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A Throughway to Functional Poly(disubstituted acetylenes): Combination of Activated Ester Strategy with Click Reaction

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We report synthetic routes to functional poly(disubstituted acetylenes) (PDSAs) through the combination of activated ester strategy and Cu(I) catalyzed azide-alkyne cycloaddition (CuAAC) reaction. Direct polymerization of disubstituted acetylene monomer with an end-alkyne group under the catalyst of WCl_6-Ph_4Sn led to poly(monosubstituted acetylene) by-product (P**1**) but not the expected PDSA bearing end-alkyne groups. Protection the end-alkyne group could lead to the expected resultant but this route had a low efficiency. Using the activated ester functionalized PDSA as a precursor (P**0**) and propargylamine as the modifier, the end-alkyne groups were easily to be attached onto the side chains of PDSA (P**2**). Based on the intermediate, the functional group could be efficiently modified onto the intermediate by reacting with azide containing reagents (using benzyl azide as a model) through the CuAAC click reaction, and finally, the triazole functionalized PDSA (P**3**) was derived. The combination of activated ester and CuAAC click reaction strategy bestows the synthetic route with the advantages of high efficiency, mild reaction condition and potentially plentiful functionalities (due to the versatile azide reagents).

Introduction

Polyacetylenes, as the prototype of conjugated polymers,[1] have been a hot research topic in the past decades.[2-9] Nowadays, the research work focuses on poly(disubstituted acetylenes) (PDSAs), owing to their improved stability and high fluorescent efficiency, in comparison with their poly(monosubstituted acetylenes) (PMSAs) counterparts.[10,11] Yet, the polymerization condition of disubstituted acetylenes is harsh, the catalysts are very sensitive to moisture and oxygen. Furthermore, the polar groups (such as amide, amine, hydroxyl, and thiol) on the disubstituted acetylene monomers can poison the catalyst systems and lead to null polymerization.[4,12] Considering these troubles, the preparation and application of functional PDSAs are greatly limited.

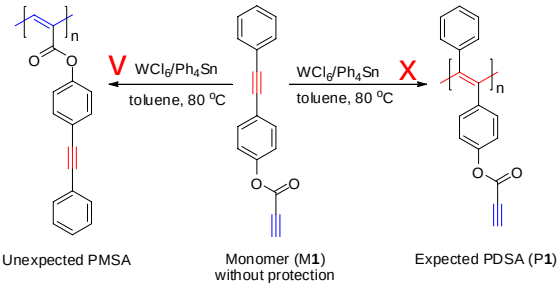
To break through the existing limitations, researchers are continously trying to find alternative strategies to the direct polymerization of the functionalized disubstituted acetylene monomers. Post-polymerization modification has been proved to be a promising strategy.[13] A representative instance is the adaption of Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition reaction between azides and alkynes (CuAAC), which is referred to as "click chemistry,[14] in the post-polymerization modification. Click chemical reactions enjoy the unique benefits of high efficiency, quantitative yield, and mild reaction conditions. A precursor PDSA can be obtained by the polymerization of a disubstituted acetylene monomers bearing a protected end alkyne group. Free end-alkynes groups are released after the deprotection procedure, and finally expected functionalities are modified to the precursor PDSA through highly efficient reaction with functional azides.[15] Or in contrary, using the azide-functionalized PDSA as precursor polymer, the target PDSA is derived from the "click" reaction between azide pendents and functionalized alkynes.[16] Besides, Pd-catalyzed coupling reaction, Michael-type addition reaction, deprotection of masked functionalities, and activated ester routes have been explored to prepare functional PDSAs that cannot be prepared by direct polymerization of corresponding functional monomers.[17-22]

The activated ester strategy, among the reports mentioned above, achieved great success in the preparation of both PMSAs and PDSAs.[11-13,23-25] These existing works have shown the possibility of this strategy to serve as a platform for the construction of functional PDSAs. Herein, we report our recent works on expanding the platform by combining activated ester strategy with alkyne-azide click reaction, introducing more functional groups into the modified PDSAs.

