Aroylacetylene Based Amino-Yne Click Polymerization toward Nitrogen Containing Polymers

Xu Chen[†], *Rong Hu*[†], *Bo Song*[†], *Anjun Qin*[*,†], *Ben Zhong Tang*[*,†,‡]

[†]State Key Laboratory of Luminescent Materials and Devices, Center for Aggregation-Induced Emission, South China University of Technology, Guangzhou 510640, China.

[‡]Department of Chemistry, Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration and Reconstruction, Institute for Advanced Study, and Department of Chemical and Biological Engineering, the Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China.

ABSTRACT: Synthesis of nitrogen containing polymers has always been a research hotspot for their broad applications as functional materials. In this work, we established a highly efficient, spontaneous, and atom-economic polymerization for constructing regio-/stereoregular nitrogen containing polymers. Aroylacetylenes were used to polymerize with amines at room temperature in air, and avoiding extra catalyst to afford poly(*β*-enaminone)s with high molecular weights (M_w up to 49 400 g/mol) in nearly quantitative yields (up to 99%). Moreover, singly *E*-configuration polymers can be obtained efficiently with secondary amines, while absolute *Z*-configuration products were prepared when using primary amines. In addition, the poly(*β*-enaminone)s can be degraded by primary amines in aqueous system to obtain definite compounds, proving their wide application prospects as degradable nitrogen containing polymers.

INTRODUCTION

Nitrogen-containing polymers not only exist widely in organisms as proteins, DNAs or RNAs, but also play a critical role in our lives in the form of synthetic polymers. Taking advantage of their excellent mechanical properties, varied shapes, chemical resistances and adjustable electrical performances, from 1950s to now, synthetic nitrogen-containing polymers such as polyamides (PAs),[1] polyimides (PIs),[2] polyurethanes (PUs),[3] nitrile rubber,[4] polyaniline(PAN)[5] and cationic polymers[6] have achieved great successes for being used as fibers or films,[7-9] elastomers,[10] conductive polymers,[11] porous materials,[12] electrolytes[13] and so on. Despite the widely use of nitrogen containing polymers, the syntheses of these polymers always require harsh reaction conditions like high temperatures or expensive metal catalysts,[14] and particularly, pre-polymerization of PUs must be operated under anhydrous condition.[15] Therefore, efficient reactions with low condition requirements for nitrogen-containing polymers are urgently needed.

Different from traditional synthetic routes, we have tried many new reactions of nitrogenous monomers like nitriles,[16] isonitriles,[17, 18] azides,[19] etc to synthetize nitrogen-containing polymers under mild conditions in good selectivity and high efficiency.[20] In addition to the above-mentioned monomers, amino compounds, as a kind of nitrogen-containing monomers, are abundant, inexpensive and easy to operate. Thus, more efficient amine-based polymerizations for preparing nitrogen-containing polymers are highly desirable. Besides, it has been demonstrated that electron-withdrawing groups could activate alkynes and increase the reactivity by improving electrophilicity of alkynes.[21] Therefore, it's a promising way to obtain nitrogen containing polymers efficiently by click polymerizations of activated alkynes with amines under mild conditions. In the past decade, several novel amino-yne click polymerizations have been developed by our group.[22-27]

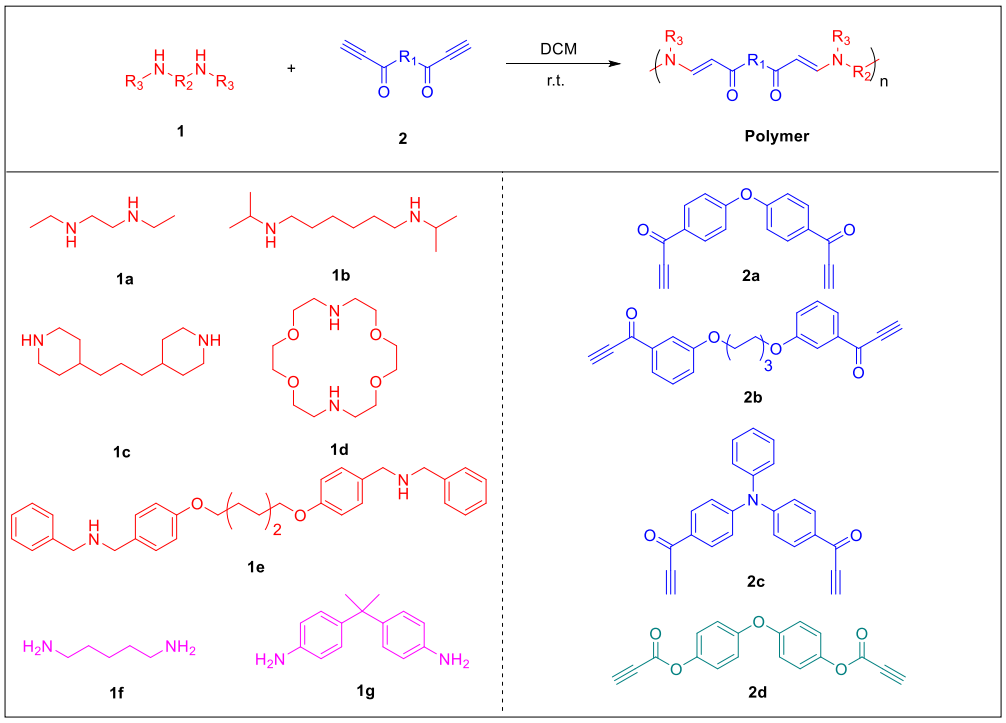
Among our previous works, the spontaneous click polymerization of propiolates and amines reported in 2017 is most attractive,[25] since it can be conducted without extra heat or catalyst to prepare all regio- and stereospecific poly(*β*-aminoacrylate)s. This report brought a new perspective to researchers, and a series of exciting applications have been raised, especially in the field of biological applications.[28, 29] However, there are still some shortcomings in this click polymerization to be overcome. Firstly, the polymerization must be carried out at high concentration to achieve complete conversion of monomers and obtain high molecular weight polymers, which might be unfavorable for heat dissipation in mass production process. Secondly, the propiolate monomers can't react with aromatic primary amines efficiently, and the polymers of propiolates with primary aliphatic amines showed poor regio- and stereoregularity. Thirdly, the propiolate monomers also have poor biocompatibility, which hinders their biological applications. More recently, our group reported a new type of amino-yne click polymerization using bis(ethynylsulfone) monomers as activated alkynes,[27] which can react with both primary and secondary aliphatic amines effectively, and shows good selectivity with primary amines. But ethynylsulfones have poor stability and the synthetic routes are complicated. Thus, a readily available synthetic route to stable activated alkynes with high reactivity is mostly needed.

