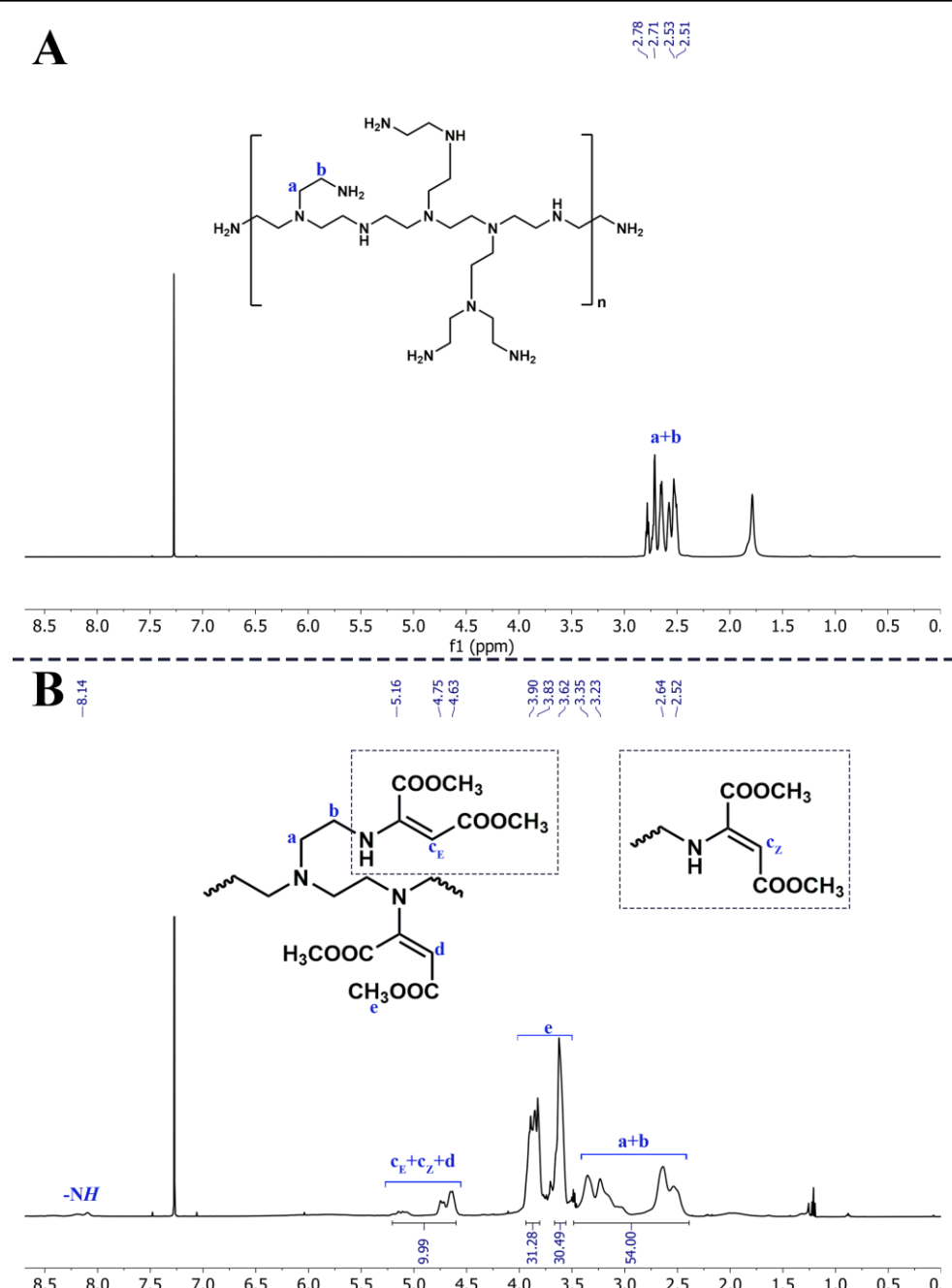


Figure 5: <sup>1</sup>H NMR spectra of PEI (A) and PEI-DMAD (B).

Table 1: Results of the PPM of branched PEI via amino-yne reaction using different electron-deficient alkynes<sup>a</sup>

Alkyne	Modified PEI	Eff. (%) <sup>b</sup>	Isolated yield (%) <sup>c</sup>
DMAD	PEI-DMAD	≥99	95
DEAD	PEI-DEAD	99	88
DPAD	PEI-DPAD	≥99	85
MP	PEI-MP	94	95
EP	PEI-EP	77/83 <sup>d</sup>	84 <sup>d</sup>
AP	PEI-AP	60/62 <sup>d</sup> /78 <sup>e</sup>	88 <sup>d</sup>
PP	PEI-PP	86	72
ETFB	PEI-ETFB	85	78

<sup>a</sup>All reactions were carried out using: 1.2 equiv. of alkyne per free amine of PEI in 1 mL CHCl<sub>3</sub> at room temperature for 2 min unless stated otherwise. <sup>b</sup>Determined by <sup>1</sup>H NMR. <sup>c</sup>Determined gravimetrically. <sup>d</sup>Reaction was carried out for 10 min. <sup>e</sup>2 equiv. of AP per amine was used.