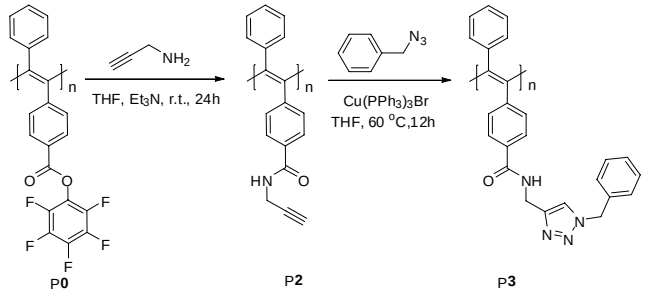
Results and Discussion

Attempt to directly polymerize disubstituted acetylene monomer containing alkyne. It is highly useful to attach alkyne onto the side chains of a precursor PDSA, then prepare functionalized PDSAs via reaction with differently functionalized azides. But this route has been proved to be obstructed. As shown in Scheme 1, the direct polymerization of alkyne-containing disubstituted acetylene monomer M**1** (the synthetic route and characterization data of M**1** are shown in Scheme S1 and Fig. S1 to S4, Electronic Supplementary Information or ESI) in the presence of WCl_6-Ph_4Sn catalyst system, which is commonly used in the polymerization of disubstituted acetylene monomers, leads to the unexpected PMSA, rather than the expected PDSA (P**1**). This is easy to be identified by the colour of the resultant

mixture. For most PDSAs, the solution appears a yellow colour, while for PMSAs, the colour is usually dark orange to red. The generation of PMSA has been confirmed by infrared and ^{1}H and ^{13}C NMR spectral data (see Experimental Section and Fig. S5 and S6 in ESI). To obtain the expected PDSA, the end alkyne must be protected with a bulky and hydrophobic trialkylsilane unit. In our previous attempt, thimethylsilane was used as the capping reagent to prevent the reaction of the alkyne functional group. But this route requires a protection-deprotection procedure, which results in low reaction efficiency and low yield.[15]



Scheme 1 Direct polymerization monomer (M**1**) containing both mono- and di-substituted acetylene moieties under WCl_6-Ph_4Sn catalyst.



Scheme 2 Synthetic route to alkyne-functionalized PDSA (P**2**) from precursor (P**0**) and the triazole-functionalized PDSA through post-polymerization modification via CuAAC reaction.

Introducing alkyne into PDSA by activated ester strategy. The problems are dissolved by aid of the activated ester strategy. As shown in Scheme 2, the end alkyne functional group can be attached onto the side chains of PDSA through the replacement of pentafluoro-phenol with propargylamine. The precursor PDSA (P**0**) was prepared according to the procedures described elsewhere.[15] The average molecular weight was 14.5 kDa and polydispersion index (PDI) was 1.79, as estimated by GPC technique using monodisperse polystyrene samples as internal calibration.

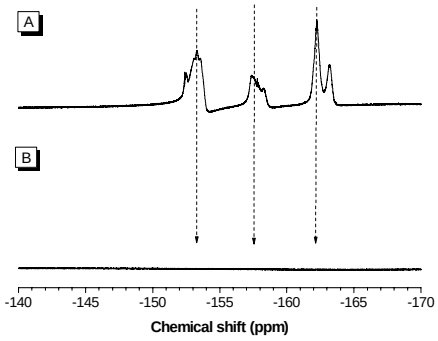


Fig. 1. ^{19}F NMR spectra of (A) the precursor PDSA (P**0**) and (B) the propargylamine modified PDSA (P**2**).

After the modification reaction, the resultant polymer has an average molecular weight of 10.6 kDa and a PDI of 1.38. The replacement reaction took place at room temperature in very high efficiency and the yield was approximate to the theoretical value (99%). Comparing the ^{19}F NMR spectra of precursor (P**0**) and the resultant PDSA (P**2**), it is found that resonant peaks for F atoms, which are clearly recognized at -152.35, -157.45, and -162.17 ppm all disappeared in the spectrum of P**2**, indicating the fully disengagement of the pentafluoro-phenol in P**0**.