In this work, carbonyl group was used to activate alkynes. Comparing with other reported activated alkynes, aroylacetylene possesses both high reactivity and good stability, as well as simple synthetic route and low biotoxicity.[30, 31] Aroylacetylene can react much more efficiently than ester activated alkynes with secondary amines under ambient conditions without any catalyst (Scheme 1). As a result, a series of regio- and stereospecific poly(*β*-enaminone)s with 100% *E*-configuration structures were obtained. Primary aliphatic or aromatic amines can also polymerize with aroylacetylenes to obtain single *Z*-configuration polymers. Notablely, the

secondary amine based polymers can be degraded by primary amine to obtain definite products. This work not only establishes an efficient click polymerization, but also provides a kind of prospective degradable nitrogen containing polymers.

RESULTS AND DISCUSSION

Synthesis of Bis(aroylacetylene) Monomers. To systematically exploring the polymerization conditions of this catalyst-free amino-yne click polymerization, bis(aroylacetylene) monomer **2a** was firstly designed and synthetized via a convenient and simple process (Scheme S1).[30, 32-33] By Sonogashira reaction of bis(aroylchloride) derivative and trimethylsilylacetylene at room temperature, trimethylsilyl group protected bis(aroylacetylene) could be obtained. Then, bis(aroylacetylene) monomer can be easily prepared after deprotection in dilute borax solution. Compared with the preparation procedures of bis(aroylacetylene) monomers **2b** and **2c**, which have been previously reported by us,[21] water sensitive ethynylmagnesium bromide and drastic reaction conditions are avoided in this method. **2a** is stable under air at room temperature, and can be preserved after purification for more than one year without deterioration.



Scheme 1. Click polymerization of amines **1** and activated alkynes **2**.

Click Polymerization. The polymerization reaction and structures of all the monomers are listed in Scheme 1. The polymerization conditions of solvent, monomer concentration, and reaction time were investigated using **1a** and **2a** as representatives.

Initial polymerization was run at the concentration of 0.1 M, and the effect of different solvents containing tetrahydrofuran (THF), 1,4-dioxane, acetone and dichloromethane (DCM) was firstly examined in parallel (Table S1). Polymers with high molecular weight (M_w) were obtained in all solvents within 1 hour, but insoluble precipitates were observed in all three solvents except DCM. In order to obtain entirely soluble polymers, DCM was chosen as the optimal solvent. We then studied the effect of monomer concentration on polymerization (Table S2). The M_w of polymers increased obviously with the rise of concentration, and polymer dispersity index ($Đ$) also increased accordingly. But our research centered on the ability of

monomers to form polymers at low concentration, so 0.05 M was chosen as the concentration for time optimization. Gel Permeation Chromatography (GPC) data shows that the polymerization was completed after 2 h (Table S3), further extending polymerization time has ignorable effect on the molecular weight. Consequently, an optimized polymerization condition of 0.05 M in DCM for 2 h was obtained. As shown in Table 1, The finally M_w of P**1a2a** (M_w = 24 000, $Đ$ = 1.93) under this optimized conditions is comparable with the reported results obtained from ethyl propiolate (M_w = 24 200, $Đ$ = 1.69) in a higher concentration of 1.0 M.[29] Moreover, similar M_w was obtained under open air in normal analytically pure DCM containing about 0.05% of water (Table 1, entry 2), proving that air and moisture condition do not directly influence the polymerization reaction.

Table 1. Click Polymerization of different secondary amines **1a~e** with activated alkynes **2a~d**.[a]

entry	polymer	time	yield (%)	M_w [b]	$Đ$ [b]
1	P**1a2a**	2h	99	24000	1.93
2 [c]	P**1a2a**	2h	99	24200	1.99
3	P**1b2a**	2h	99	19900	1.65
4	P**1c2a**	0.5h	91	11800	1.43
5	P**1d2a**	2h	99	26200	1.63
6	P**1e2a**	2h	96	49400	2.28
7	P**1a2b**	1h	82	6200(Δ)[d]	1.61
8	P**1b2b**	2h	59	17000	1.61
9	P**1c2b**	5 min	91	14800	1.30

10	P**1d2b**	1h	81	13400(Δ)[d]	1.09
11	P**1e2b**	2h	77	22500	1.86
12	P**1a2c**	2h	99	15300	1.68
13	P**1b2c**	2h	99	25800	1.62
14	P**1c2c**	1h	99	6290(Δ)[d]	1.25
15	P**1d2c**	2h	86	20900	1.78
16	P**1e2c**	2h	95	24300	1.82
17	P**1a2d**	2h	98	11000	1.54

[a] Carried out under nitrogen in DCM at 25 °C for 2 h, [M] = 0.05 M; [b] Determined by GPC in N, N-dimethylformamide (DMF) using linear polymethyl methacrylate (PMMA) for calibration; [c] Carried out under open air in analytically pure DCM at 25 °C; [d] Soluble part in DMF.

