Click Polymerization

Phenol-yne Click Polymerization: An Efficient Technique to Facilely Access Regio- and Stereoregular Poly(vinylene ether ketone)s

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Abstract: 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 study, 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 stereoregular poly(vinylene ether ketone)s (PVEKs) with high molecular weights (up to 35200) were obtained in excellent yields (up to 99.0%). 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-liable linkage, the polymers could be decomposed under acid conditions, rendering them applicable in biomedical and environmental fields.

Establishment and development of new polymerization techniques to facilely synthesize functional polymeric materials is of vital importance to the polymer and materials sciences. Currently, an increasing number of polymerizations developed

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Supporting information and the ORCID identification numbers for the authors of this article can be found under https://doi.org/10.1002/ chem.201702966.

from reported efficient organic reactions have been promoted. However, on account of the rather complicated process of polymerization, the number of organic reactions for further development to polymerizations is limited. To make organic reactions suitable for developing into polymerizations, several essential criteria should be considered and satisfied: a) high efficiency and excellent yields of organic reactions; b) satisfying physical and chemical stabilities of catalytic system; c) mild reaction conditions, together with d) simple preparation procedures and general availability of monomers.^[1]

Among the well-known organic reactions, click chemistry is the most ideal candidate to be developed into a powerful tool for efficient polymerizations.^[2] Click chemistry represents a novel chemical reaction that possesses the attractive advantages of high efficiency, good selectivity, mild reaction conditions, functional group tolerance, simple work-up procedures, and no or benign byproducts.^[2a,c] Therefore, with the enthusiastic efforts of polymer scientists, click reactions have been successfully developed into powerful click polymerizations, which include the Cu¹- and Ru^{II}-catalyzed azide–alkyne click polymerizations (AACPs),^[3] metal-free azide–alkyne click polymerizations (MFCPs),^[1a] thiol-yne click polymerization,^[4] amino-yne click polymerization,^[5] and so on.^[6]

Although all of these polymerizations are effective, some drawbacks are unavoidable, such as the insecurity of the azide monomers used in the AACPs and MFCPs, the strongly pungent aroma of thiol compounds in the thiol-yne click polymerizations, and the existence of stereoisomer mixtures in the MFCPs. Thus, other efficient and powerful alkyne-based click polymerizations that are free from such drawbacks remain to be developed.

Inspired by our recently established spontaneous thiol-yne click polymerization and amino-yne click polymerizations, we wondered whether the polyhydroalkoxylation of alkynes would occur if sulfur in the mercapto-group and nitrogen in the amino group are replaced by oxygen atom in the hydroxyl group since they are from the same group or period in the periodic table, respectively. Surprisingly, to the best of our knowledge, only Endo and co-workers have reported the polymerization of activated diynes with aliphatic diols in the presence of the organophosphorus catalyst of *n*Bu₃P.⁽⁷⁾ However, the scope of the diols, and the unpleasant smell of the catalyst as well as the harsh anaerobic conditions have limited the application of this polymerization.

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Herein, different from Endo's work, we succeeded in establishing a novel polymerization of aromatic diols and diynes under the catalyst of a solid Lewis base of 4-dimethylaminopyridine (DMAP). Simply mixing the diynes and diphenols in THF in the presence of DMAP at ambient conditions readily produced regio- and stereoregular poly(vinylene ether ketone)s (PVEKs) in excellent yields after only 4 h. This polymerization has many remarkable advantages, for instance, the avoidance of expensive transition-metal catalyst,^[8] the mild reaction conditions, the high efficiency, and no byproducts. Thus, we successfully established a new kind of click polymerization, that is, the phenol-yne click polymerization.

Furthermore, the PVEKs prepared by the phenol-yne click polymerization are thermally stable at temperatures as high as 259°C with only 5% loss of weight. Thanks to their containing vinyl ether groups, the PVEKs can be rapidly hydrolyzed in strongly acidic solutions with a concentration of hydrochloric acid [c(HCI)] higher than $10^{-3.2} \text{ mol L}^{-1}$, while remaining chemically stable below this value.

To develop the phenol-yne click polymerization, the activated diyne of aroylacetylene 1 a and another commercially available bisphenol A (2a) were initially used as model monomers to optimize the reaction conditions such as reaction time, the reaction solvent, the concentrations of monomer and catalyst, and the reaction temperature (Scheme 1). Monomer 1a was synthesized according to the reported methods as shown in the Supporting Information.^[9]

The time course investigation indicated that the weightaverage molecular weights (M_w) of PVEKs no longer increased after successive reactions for 4 h (Table S1). Thus, 4 h was selected as the optimized polymerization time.