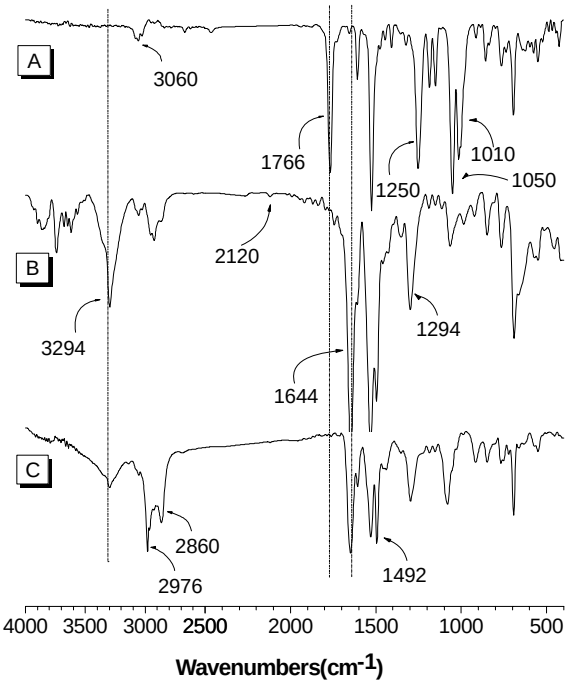


Fig. 2. FTIR spectra of the precursor PDSA (P**0**) and propargylamine modified PDSA (P**2**) and triazole functionalized PDSA (P**3**).

The successful replacement of activated ester (pentafluoro-phenol) group by propargylamine was also confirmed by the Fourier transition infrared (FTIR) spectra of P**0** and P**2**. For FTIR spectrum of P**0** (Fig. 2A), the absorption band peaked at 3060 cm^{-1} is assigned to the stretching vibration of C–H bond on phenyl. Concomitantly, the absorption bands at around 1605, 1520, 844 and 690 cm^{-1} (not marked) provide the proofs of the existence of phenyl group, and the latter two bands are fingerpints of 1,4-disubstituted and mono-substituted phenyl groups. These bands show up in all of the PDSAs' spectra in this work (Fig. 2, S1 and S4). The absoprtion band at 1766 cm^{-1} origins from the carbonyl in the ester group, which comes along with the absorption bands at around 1250 and 1050 cm^{-1}, indicating the presence of aromatic ester group. For the spectrum of P**2**, the absorption band of the stretching mode of carbonyl appears at 1644 cm^{-1}, indicating the transition of ester to amide group. The absorption band at 1294 cm^{-1} is a side proof of the amide group. Different from spectrum A, some new bands show up. The band with a peak at 3294 cm^{-1} is assigned to the stretching vibration of C–H bond on alkyne. In principle, this band should be sharp one. The broadening observed here is ascribed to the overlapping with the stretching mode of N–H bond in amide group. The weak but obvious band at around 2120 cm^{-1} can be assigned to the anti-symmetric vibration of the C≡C bond. In addition to the

absorption bands for amide and alkyne groups, new bands also appear at 2926~2850 cm^{-1}, which are assigned to the anti-symmetric and symmetric stretching vibrations of C–H bond of methylene group. Incidentally, the band for bending mode of C–H bonds in the methylene group appears at around 1492 cm^{-1}. The simultaneous appearance of these bands clearly prove the presence of propargyl-groups in P**2** and the transformation of the ester to the amine group. It is worthy of note that the absorption band of C–F bond at around 1010 cm^{-1}, which is shown clearly in spectrum A, totally disappears in spectrum B. This change suggests the complete replacement of pentafluoro-phenol by amine groups.