With the optimized conditions in hand, we further extended the monomer scope to test the robustness and universality of this polymerization reaction. Since the nucleophilic additions of amines with aroylacetylenes are highly reliable to the nucleophilicities of amines,[34] it's fundamental to primarily investigate the reactivity of aroylacetylenes with different amines. According to our experiment results (Chart 1), the reactivity of amines with phenylpropynone is weakened with the nucleophilicity decreasing. As the nucleophilicity of aniline is not strong enough, the effect of solvent becomes notable, which is possibly affected by the different hydrogen-bond stabilization effect of solvents.[35] Thus, aniline can react with aroylacetylenes in THF at room temperature, but the reaction can't be conducted in DCM without extra heat.

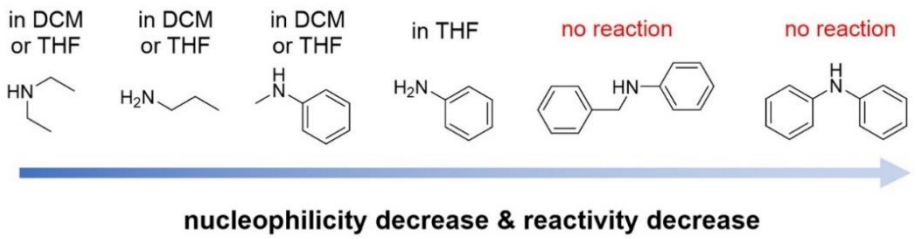


Chart 1. Comparison of the reactivity of different amines with phenylpropynone in DCM or THF at room temperature.

The polymerization of bis(aroylacetylene)s with all the secondary amines **1b~e** can be conducted spontaneously (Table 1) and producing polymers with considerable M_w (up to 49 400 g/mol) and high yields (up to 99%). In order to comparing the reactivity of aroylacetylenes with propiolates, oxybis(4,1-phenylene) dipropiolate (**2d**) was synthetized, which has similar skeleton structure as **2a**. The molecular weight of P**1a2d** (Table 1, entry 17) is much lower than that of P**1a2a** under the same polymerization condition, indicating that the reactivities of aroylacetylenes are much higher than propiolates.

Table 2. Click Polymerization of primary amines **1f** and **1g** with activated alkynes **2a~d**.[a]

entry	polymer	solvent	time (h)	yield (%)	M_w [b]	$Đ$ [b]	Z/E [c]
1	P**1f2a**	DCM	0.5	93	12 300	1.58	100/0
2	P**1f2b**	DCM	0.5	90	22 700	1.88	100/0
3	P**1f2c**	DCM	0.5	97	15 900	1.63	100/0
4	P**1f2d**	DCM	0.5	96	13 400	1.73	40/60
5	P**1g2a**	DCM	14	--	--	--	--
6	P**1g2a**	THF	14	40	19 100	2.16	100/0

7	P**1g2a**	toluene	14	45	16 500	1.93	100/0
8 [d]	P**1g2a**	THF/H_2O	14	Δ[e]	--	--	--

[a] Carried out under nitrogen at 25 °C, [M] = 0.05 M. [b] Determined by GPC in DMF using linear PMMA for calibration. [c] *Z*/*E*-isomeric unit ratio of the products are determined by ^{1}H NMR spectra. [d] Carried out under nitrogen in THF/H_2O=1/1 at 25 °C, [M] = 0.05 M. [e] Insoluble.

Then, we also tried the polymerization with primary aliphatic or aromatic amines (Table 2). Primary aliphatic amine **1f** can polymerize effectively with all the activated alkyne monomers (**2a**~**d**), but only the aroylacetylene based polymers show good selectivity with exact *Z*-configuration structures. For better solubility in DCM, the reaction time was controlled to 30 minutes. As to primary aromatic amine **1g**, 100% *Z*-configuration polymer P**1g2a** can also be obtained, but the weakened nucleophilicity of **1g** lead to greatly reduced reaction rate and sharply decreased yield. At the same time, under the influence of solvent effect, the polymerization can only be carried out well in THF and toluene. According to previously reported results,[34] the nucleophilicity of primary aromatic amine might be enhanced in water containing system, but the obtained polymer (Table 2, entry 8) became insoluble in general solvents and can't be characterized by GPC.

Structural Characterization. The structures of the as-prepared polymers were characterized by Fourier transform-infrared spectroscopy (FT-IR) and nuclear magnetic resonance (NMR) spectra. P**1a2a** and P**1f2a** are used as examples here, the spectra of other polymers are contained in Supporting Information. To facilitate the structural characterization, model compounds **3** and **4** have been prepared for comparation.