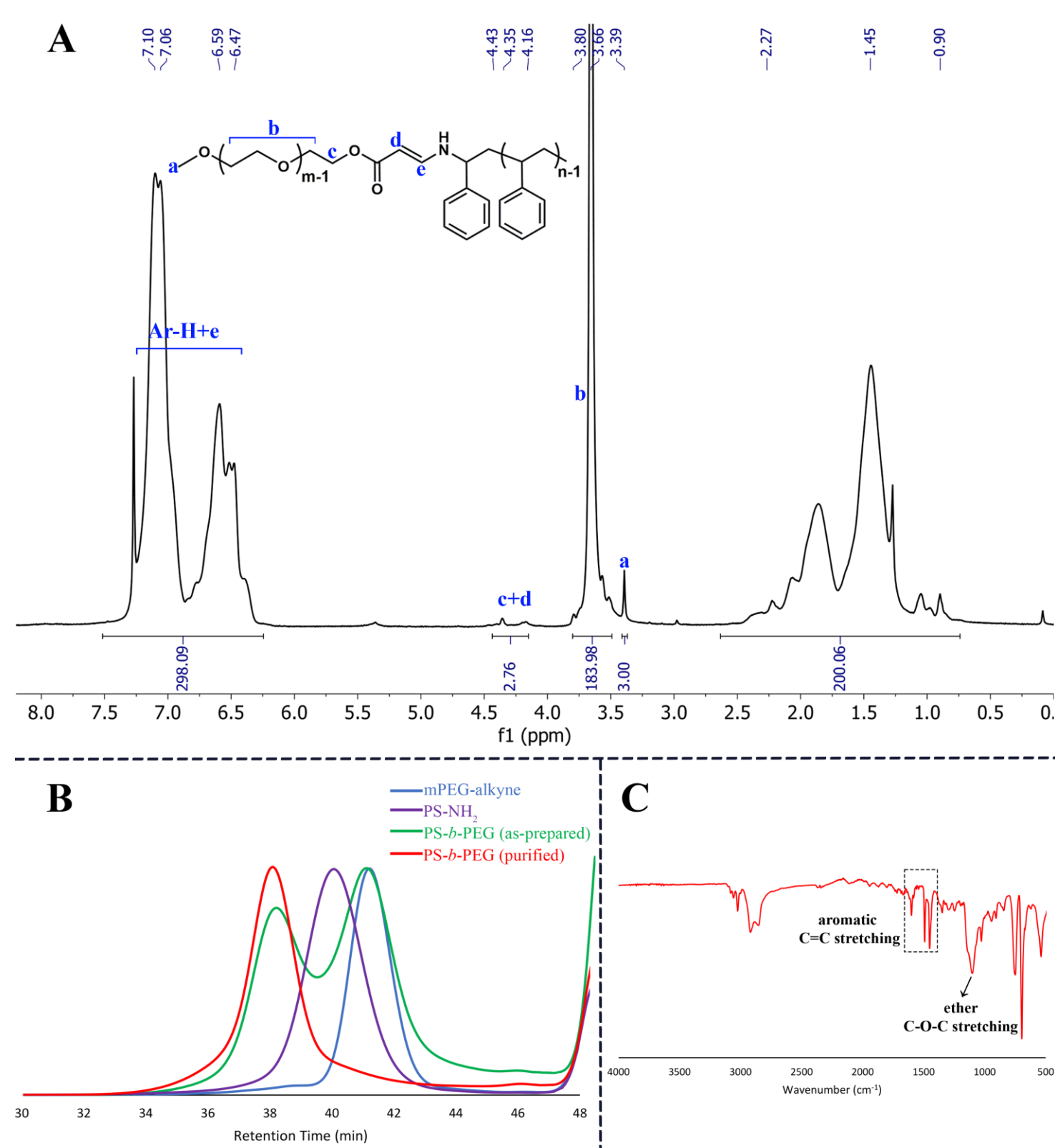


Figure 2: <sup>1</sup>H NMR spectrum, overlaid GPC traces and FT-IR spectrum of PS-b-PEG.