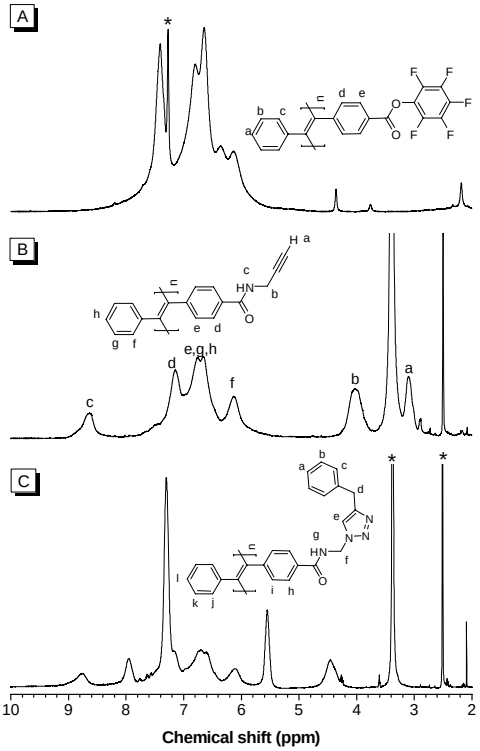
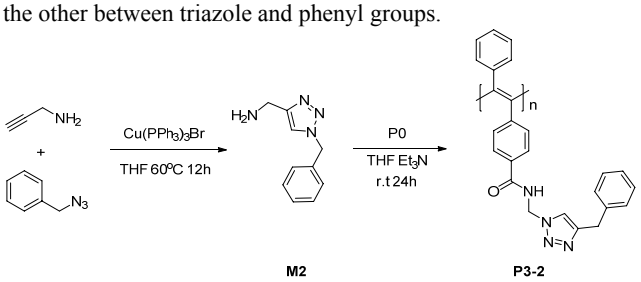


Fig. 3. ^{1}H NMR spectra of (A) the matrix polymer, (B) the alkyne modified and (C) the triazole functionalized PDSAs. The solvent peaks are marked as asterisks.

^{1}H NMR spectra provide further evidences to support the transformation of P**0** to P**2** (Fig. 3). For P**0**, only resonant peaks in the range of 7.24 to 7.60 ppm are observed, which are contributed by two phenyl groups in the polymer skeleton. For P**2**, the characteristic resonant peaks at 3.09 and 4.04 ppm are assigned to the protons on the alkyne and methylene, repsectively. Together with the ^{19}F NMR and FTIR spectra, all of the spectral data sufficiently prove the achievement of alkyne-functionalized PDSA (P**2**) from the activated ester precursor (P**0**). Moreover, in comparison with the previous protection-deprotection strategy, the activated ester strategy is more efficient and facile.

Post-polymerization modification of PDSA by alkyne-azide click reaction. Based on the propargyl group, Cu(I) catalyzed azide-alkyne cycloaddition (CuAAC) reaction can be carried out to furnish P**2** with different functionalities. As shown in Scheme 2, benzyl azide was used as a simple model compound to modify P**2** through the CuAAC click reaction with propargyl group and the triazole-functionalized PDSA (P**3**) was derived. The average molecular weight Mw and PDI of P**3** were masured to be 9.6 kDa and 1.23, respectively. The lowered molecular weight does not mean the polymer degradation induced by post-polymerization modification. Because, on one hand, the chemical structure and solubility of P**0**, P**2**, P**3** are distinct, the same polymerization degree cannot be counted on by using the same polystyrene (PS) calibration. The adjactive phenyl goups on the pendents of P**3** may have stronger interation with PS and result in longer retention time. On the other hand, from chemcial view of point, the CuAAC reaction proceeded in a mild condition that is harmless to polymer structure. The transformation of P**2** to P**3** has also been confirmed by ^{1}H NMR spectroscopic evidence. For P**2**, the chemical shifts of the proton on propagyl appears at 3.09 ppm, corresponding to H^{a} in Fig. 3B. After modification reaction, this peak totally disappears and a new peak appears at around 7.95 ppm, which corresponds to the transition from a proton on alkyne to the one on triazole ring (H^{e} in Fig. 3C). The magnetic shielding effect and electron-deficient nature of the triazole moiety allow the resonance of the proton to come forth at much lower field. The chemical shift for the methylene protons on propargyl group of P**2** is about 4.04 ppm; it shifts to about 4.45 ppm in P**3**. This low-field shift is ascribed to the electron-withdrawing effect of the triazole moiety. The chemical shift at about 5.56 ppm comes from the methylene protons contributed by benzyl azide. It appears at relative lower field if compared with the protons on normal methylene groups because of the mutual interaction of the triazole and phenyl rings.