Secondly, we studied the effect of solvent on the polymerization results. After testing several solvents including tetrahydrofuran (THF), dichloromethane (DCM), toluene, chloroform



Scheme 1. Syntheses of poly(vinylene ether ketone)s by organocatalytic phenol-yne click polymerizations of bis(aroylacetylene)s 1 and diphenols 2.

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and N,N-dimethylformamide (DMF), we assigned THF as the most suitable solvent when considering the balance of solubility, M_w and yields of the products (Table S2).

Thirdly, the monomer concentration investigation showed that with the concentration of 0.1 M, the best $M_{\rm w}$ (15400) and yield (92.9%) of the product was obtained (Table S3). So 0.1 M was chosen as the optimal monomer concentration.

Fourthly, we studied the effects of the concentration of DMAP on the polymerization results. When the concentration of DMAP increased from 0.008 to $0.02 \,\mathrm{M}$, the $M_{\rm w}$ and yield of the product were almost constant (Table S4). Thus, the catalyst concentration of 0.008 M was used in our experiments.

Finally, the temperature investigations suggested that it exerts little influence on the polymerization results (Table S5). To save energy and simplify the operation, 25 °C was selected as the preferable temperature.

With the optimized reaction conditions in hand, we set out to explore the universality of the polyhydroalkoxylation of the activated bis(aroylacetylene)s 1a, 1b and bisphenols 2a, 2b (Scheme 1). All the polymerizations proceeded smoothly and PVEKs of P1a2a–P1b2b with high M_w (up to 35200) were produced in excellent yields (up to 99.0%; Table 1). Generally, the

Table 1. Phenol-yne click polymerizations of bis(aroylacetylene)s 1 and diphenols $2^{(a)}_{\cdot}$							
Entry	Monomer	Polymer	Yield [%]	<i>M</i> _w ^[b]	$M_{\rm w}/M_{\rm n}^{\rm [b]}$		
1	1 a + 2 a	P1a2a	96.8	18600	1.72		
2	1 a + 2 b	P1a2b	99.0	35 200	2.05		
3	1 b + 2 a	P 1b2a	86.5	17 500	2.00		
4	1 b + 2 b	P1b2b	93.2	35 000	1.84		
[a] Carried out in THE at 25°C in air for 4 h: $[M] = 0.10 \text{ M} \cdot [DMAP] = 100000000000000000000000000000000000$							

0.008 м. [b] Estimated by gel-permeation chromatography (GPC) in THF on the basis of polystyrene calibration. $M_{\rm w}$ = weight-average molecular weight; $M_n =$ number-average molecular weight; $M_w/M_n =$ polydispersity index (PDI).

 $M_{\rm w}$ values of polymers generated from **2b** are higher than those from 2a probably due to the larger molecular weight of the former and the easier deprotonation. The results demonstrate the general applicability of this powerful polymerization methodology.

All the obtained polymers are completely soluble in commonly used organic solvents, such as THF, chloroform, DCM and DMF. The PVEKs are also thermally stable; 5% loss of weights was observed at temperatures higher than 259°C under nitrogen (Figure S1).

Owing to the good solubility of P1a2a-P1b2b, the structures of all polymers were characterized by FT-IR and ¹H NMR spectra (see the Experimental Section and Figures S2-S8 in Supporting Information for details). For example, in the FT-IR spectra of polymer P1a2a and its monomers 1a and 2a in Figure S2, the stretching vibrations of \equiv C–H and C \equiv C in **1a** and O-H group in **2a** appeared at 3210, 2090 and 3344 cm⁻¹, respectively. These characteristic peaks, however, could not be observed in the spectrum of P1a2a, indicating that the ethynyl

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Figure 1. ¹H NMR spectra of: A) monomer 1 a, B) monomer 2 a, C) polymer P1a2a, and D) model compound 13 in $[D_1]$ CHCl₃. The solvent peaks are marked with asterisks.

groups in **1a** and the phenol groups in **2a** have reacted. Similar results were obtained from FT-IR spectra of P**1a2b**–P**1b2b**.

Figure 1 shows the ¹H NMR spectra of P**1a2a** and its monomers in CDCl₃ as an example. The ethynyl and phenol protons of **1a** and **2a** resonated at δ =3.43 and 4.65 ppm, respectively. These peaks, however, almost disappeared in the spectrum of P**1a2a**, further substantiating the conclusion drawn from the FT-IR analysis. Moreover, all the peaks are assignable when compared with the monomers except for the new peak at δ = 7.97 ppm.

