



Phenol-yne Click Polymerization: A Novel Technique to Facilely Access Regio- and Stereo-regular Poly(vinylene ether ketone)s

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Abstract: The alkyne-based click polymerizations have been well-established, however, in order to expand the family to synthesize polymers with new structures and novel properties, new types of click polymerizations are highly demanded. In this paper, for the first time, we established a new efficient and powerful phenol-yne click polymerization. The activated diynes and diphenols could be facilely polymerized in the presence of the Lewis base catalyst of 4-dimethylaminopyridine (DMAP) under mild reaction conditions. Regio- and stereo-regular poly(vinylene ether ketone)s (PVEKs) with high molecular weights (up to 29,000) were obtained in excellent yields (up to 98.2%). The reaction mechanism was well explained under the assistance of density functional theory (DFT) calculation. Furthermore, since the vinyl ether sequence acts as a stable but acid-labile linkage, the polymers could be decomposed at pH values lower than 3.2, enabling them to be applicable in biomedical and environment fields.



Phenol-yne click polymerization

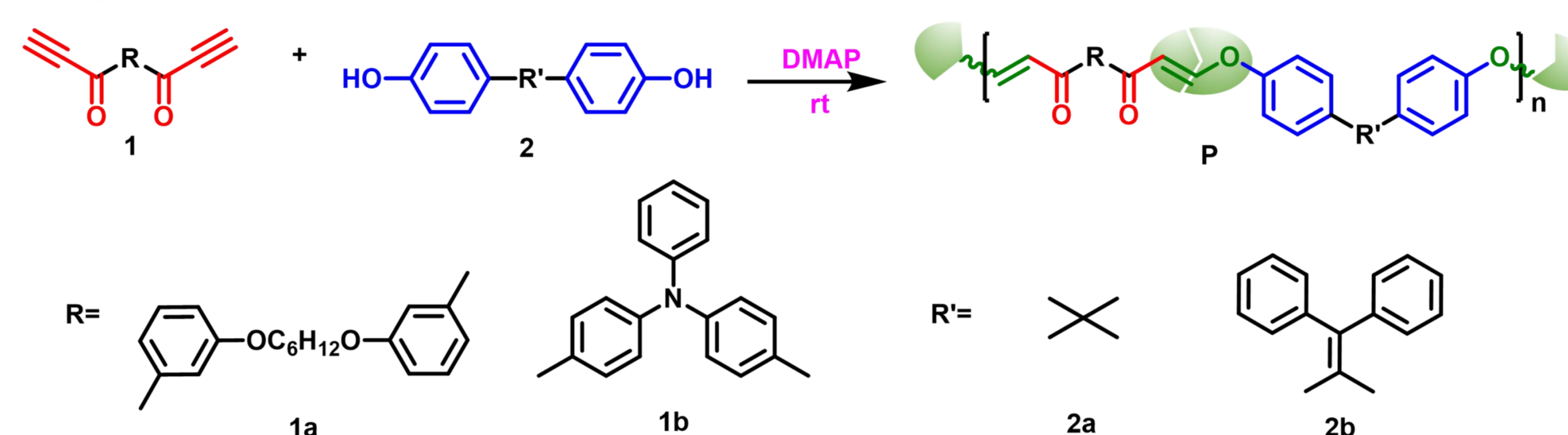


Fig. 1. Syntheses of poly(vinylene ether ketone)s by organocatalytic phenol-yne click polymerizations of bis(arylacetylene)s and diphenols.