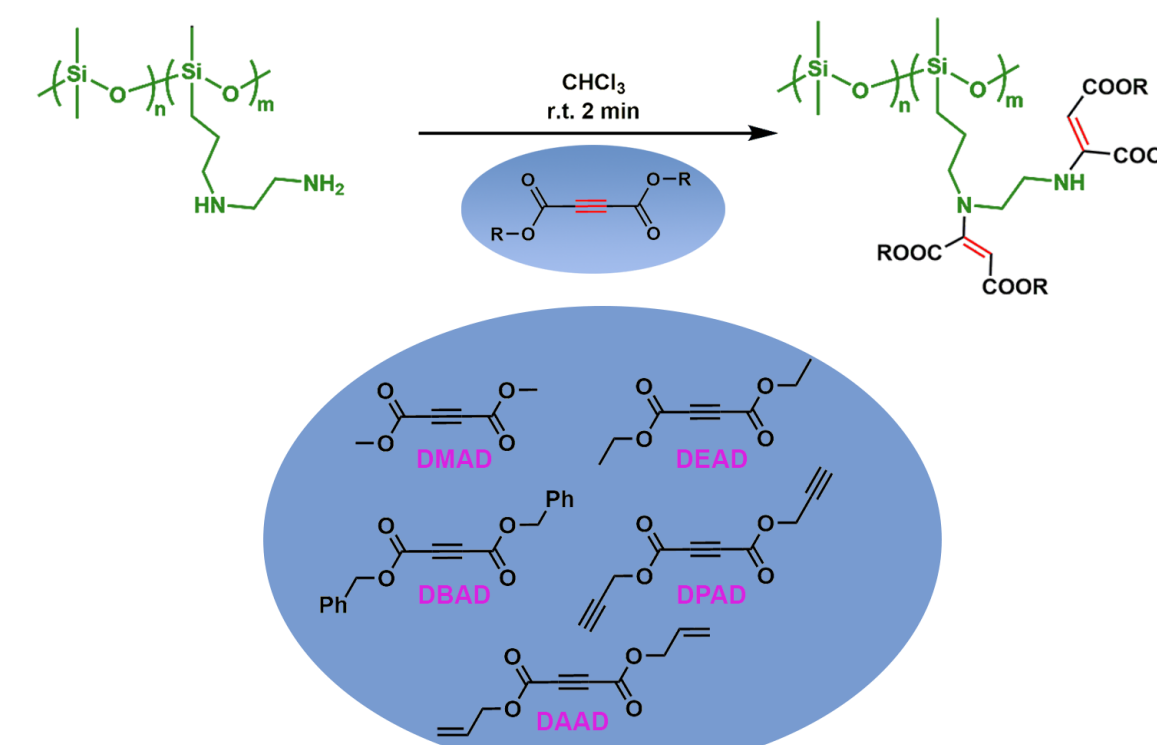


Table 2: Results of the modification of poly(AEAPMS-co-DMS) via amino-yne reaction using different difunctional propiolates<sup>a</sup>

Alkyne	Eff. (%) <sup>b</sup>	M <sub>n</sub> (g/mol) <sup>c</sup>	D <sup>d</sup>	Isolated yield <sup>d</sup> (%)
DMAD	≥99	34000	1.58	76
DBAD	≥99	32000	1.59	74
DEAD	≥99	33000	1.51	76
DPAD	≥99	36000	1.60	73
DAAD	≥99	35000	1.65	74

<sup>a</sup>All reactions were carried out using: 1.2 equiv. of alkyne per amine groups of the copolymer in 1 mL CHCl<sub>3</sub> at room temperature for 2 min. <sup>b</sup>Determined by <sup>1</sup>H NMR. <sup>c</sup>Determined by GPC using linear PS standards in THF. <sup>d</sup>Determined gravimetrically.

## Conclusion

The amino-yne click reaction has been effectively applied to polymer-polymer conjugation and post-polymerization modification (PPM) of amine-functional commercial polymers, showcasing its versatility. For conjugation, amine-end-functional polystyrene (PS-NH<sub>2</sub>) and poly(N-isopropylacrylamide) (PNIPAM-NH<sub>2</sub>) were reacted with alkyne-end-functional poly(ethylene glycol) (PEG-alkyne), achieving high efficiencies, as verified by several spectroscopic and chromatographic techniques. In PPM, hyperbranched poly(ethylene imine) (PEI) and a polysiloxane-based polymer were modified with propiolate derivatives in just two minutes at room temperature. Difunctional propiolates showed near-quantitative modification, while monofunctional ones achieved good to high efficiencies. This catalyst-free, room-temperature method, enabled by accessible electron-deficient alkynes, offers a simple, greener, and energy-efficient alternative to traditional polymer modification strategies, imparting valuable functionalities for diverse applications across chemistry.

## References

- [1] Fu, X.; Qin, A.; Zhong Thang, B.; X-yne click polymerization. *Aggregate*, 2023, 4(5), e350. DOI: 10.1002/agt2.350.
- [2] Akar, E.; Luleburgaz, S.; Saim Gunay, U.; Kumbaraci, V.; Tunca, U.; Durmaz, H.; Amino-yne reaction: An exquisite method for polymer-polymer conjugation and post-polymerization modification. *European Polymer Journal*, 2023, 199, 112470. DOI: 10.1016/j.eurpolymj.2023.112470.