Theoretically, as shown in Scheme 2, the reaction of phenol group with aroylacetylene will generate three isomers, two anti-Markovnikov products with *E*- and *Z*-configurations, and one Markovnikov product.^[4b, 5, 10] To assign the new peak and to check the regio- and stereoselectivity of our developed polymerization, we carried out the model reaction using benzoylacetylene **11** and phenol **12** as the starting materials under exactly the same conditions as the polymerization. The gas chromatography-mass spectrometry (GC-MS) measurement of the crude product showed only one isomer with molecular weight of 223 (Figure S9). After purification, only one product **13** was indeed obtained in 92% yield. The ¹H NMR spectrum of **13** showed distinct doublet peaks assigned to the proton resonances of the linear vinyl groups at δ =6.72 and 8.00 ppm, representing a linear anti-Markovnikov product (Figure 1D). The ¹³C NMR spectrum also confirmed the vinyl ether ketone structure of **13** (Figure S10).

Moreover, the coupling constants (J_{HH}) of these two peaks are both 12.8 Hz, suggesting the vinyl groups own an *E*-isomeric configuration.^[11] These results also agree well with previous reports.^[12] Thus, this reaction is regio- and stereoselective. Combined with the high efficiency, this reaction is a new kind of click reaction. Compared with the ¹H NMR spectrum of the model compound **13**, the new formed peak of P**1a2a** (δ = 7.97 ppm) is readily assignable to its *E*-isomers (Figure 1 c) although another peak at δ = 6.69 ppm overlaps with that of benzene rings. It is worth noting that no other isomeric resonance was observed in the ¹H NMR spectrum of P**1a2a**. Similar results were obtained in the ¹H NMR spectra of other PVEKs (Figures S6–S8).

These results suggest that such polymerization could furnish unitary products with high regio- and stereoregularity. Consequently, it is a new kind of click polymerization, that is, a phenol-yne click polymerization.

For this click polymerization, the organocatalyst of DMAP plays a critical role, therefore three other catalysts were chosen to confirm the indispensable nucleophilicity of the catalyst, and comparable results were obtained in Table S6. Triethylamine (TEA), a base with weak nucleophilicity, can catalyze this reaction. However, the non-nucleophilic bases of 1,8-diazabicy-clo[5.4.0]undec-7-ene (DBU) and inorganic KOH were ineffective, although their pK_a values are similar to that of DMAP.^[13]

We thus propose a plausible mechanism for this polymerization based on related reports^[7,13,14] and density functional



Scheme 2. The possible isomeric structures of the phenol-yne click reaction.

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Figure 2. DFT calculated profiles of nucleophilic addition and proton transfer steps of *E*- (black) and *Z*-configuration pathways (red), as well as the transformations between anionic intermediates (blue) and vinyl products (olive). All numbers are given as relative Gibbs free energy in kcalmol⁻¹.

theory (DFT) calculations.^[15] Similar with starting materials of the model reaction, we used the benzoylacetylene **11** and phenol **12** to demonstrate this process. Two elementary reactions were discovered, which include nucleophilic-addition and proton-transfer reactions. Moreover, two transformation pathways between anionic and stable intermediates were observed. These routes are shown in Figure 2 and Scheme 3 with

selected 3D geometries and coordinates in the Supporting Information (Figure S11).

In the first step, phenol anion is formed from **12** through hydrogen-abstraction reaction with DMAP. This anion attacks the terminal carbon of **11** to produce an anionic transition intermediate. Due to the steric hindrance of anion with both phenyl and carbonyl, a transition state in *E*-configuration is



Scheme 3. Proposed reaction mechanism.

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forbidden, which was not observed in calculations after many attempts. The addition step exhibits a Gibbs energy barrier of 14.42 kcal mol⁻¹ in *Z*-configuration (**Z_TS1**) route. Subsequently, a configuration exchange through allene-type TS occurs with a negligible Gibbs energy barrier of only 0.18 kcal mol⁻¹, and almost all *Z*-configuration intermediates (**Z_1**) transfer to *E*-isomers (**E_1**) due to the energy benefit of 2.04 kcal mol⁻¹.