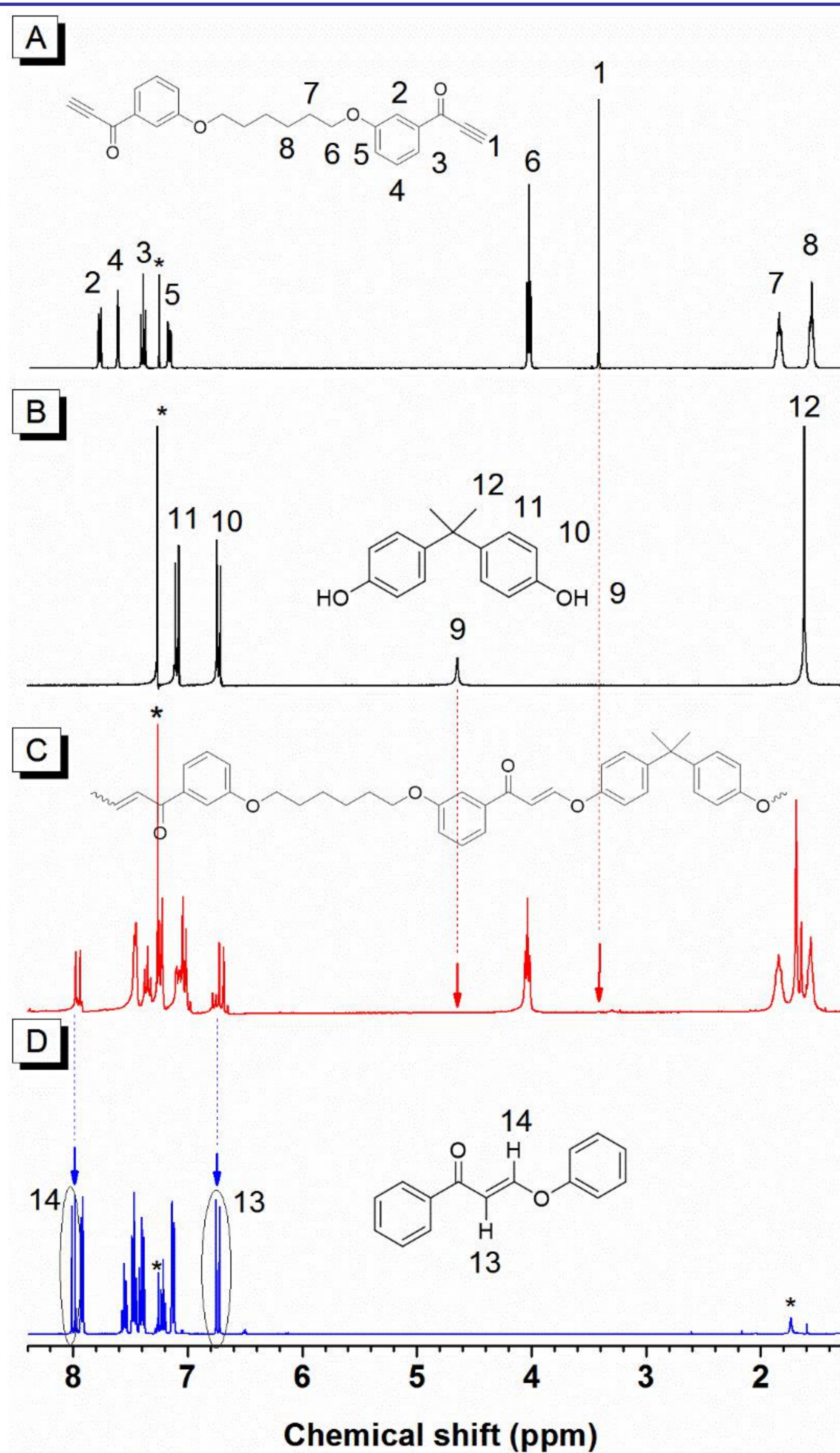


Fig.2 ^1H NMR spectra of (A) monomer 1a, (B) monomer 2a, (C) polymer P1a2a and (D) model compound in CDCl_3 . The solvent peaks are marked with asterisks.