The transition from P**2** to P**3** has been also confirmed by the changes in their FTIR spectra (Fig. 2, spectra B and C). For P**2**, the broad band ranging from 3400 to 3000 cm^{-1} with a sharp peak at around 3294 cm^{-1} corresponds to the overlapping of the stretching vibration of C–H bond on alkyne and the stretching band of N–H bond on imide group. For P**3**, the sharp peak becomes obtuse and the broad band becomes weaker, indicating that the alkyne group has been exhausted while the amide group is retained. Due to the contribution from the benzyl, the absorption band of methylene becomes evident stronger in P**3** than that in P**2**. Meanwhile, the band splits into two groups of sub-bands because the methylene groups are in two different chemical atmospheres, one lies between amide and triazole and the other between triazole and phenyl groups.



Scheme 3 Synthetic route to the triazole functionalized PDSA (P**3**) from P**0** through post-polymerization modification via activated ester strategy.

Post-polymerization modification of PDSA by alkyne-azide click reaction. P**3** can be derived from an alternative combination of the ativated ester with CuAAC strategy (Scheme 3). Different from the route shown in Scheme 2, where the CuAAC reaction was used in the step of post-polymerization modification, the CuAAC reaction is used in the step of the construction of the modifier agent containing triazole moiety.

Afterwards, the triazole moieties are grafted onto the P**0** from the primary amine functionalized triazole intermediate via activated ester strategy. The average molecular weight of Mw and PDI are 10.2 kDa and 1.36 respctively, which are comparable with the resultant P**3** derived from Scheme 2. The ^{1}H NMR spectrum is quite similar to that recorded for the resultant P**3** from Scheme 2 (Fig. S8), indicating the same polymer derived from different synthetic routes.

In summary, we have shown an improved preparation method of functional PDSAs through the synthetic route of combining activated ester and CuAAC click reaction. The structures of the derived PDSAs have been characterized by multiple spectroscopic techniques including GPC, FTIR, ^{1}H NMR, and ^{19}F NMR. The characterization data confirmed the validity of the expected polymer structures, thus confirmed the accessability of the predesigned synthetic route. In comparison with the widely used activated ester strategy, the combination with CuAAC reaction offers the possibility of modification the precursor PDSA with azide-containing compounds, thus expands the platform of functional PDSAs. In comparison with the previously reported route, which used the end-alkyne-containing PDSA as precursor, the protection-deprotection steps have been omitted, thus the efficiency has been evidently improved. With the rapid development of azide- and alkyne- chemistry, more and more functional agents containing azide and alkyne groups will be designed and prepared, and we expect the combination strategy demonstrated in the present work to be helpful to fabricate novel and useful PDSAs.

Experimental Section

Materials

Toluene was distilled before use. Tetrahydrofuran (THF) was distilled under normal pressure from sodium benzophenone ketyl under nitrogen immediately prior to use. Triethylamine (Et_3N) was distilled and dried over potassium hydroxide. WCl_6 and Cu $(PPh_3)_3Br$ were bought from Aldrich. Ph_4Sn was bought from ABCR. Propagylamine and benzil azide were perchased from Acros. DMAP, TsOH was bought from Alfa. Other solvents, including N,N-dimethylformamide (DMF), chloroform, methanol, ethyl acetate, chloroform ($CHCl_3$), dichloromethane (DCM), hexane and petroleum ether (PE, b. p. 60~90 ^{o}C) were purchased from Sinopharm Co. Ltd. They were in analytical grade and directly used as received without further purification.

Instruments

^{1}H and ^{19}F NMR spectra were measured on a Bruker ARX 500 NMR spectrometer using tetramethylsilane (TMS; δ = 0 ppm) as internal standard. FTIR spectrum was measured on a Perkin Elmer 16 PC FT-IR spectrophotometer. High-resolution mass spectra (HRMS) were taken on a GCT premier CAB048 mass spectrometer operating in a MALDI-TOF mode. Molecular weights (M_w and M_n) and polydispersity indexes (PDI, M_w/M_n) of the polymers were estimated in THF by a Waters gel permeation chromatography (GPC) system. A set of monodisperse polystyrene standards covering molecular weight range of 10^3-10^7 were used for molecular weight calibration.