In the second step, stable products are obtained through an intermolecular-proton-transfer pathway. If potential (*Z*)-**13** kinetically formed, it would transform to (*E*)-**13**, which is evidenced by the "oxygen-activated double bond reaction". The (*E*)-**13** is more stable than (*Z*)-**13** with a Gibbs energy difference of $3.79 \text{ kcal mol}^{-1}$; this indicates the complete formation of favored (*E*)-**13** product.

Since many elegant studies have reported the vinyl ether linkage can be cleaved through acid hydrolysis, it means that our prepared PVEKs possess hydrolytic degradability.^[16] The corresponding mechanism (Scheme S1) indicates that the acidcatalyzed vinyl ether process involving the intramolecular proton transfer to β -carbon is the rate-determining step. Several previous reports also provide second-order hydrolysis rate constants of simple vinyl ethers with different substituents at α or β positions.^[17] Indeed, the PVEKs are highly acid responsive with ultrafast hydrolytic degradability in aqueous HCI/THF solution with a $-\lg c(\text{HCI})$ value below 3.2. For example, the M_w value of P**1a2a** dramatically decreased from 11000 to nearly 2000 in a few tens of seconds (Table S7).

The molecular-weight evolution of P1a2a in different acidic solutions was monitored by gel permeation chromatography (GPC) by using THF as eluent. As shown in Figure 3, the M_w value of the example polymer P1a2a sharply decreases under strong acid conditions, whereas it remains almost unchanged even after 10 min when the $-\lg c(HCI)$ value is higher than 3.2 (Figure S12). In addition, the degradation degree determined by integration of the peak areas confirmed that the polymer was fully degraded.

Kirby and co-worker^[16d] have extensively studied the apparent rate constant (k_{obs}) and second-order rate constant (k_{H}) of *E*-vinyl ether structure which is similar to PVEK units. With



Figure 3. The plots of weight-average molecular weight (M_{w} solid blue line) and percentage of degradation (dash pink line) of P**1a2a** versus different concentrations of hydrochloric acid.

-lg c(HCl) higher than 3.2, the k_{obs} drops below 10^{-3} s^{-1} and signifies a sluggish proton transfer to β-carbon of vinyl group. Kresge's and co-workers^[17a] have presented the same evidence. In reference to these results, the $-\lg c(\text{HCl})$ value of vinyl ether cleavage suggested is specific and reliable. Thus, these acid-responsive PVEKs are promising for application in biomedical and environmental fields.^[18]

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(aroylacetylene)s 1 and diphenols 2, and regio- and stereoregular PVEKs with high molecular weights could be produced in excellent yields at room temperature after 4 h. Strong evidence suggests that the nucleophilicity of base catalyst plays a crucial role for this polymerization. ¹H NMR spectra revealed that solely anti-Markovnikov additive products with 100% E-isomer were obtained. DFT calculation unveiled the intrinsic mechanism of this phenol-yne click polymerization. The obtained PVEKs are completely soluble in commonly used solvents and are thermally stable. Furthermore, the polymers are chemically stable in neutral and basic conditions but could be swiftly decomposed when the $-\lg c(HCI)$ value is lower than 3.2. Thus, these PVEKs are promising for application in biomedical and environmental fields, and the phenol-yne click polymerization will open new avenues in the synthesis of functional polymers.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (21525417 and 21490571); the key project of the Ministry of Science and Technology of China (2013CB834702); The National Program for Support of Top-Notch Young Professionals; the Fundamental Research Funds for the Central Universities (2015ZY013) and the Innovation and Technology Commission of Hong Kong (ITC-CNERC14S01). A.J.Q. and B.Z.T. thank the support from Guangdong Innovative Research Team Program (201101C0105067115).

Conflict of interest

The authors declare no conflict of interest.

Keywords: organocatalysts · polymers · polymerization · poly(vinylene ether ketone)s · regio- and stereoselectivity

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Manuscript received: June 28, 2017 Accepted manuscript online: July 2, 2017 Version of record online:

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COMMUNICATION

Cut to the click: The first example of phenol-yne click polymerization was established. Bis(aroylacetylene)s and diphenols could be efficiently polymerized in the presence of organic bases under mild conditions, and regio- and stereoregular polymers with high molecular weights could be produced in excellent yields. An intrinsic mechanism is proposed with the assistance of DFT calculations. The polymers could be completely decomposed when the $-\lg c(HCI)$ is lower than 3.2, but are chemical stable above this value.



Click Polymerization

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Phenol-yne Click Polymerization: An Efficient Technique to Facilely Access Regio- and Stereoregular Poly(vinylene ether ketone)s