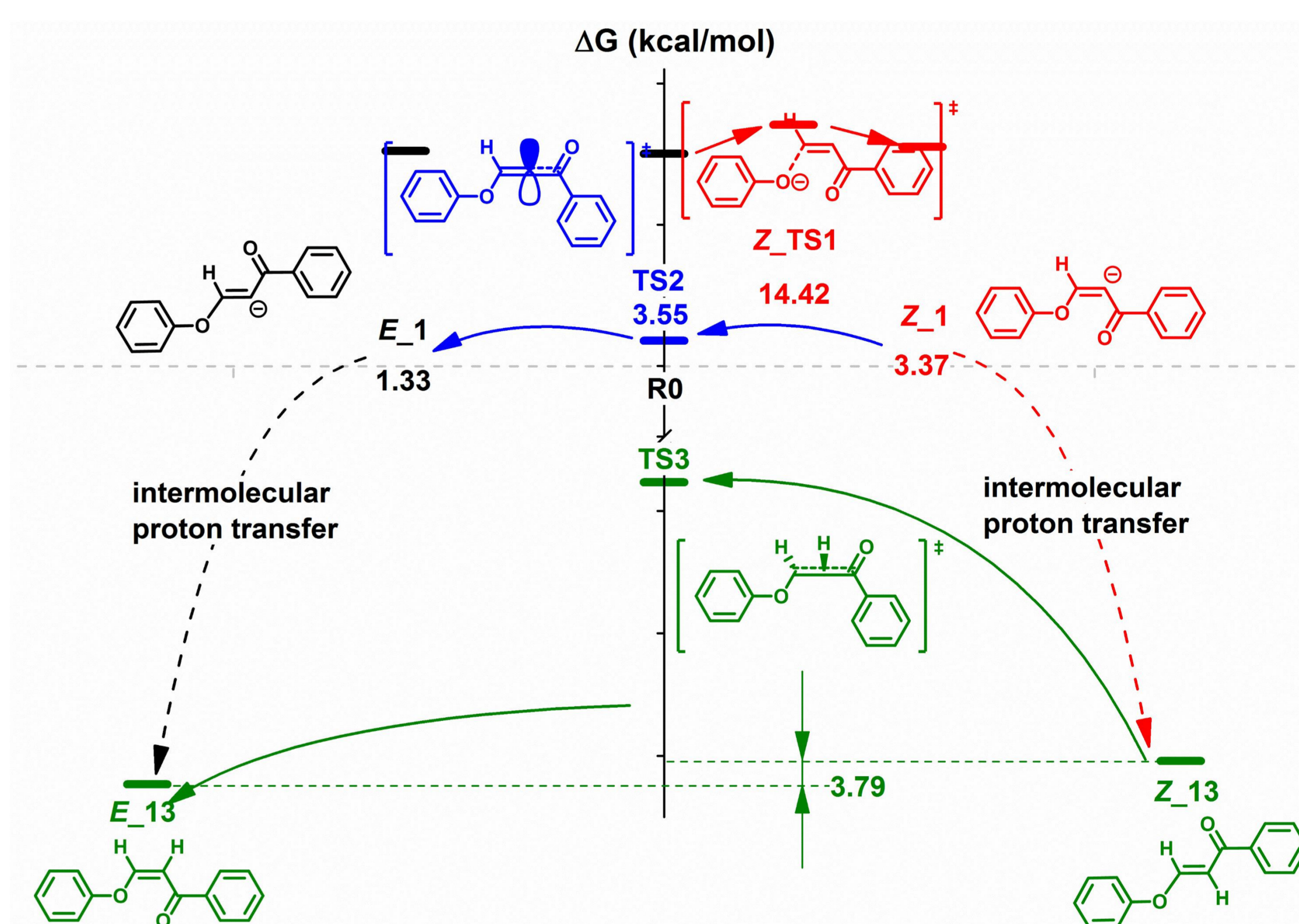


Fig. 3. DFT calculated profiles of nucleophilic addition and proton transfer steps of E- (black) and Z-configuration pathways (red).