Polymer synthesis

Preparation of monomer 1 (M1). The synthesis methods of monomer are shown in scheme S1. In a two-necked round bottom flask was added 3.3 g (15 mmol) 4-idiophenol and stirrer. The flask was flushed with nitrogen for three times in the glove box. Then three kinds of catalysts: 210.6 mg (0.3 mmol) $PdCl_2(PPh_3)_3$, 114.3 mg (0.6 mmol) CuI and 236.1 mg (0.9 mmol) PPh_3 were added in the flask, respectively. Afterwards, 80 mL freshly distilled THF and 50 mL dried triethylamine was injected into the flask. The mixture was stirred at room temperature for 24 hrs. The filtrate was removed and the solution was concentrated by rotatory evaporator. Extracted with DCM for several times, the crude product was purified by column gel using PE: ethyl acetate = 30:1 (by volume). At last, light yellow solid was obtained with 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$, Fig. S1), δ (TMS, ppm): 7.51 (d, 2H), 7.43 (d, 2H), 7.34 (t, 1H), 7.32 (t, 2H), 6.81 (d, 2H), 5.07 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, Fig. S2), δ (TMS, ppm): 155.6, 133.3, 131.5, 128.4, 128, 123.5, 115.7, 115.5, 89.2, 88.1. HRMS (m/z): calcd for M**0**, 194.0732; found, 194.0727. Continuously, 1.942 g (10 mmol) M**0**, 3.093 g (15 mmol) DCC, 73.3 mg (0.6 mmol) DMAP and 114 mg (0.6 mmol) TsOH was added into the flask. 100 mL freshly distilled DCM was poured into the system as solvent. Lastly, 0.7 g (10 mmol) propagylamine was added. The solution color turned to be dark brown. After two day's stirring at room temperature, the crude product was evaporated and extracted with DCM. By purification with eluent containing PE and EA (from 100:1 to 40:1), white solid was got with the yield of 57.6%. ^{1}H NMR (400 MHz, $CDCl_3$, Fig. S3), δ (TMS, ppm): 7.56 (d, 2H), 7.52 (t, 2H), 7.36 (d, 1H), 7.35 (d, 2H), 7.15 (d, 2H), 3.10 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, Fig. S4), δ (TMS, ppm): 150.7, 149.7, 132.9, 131.7, 128.5, 128.4, 122.9, 121.9, 121.4, 89.9, 88.3, 77.2, 74.1. HRMS (m/z): calcd for M**1**, 246.0681; found, 246.0674.

Polymerization of M1. In a Schlenk tube with side arm was added 144 mg (0.5 mmol) M**1** and flushed with nitrogen for 3 times. While in another Schlenk tube was added 4 mg (0.01 mol) WCl_6, 4.2 mg (0.01 mmol) Ph_4Sn in the glove box. Both of the two Schlenk tubes was injected 1 mL freshly distilled toluene. After being aged at 80 ^{o}C for 15 min, the monomer solution was transferred to the catalyst solution immediately, and polymerized at 80 ^{o}C for 24 h. The polymerization solution was poured into 180 mL hexane/$CHCl_3$ (5:1 by volume) and filtrated. At last 30 mg red-orange resultant was obtained and the yield was only 20.8%. The low yield was ascribed to the fact that the polymerization temperature was in accordance with the items prepared for PDSAs, and the polymer had poor solubility at that temperature, which caused a large loss. GPC: Mw = 9500, Mw/Mn = 5.09 (for the soluble fraction). ^{1}H NMR (400 MHz, $CDCl_3$, Fig. S5), δ (TMS, ppm): 7.60~7.45, 7.40~7.30 (aromatic ring). FTIR spectrum (thin film, Fig. S6), ν (cm^{-1}): 3060, 2120, 1740, 1504, 1190, 900, 830, 750, 685.