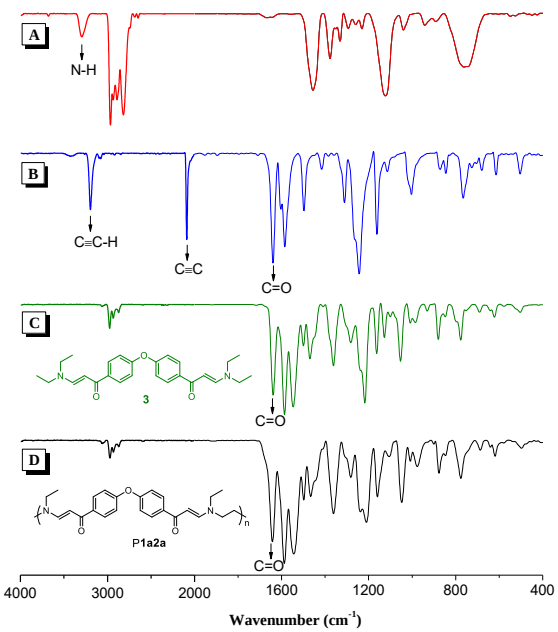


Figure 1. FT-IR spectra of (A) monomer **1a**, (B) monomer **2a**, (C) model compound **3**, and (D) polymer P**1a2a**.

According to the FT-IR spectrum of secondary amine based polymer P**1a2a** displayed in Figure 1, the peaks at 2090 and 3195 cm^{-1} corresponding to alkyne group disappeared in the spectra of both polymer and model compound **3**, and so does the N-H stretching vibration peak of **1a** at 3306 cm^{-1}, which reveals that all the triple bonds of **2a** and amino hydrogens of **1a** have been consumed during the polymerization. For polymerization with primary amine (Figure 2), though the alkyne group signal disappeared, a peak corresponding to secondary amine is retained at 3267 cm^{-1} for P**1f2a**, so as the peak at 3386 cm^{-1} for model compound **4**. Because of the strong electron-withdrawing vinyl ketone group, the nucleophilicity of remained secondary amine in P**1a2f** is limited, and can't further react with another alkyne group.

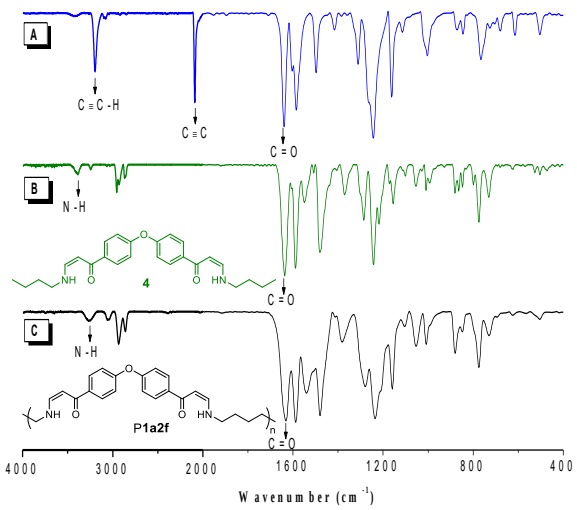


Figure 2. FT-IR spectra of (A) monomer **2a**, (B) model compound **4**, and (C) polymer P**1f2a**.

More detail information about the polymer structures were further analyzed by ^{1}H and ^{13}C NMR spectra. In Figure 3, the acetylene proton of monomer **2a** resonated at δ 3.44 completely disappeared in the spectra of model compound **3** and P**1a2a**, indicating the consumption of monomer **2a**, which is in consistent to the conclusion drawn from FT-IR analysis. The peaks at δ 7.83 and 5.76 in the spectrum of model compound **4** are assigned to the protons of double bond in newly formed enaminone group. And the coupling constants are 12.3 and 12.5 Hz, respectively, proving that the polymer structures are exact *E*-configurations. The double bond hydrogen peaks of P**1a2a** appeared at δ 7.76 and 5.83, which is near to the position of model compound, and no additional double bond peak was observed, thus the structure of polymer is inferred as single *E*-configuration, too.

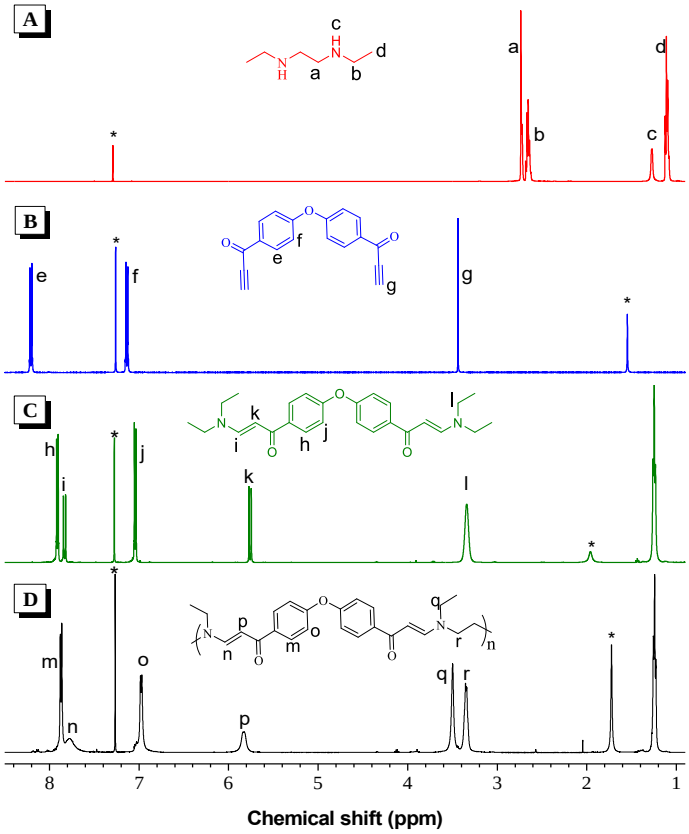


Figure 3. ^{1}H NMR spectra of (A) monomer **1a**, (B) monomer **2a**, (C) model compound **3**, and (D) polymer P**1a2a** in $CDCl_3$. The solvent peaks are marked with asterisks.