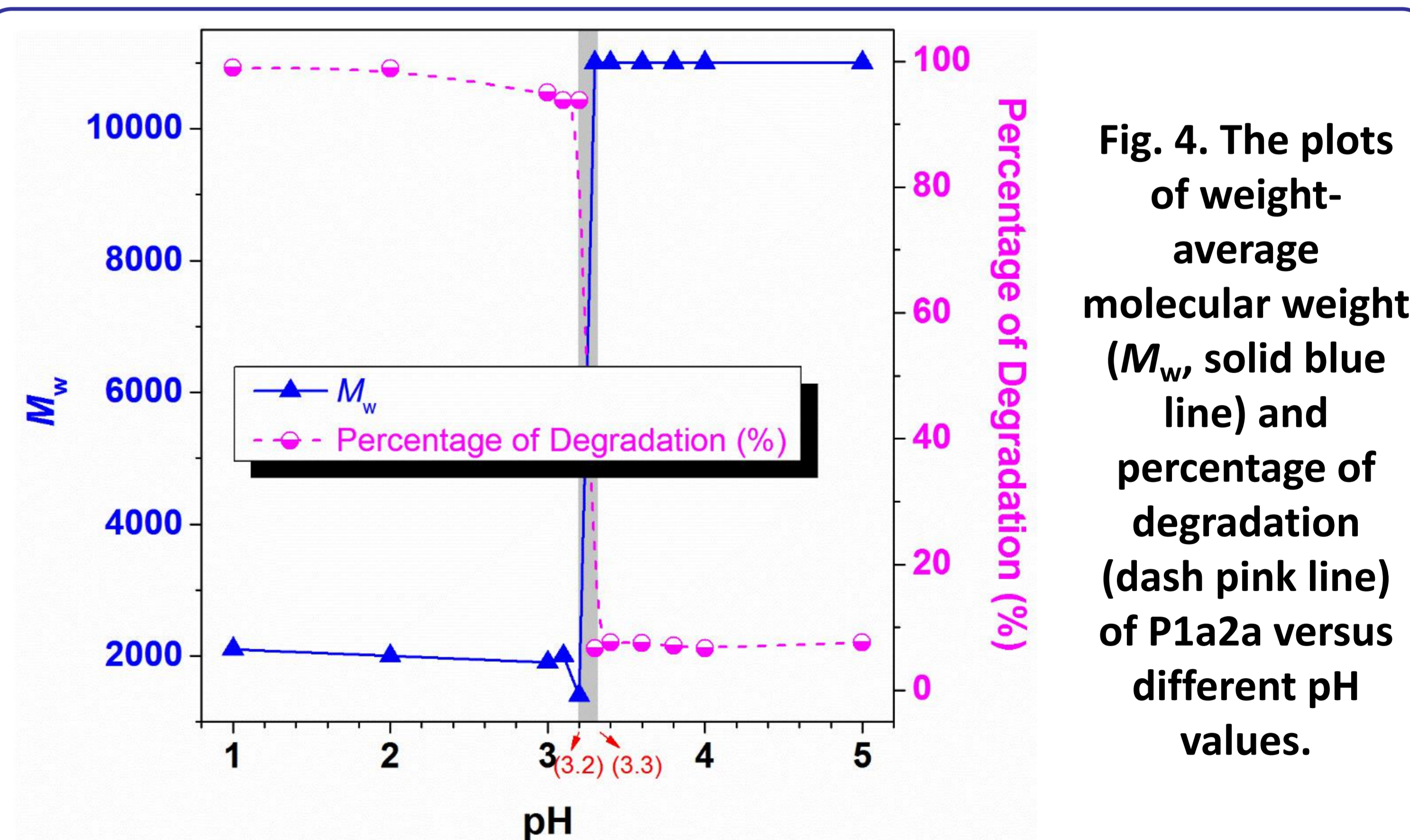


Fig. 4. The plots of weight-average molecular weight (M_w , solid blue line) and percentage of degradation (dash pink line) of P1a2a versus different pH values.

Conclusions: In summary, we have established the first example of phenol-yne click polymerization. Under very mild reaction conditions, the Lewis base of DMAP could efficiently catalyze the polymerization of bis(arylacetylene)s 1 and diphenols 2, and regio- and stereo-regular PVEKs with high molecular weights could be produced in excellent yields at room temperature after 4 hours. ^1H NMR spectra analysis revealed that solely anti-Markovnikov additive products with 100% E-isomer were obtained. DFT investigation has well unveiled the intrinsic mechanism of this phenol-yne click polymerization. Furthermore, the polymers are chemically stable in neutral and basic conditions but could be swiftly decomposed when the pH value is lower than 3.2. Thus, these PVEKs are promising to be applied in biomedical and environmental fields, and the phenol-yne click polymerization will open up a new avenue in the synthesis of functional polymers.

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References:

- Shi, Y.; Qin, A.; Tang, B. Z. *et al. Patent*: 201510200387X. Issue date: Jan 11th, 2017.
- Shi, Y.; Qin, A.; Ling, J.; Tang, B. Z. *Submitted*.