Preparation of P2. 194 mg (0.5 mmol) of P**0**, 27.5 mg (0.5 mmol) propargylamine was added into a Schlenk tube. About 8 mL THF was added to dissolve the polymer, 1 mL fresh trimethylamine was used for accelerating the reaction. The mixture was stirred at room temperature for 24 hours. By precipitation, 125 mg yellow solid was obtained with high yield of 99.2%. ^{1}H NMR (400 MHz, DMSO-d6) (δ, ppm): 8.68 (amide proton), 7.20-6.16 (aromatic ring), 4.05, 3.10 (alkyne H). FTIR spectrum (thin film), ν (cm^{-1}): 3294, 3060, 2960, 2926, 2846,

2120, 1644, 1528, 1492, 1294, 1064, 847, 762, 687.

Preparation of P3. 52 mg (0.2 mmol) P**2** was added into a Schlenk tube. The tube was flushed with N_2 in glove box and 3.7 mg (0.004 mmol) Cu $(PPh_3)_3Br$ was added. 26.6 mg (0.2 mmol) benzyl azide was dissolved in 3 mL distilled THF and was injected into the Schlenk tube. The mixture was heated to 60 °C and reacted for 12 hours. After precipitation treatment and drying in vacuum oven at 60 °C over night, 65 mg yellowish-green solid (P**3**) was gotten and the yield was 82.9%. ^{1}H NMR (400 MHz, DMSO-*d*6) (δ, ppm): 8.78, 7.96, 7.12~6.10 (aromatic protons), 4.45 (protons on methylene group linking to triazole). FTIR spectrum (thin film), ν (cm^{-1}): 3292, 2976, 2860, 1648, 1531, 1492, 1295, 1080, 914, 848, 693.

Preparation of P3 from an alternative route. The synthetic route is shown in Scheme 3. Into a round-bottom flask was added 37 mg (0.04 mmol) Cu $(PPh_3)_3Br$ under N_2 atmosphere. 266 mg (2 mmol) benzyl azide was dissolved in 15 mL distilled THF and was injected into the flask. 110 mg (2 mmol) propargylamine dissolved in another 15 mL distilled THF was injected into the flask. The mixture solution was stirred at 60 °C for 12 hours. After filtration and extraction, the crude product was purified by column chromatography using DCM/methanol (10:1 by volume) as eluent. 102 mg target product was obtained with the yield of 27.1%. ^{1}H NMR (400 MHz, DMSO-d6), δ (TMS, ppm): 7.92 (s, 1H), 7.39~7.31 (m, 5H), 5.56 (s, 2H), 3.74 (s, 2H). 18.8 mg (0.1 mmol) M**2** (obtained in last step) and 38.9 mg (0.1 mmol) P**0** was added to a Schlenk tube. 5 mL THF together with several drops of triethylamine was added to dissolve the solid. The solution was stirred for 24 hours at room temperature. The solution was then poured into hexane/$CHCl_3$ (5:1 by volume) and after filtration, the expected polymer was gotten with a yield of 95%. ^{1}H NMR (400 MHz, DMSO-d6, Fig. S7), δ (TMS, ppm): 8.00~6.10 (aromatic ring), 5.45 (2H, methylene linking to amido group), 4.50 (2H, methylene linked to triazole group).

Acknowledgements

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Notes and references

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† Electronic Supplementary Information (ESI) available: FTIR and ^{1}H NMR spectra of **PMSA**; ^{1}H NMR and ^{13}C NMR spectra of **M0, M1**; ^{1}H NMR spectrum of **M2**, **P0** and **P3-2**. See DOI:10.1039/b000000x/

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Graphical Abstract for Polymer Chemistry

A Throughway to Functional Poly(disubstituted acetylenes): Combination of Activated Ester Strategy with Click Reaction

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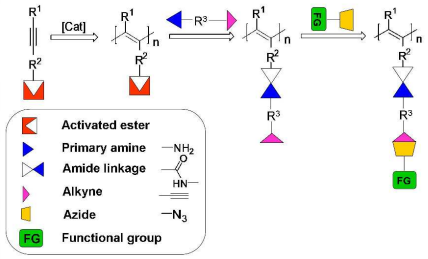

We report a facile and efficient synthetic route to functional poly(disubstituted acetylenes) by the combination of activated ester strategy with alkyne-azide click reaction.