In order to further verify the polymeric structure, ^{13}C NMR spectra of P**1a2a**, model compound **3** and monomers **1a** and **2a** are depicted in Figure 4. For model compound **3**, the two peaks of carbon in acetylene at δ 80.48 and 80.13 disappeared, accompanied with the appearance of two new peaks at δ 152.35 and 91.29 corresponding to double bond carbon. The spectrum of P**1a2a** is similar to that of compound **3**, in which the double bond carbons' peaks appear at δ 152.15 and 92.80. The signals of alkyl carbon in model compound **3** and P**1a2a** are not obvious and divided into two groups due to the phase flipping of nitrogen, which has been verified by the results in literature.[36]

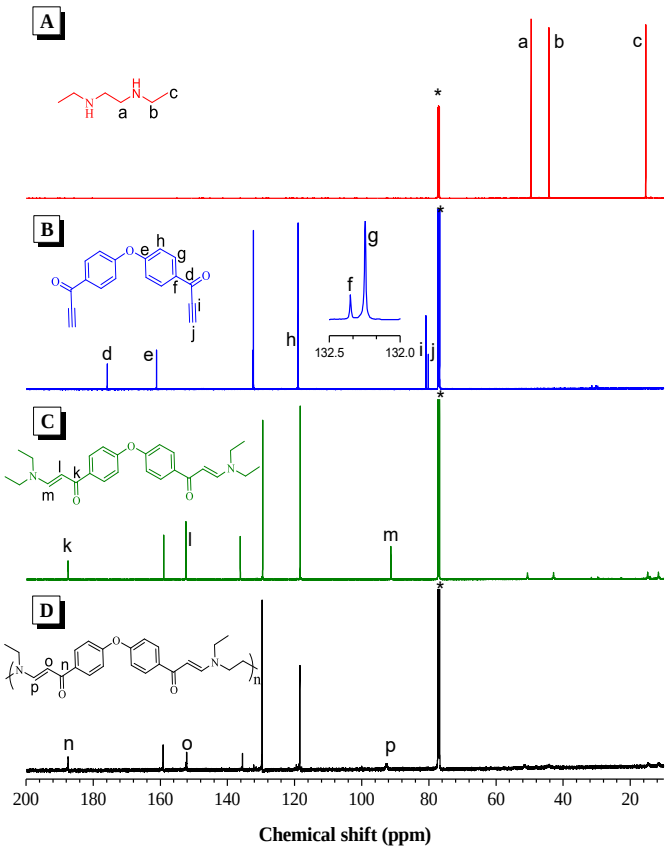


Figure 4. ^{13}C NMR spectra of (A) monomer **1a**, (B) monomer **2a**, (C) model compound **3**, and (D) polymer P**1a2a** in $CDCl_3$. The solvent peaks are marked with asterisks.

The polymers obtained from primary amine has also been characterized by NMR spectra. As shown in Figure 5, the resonance peaks at δ 6.92 and 5.65 in model compound **4** are associated to the protons of new alkene group. Influenced by the hydrogen of amine in β-enaminone, the signal at δ 6.92 is multiple peak. The coupling constant at δ 5.65 is 7.4 Hz, indicating that the structures of polymers are *Z*-configurations. Double bond protons' signals of P**1f2a** appeared at δ 6.91 and 5.65, and the coupling constant at δ 5.65 is also 7.4 Hz, which is consistent with model compound **4** and confirms the absolute *Z*-configuration of P**1f2a**. The completely opposite stereoselectivity of primary amine from secondary amine is caused by the inductive effect of

hydrogen bond between carbonyl group and retained amino hydrogen.[37-39] ^{13}C NMR spectrum of P**1f2a** also proves that the generated structure is correct (Figure S15).

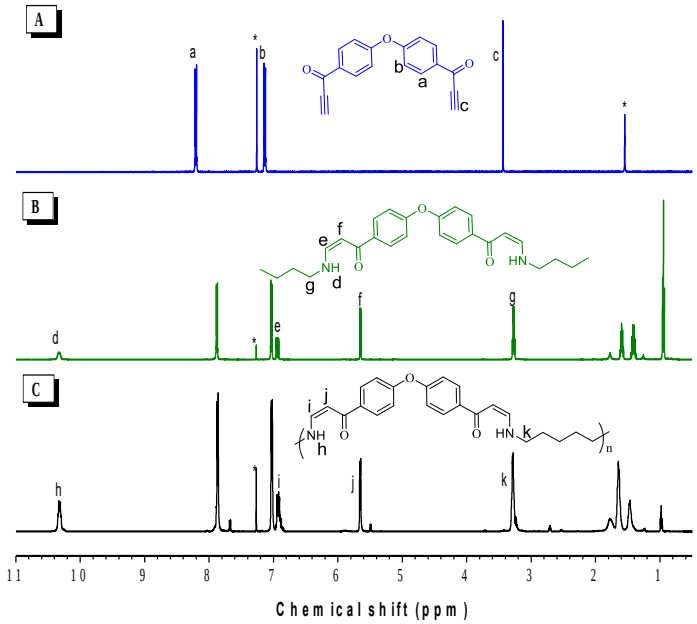


Figure 5. ^{1}H NMR spectra of (A) **2a**, (B) model compound **4**, and (C) P**1f2a** in $CDCl_3$. The solvent peaks are marked with asterisks.

Biocompatibility of Aroylacetylene and Propiolate. In consideration of the possible biological applications, the biocompatibilities of aroylacetylene monomer (**2a**) and propiolate monomer (**2d**) with similar skeleton structure were evaluated. HeLa cell was selected as the representative, and incubated with different concentrations of **2a** and **2d**, respectively. Cell viability results (Figure 6) demonstrated that **2a** shows good biocompatibility under low concentration. While low cell viability was detected even when the concentration of **2d** is as low as 1 μM. It means that the biocompatibility of **2a** is better than that of **2d**, showing great promise of aroylacetylenes in biological orthogonal and related applications.

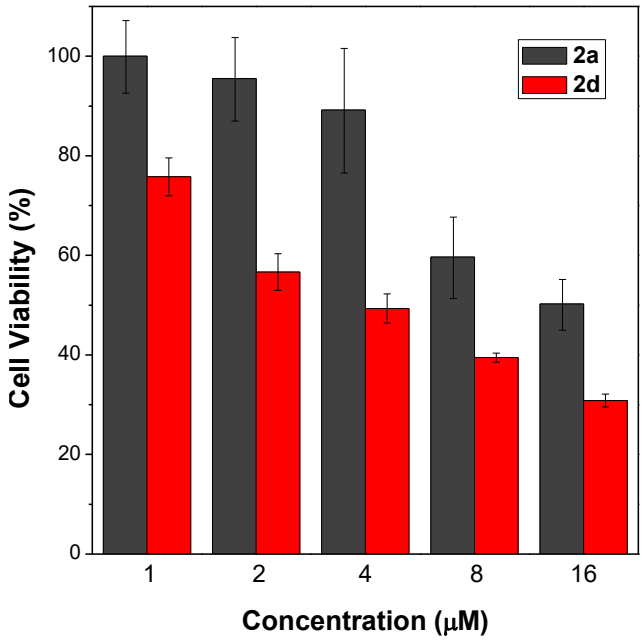


Figure 6. Cell viability of HeLa cells incubated with aroylacetylene monomer (**2a**) and propiolate monomer (**2d**), respectively.

Solubility and Thermal Properties. Since the poly(*β*-enaminone)s possess high polarity, their solubility in polar solvents were tested. All the poly(enaminone)s are soluble well in DCM and chloroform except P**1f2d** and P**1g2a**. Most of the polymers show good solubilities in DMF, but some of them are partly soluble possibly because of the strong intermolecular interactions.

The thermal stabilities of polymers obtained from secondary amines were studied by thermogravimetric analysis (TGA) (Figure 7A), the TGA thermograms are contained in Supporting Information (Figure S1A). The degradation temperatures (T_d, the temperatures for 5% weight loss) of the polymers are all higher than 300 °C under nitrogen, indicating their strong resistance to thermolysis. The glass transition temperatures (T_g) of polymers were further evaluated by differential scanning calorimetry (DSC) measurement (Figure 7B), see supporting information for detail DSC grams (Figure S1B, C, D). According to the results, the more alkyl

chains polymers contain, the lower their T_g will be. However, the T_g values of polymers containing **1c** are especially higher than that of the others (up to 211 °C). The abnormal phenomenon, together with their poorer solubilities prove the strong intermolecular interactions of these polymers. The results above illustrate good solution processability and thermal stability of the polymers obtained by this polymerization reaction.

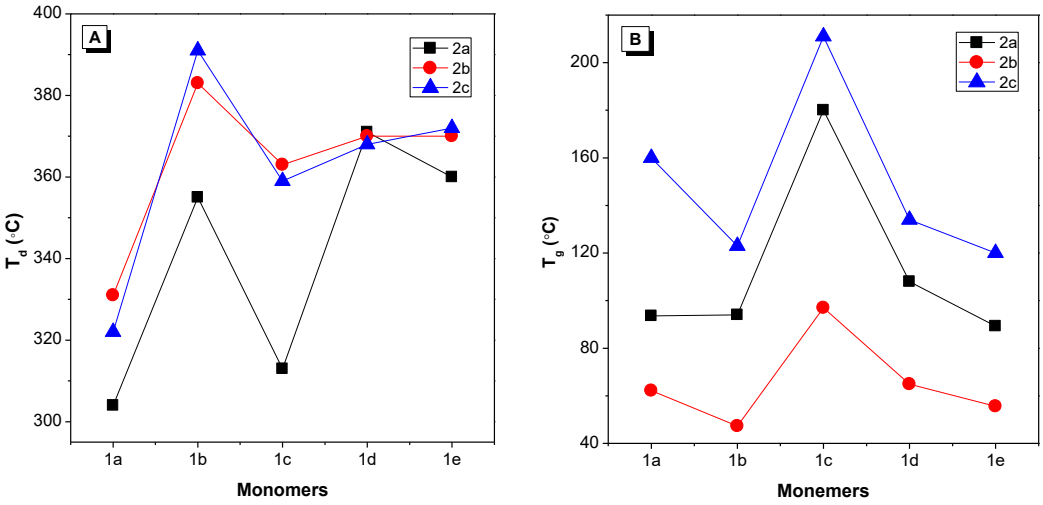


Figure 7. (A) Degradation temperatures (T_d) and (B) glass transition temperatures (T_g) of secondary amine based poly(β-enaminone)s.

Amine Exchange of Polymers with Secondary Amine. During the experiment, we accidently find a slow decrease of M_w after adding overdose of diethylamine into P**1a2a** solution. As shown in Figure 8A, the M_w of P**1a2a** in DMF became lower after the addition of 10 equivalent of diethylamine, and it reached to an equilibrium after 72 h. The gradually decreasing trend suggests that the degradation of polymer is a random process.

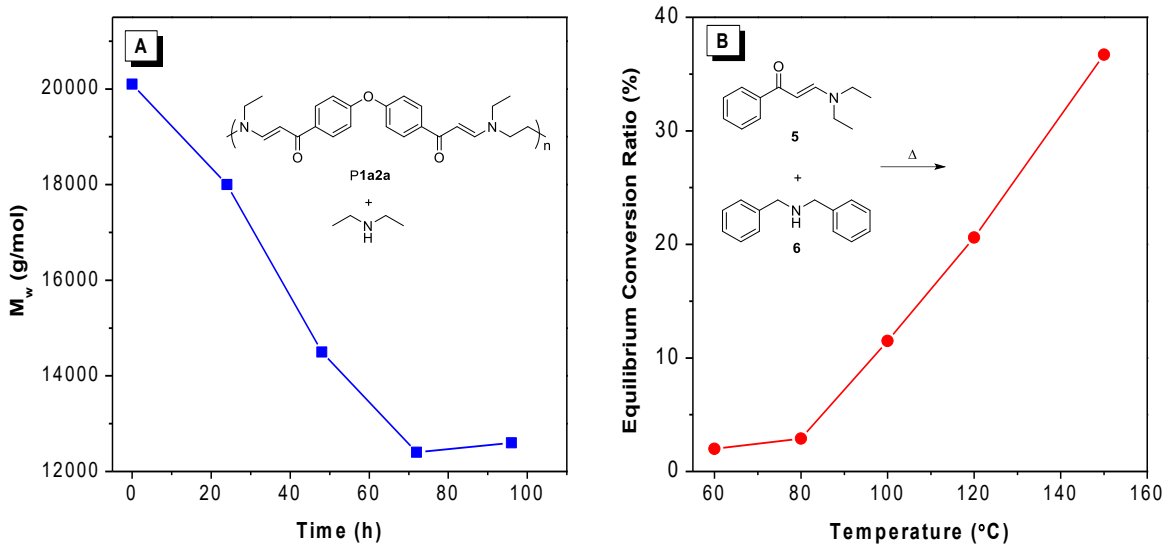
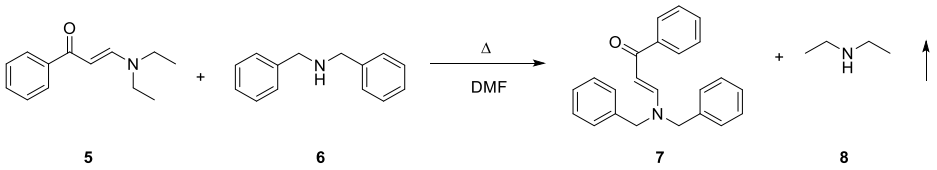


Figure 8. (A) Molecular weight of P**1a2a** (0.1 mol in 2 mL of DMF) changes with time after adding 100 μL of diethyl amine tested by GPC; (B) Conversion rate from compound **5** to **7** and corresponding temperatures calculated from the integral area in NMR spectra, equilibrium conversion ratio is equal to the integral area of **7** decided by the total integral area of **7** and **5** and then multiplied by 100%.

Despite the good thermal stabilities of poly(*β*-enaminone)s, enaminone possesses an electron-donating amino group at one end and an electron-withdrawing carbonyl group at the other end, which endow the double bond with high polarity and high reactivity.[39] Thus, we assumed that there was a slow process of amine exchange between polymer and diethylamine. Though the enaminone formed by primary amine is commonly recognized as one kind of dynamic bond,[40] little attention has been paid to secondary amine based enaminone, which seems more stable. To verify the hypothesis of amine exchange above, small molecular (*E*)-3-(diethylamino)-1-phenylprop-2-en-1-one (compound **5)**, which possesses similar structure as polymers was synthetized. As shown in Scheme 2, upon heated together with excessive dibenzylamine (compound **6**, 10 eq.) in DMF, the ^{1}H NMR (Figure S2) results illustrate that part

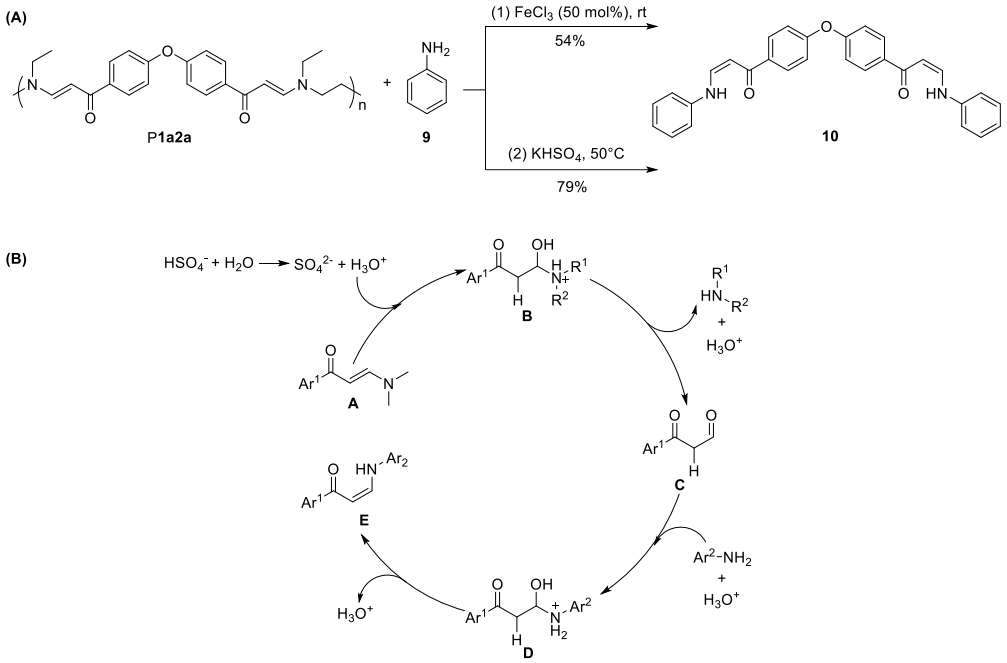
of compound **5** have been converted to (*E*)-3-(dibenzylamino)-1-phenylprop-2-en-1-one (compound **7**). Calculated from the integral areas of characteristic peaks at δ 6.05 for compound **5** and δ 5.82 for compound **7**, the conversion ratios from compound **5** to compound **7** and corresponding temperatures are shown in Figure 8B. With the temperature increasing, more compound **7** can be obtained, because high temperature is not only helpful to increase the reaction speed but also accelerates the release of compound **8** and moves the balance forward.



Scheme 2. Reaction of compound **5** and **6** heated in DMF.

Exact Degradation of Polymers by Lewis acid. Though the exchange products above can be deduced from small molecule reaction, only fragments of polymers could be obtained with undetermined structures. Besides, high temperature must be used, which is irreconcilable with the concept of green chemistry. Previous works have reported that the secondary amine of enaminone can be replaced by aniline under the catalysis of Lewis acid (Scheme 3A),[41, 42] which gave us an inspiration to get exact degradation products by dealing polymers with Lewis acid and primary amine. After optimization, it was found that Fe^{3+} can catalyze the reaction of P**1a2a** with aniline at room temperature, but only 54% of **10** can be separated out. And a large amount of Fe^{3+} which is easy to coordinate with enaminone has also been drawn in and difficult to remove. While by using $KHSO_4$ instead, a high yield of 79% was realized. After simple filtration and extraction procedures, the product **10** in single *Z*-configuration was obtained. Besides, to further improve the catalysis efficiency, a little amount of DMF have been used to help the polymer form small size particles in aqueous solution and increase the contact area with water.

As a result, the degradation of secondary amine based poly(*β*-enaminone)s has been realized under aqueous conditions efficiently.



Scheme 3. (A) Degradation of P**1a2a** by aniline under the catalysis of Lewis acid; (B) Possible mechanism of polymer degradation process under the catalysis of $KHSO_4$.

To validate the effect of Lewis acid and aniline in this process, degradation of P**1a2a** has been conducted by adding only $KHSO_4$ or aniline respectively. From the GPC results (Figure S5, Table S5), when adding only $KHSO_4$ to the suspension, the M_w of P**1a2a** was evidently decreased (from 24 200 g/mol to 4 960 g/mol), indicating that the enaminone groups in polymer have already been cleaved before addition of aniline. While, only a slight decrease of M_w was observed when adding aniline singly, which proves that Lewis acid acts as a critical role in earlier degradation and the addition of aniline continues to complete this process. Besides, the structures of degradation products in the presence of singly $KHSO_4$ is complicated, while when

adding both $KHSO_4$ and aniline, the degradation product is unique, proving that there might also be a synergistic effect between $KHSO_4$ and aniline.

According to the literatures,[42-44] the possible mechanism of degradation process is shown in Scheme 3B. Intermediate **B** will be formed by enaminone **A** with water under acid condition, followed with the left of secondary amine to obtain **C**. It's easy for primary amine to combine with **C** and form intermediate **D**, which can be continually converted into the new enaminone **E**. The polymer will be degraded during the process from **A** to **C**, and small molecular products can be spontaneously formed upon the addition of primary amine. The new enaminones degraded from polymers are still useful monomers or building blocks for complex organic compounds, and can also be used as ligands of metal catalysts.

CONCLUSION

In summary, we successfully developed an efficient polymerization based on primary or secondary amines and aroylacetylenes. Aroylacetylenes possesses unique properties of high reactivity, good stability, relatively easy synthesis process, and low biotoxicity. By using bis(aroylacetylene) monomers as activated alkynes, the amino-yne click polymerization can be conducted under air and room temperature without any catalyst to obtain poly(*β*-enaminone)s in high yield (up to 99%). It was found that the polymerizations of aroylacetylenes with different amines are greatly different. When secondary amine is used, polymers with singly *E*-configuration structures can be obtained, but 100% *Z*-configuration polymers were prepared using primary amine for polymerization. Taking advantage to the dynamic bond in poly(*β*-enaminone)s, the degradation reaction of secondary amine based polymers was

systematically investigated to obtain useful degradation products. This work provides an efficient amino-yne click polymerization for synthesizing degradable nitrogen containing polymers.

ASSOCIATED CONTENT

Supporting Information.

Materials; instruments and measurements; experiment details of synthesis, characterization data of some intermediate products and polymers and detail degradation procedures (Figure S1~19 and Table S1~5). (PDF)

AUTHOR INFORMATION

Corresponding Author

* E-mail: msqinaj@scut.edu.cn (A.J.Q.).

* E-mail: tangbenz@ust.hk (B.Z.T.).

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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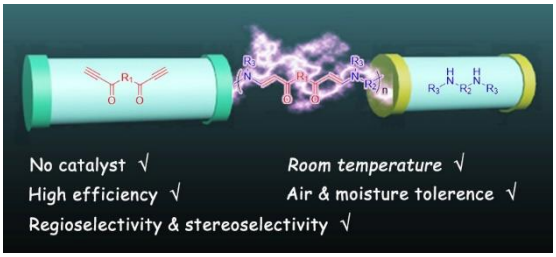

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