Polymer Chemistry

PAPER

View Article Online
View Journal | View Issue

Cite this: *Polym. Chem.*, 2015, **6**, 7958

A throughway to functional poly(disubstituted acetylenes): a combination of the activated ester strategy with click reaction†

Xiao Wang,[a] Han Hu,[a] Wenjie Wang,[a] Anjun Qin,[b] Jing Zhi Sun*[a] and Ben Zhong Tang*[a,b,c]

Received 2nd September 2015,
Accepted 20th September 2015

DOI: 10.1039/c5py01408e

www.rsc.org/polymers

We report synthetic routes to functional poly(disubstituted acetylenes) (PDSAs) through the combination of the activated ester strategy and Cu(I) catalyzed azide–alkyne cycloaddition (CuAAC) reaction. Direct polymerization of a disubstituted acetylene monomer with an end-alkyne group under the catalysis of WCl_6-Ph_4Sn led to the poly(monosubstituted acetylene) by-product (P**1**) but not the expected PDSA bearing end-alkyne groups. Protection of the end-alkyne group could lead to the expected product but this route has low efficiency. Using the activated ester functionalized PDSA as a precursor (P**0**) and propargylamine as the modifier, the end-alkyne groups were easily 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 the activated ester and the CuAAC click reaction strategy bestows the synthetic route with the advantages of high efficiency, mild reaction conditions 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 few decades.[2–9] Nowadays, research work is focused on poly(disubstituted acetylenes) (PDSAs), owing to their improved stability and high fluorescence efficiency, in comparison with their poly(monosubstituted acetylene) (PMSA) counterparts.[10,11] Yet, the polymerization conditions of disubstituted acetylenes are harsh, and the catalysts are very sensitive to moisture and oxygen. Furthermore, the polar groups (such as amide, amine, hydroxyl, and thiol) on disubstituted acetylene monomers can poison the catalyst systems and lead to null polymerization.[4,12] Considering these problems, the preparation and application of functional PDSAs are greatly limited.

To break through the existing limitations, researchers are continuously trying to find alternative strategies to the direct polymerization of the functionalized disubstituted acetylene monomers. Post-polymerization modification has been proven 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 disubstituted acetylene monomers bearing a protected end alkyne group. Free end-alkyne groups are released after the deprotection procedure, and finally the expected functionalities are modified to the precursor PDSA through highly efficient reaction with functional azides.[15] Or on the contrary, using the azide-functionalized PDSA as the 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 the corresponding functional monomers.[17–23]

[a]*MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China. E-mail: sunjz@zju.edu.cn; Fax: +86-571-87953734; Tel: +86-571-87953734*

[b]*Guangdong Innovative Research Team, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China*

[c]*Department of Chemistry, Jockey Club Institute for Advanced Study, Institute of Molecular Functional Materials, State Key Laboratory of Molecular Neuroscience, and Division of Biomedical Engineering, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China. E-mail: tangbenz@ust.hk; Fax: +852-2358-7375; Tel: +852-2358-1594*

†Electronic supplementary information (ESI) available: FTIR and ^{1}H NMR spectra of PMSA; ^{1}H NMR and ^{13}C NMR spectra of M**0**, M**1**; ^{1}H NMR spectrum of M**2**, P**0** and P**3**–**2**. See DOI: 10.1039/c5py01408e

The activated ester strategy, among the reports mentioned above, achieved great success in the preparation of both PMSAs and PDSAs.[11–13,24–26] These existing reports have shown the possibility of this strategy to serve as a platform for the construction of functional PDSAs. Herein, we report our recent work on expanding the platform by combining the activated ester strategy with alkyne–azide click reaction, introducing more functional groups into the modified PDSAs.

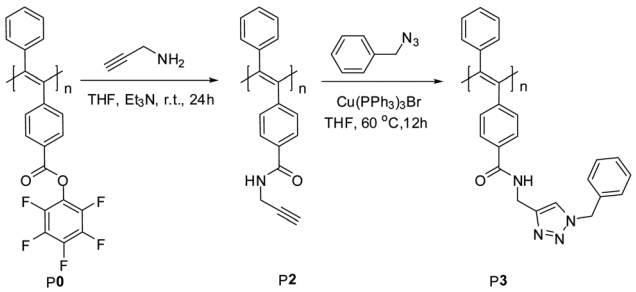
Results and discussion

Attempt to directly polymerize the disubstituted acetylene monomer containing alkyne

It is highly useful to attach the 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 the alkyne-containing disubstituted acetylene monomer **M1** (the synthetic route and characterization data of **M1** are shown in Scheme S1 and Fig. S1–S4, ESI†) in the presence of the WCl_6-Ph_4Sn catalyst system, which is commonly used in the polymerization of disubstituted acetylene monomers, leading to the unexpected PMSA, rather than the expected PDSA (**P1**). This is easily identified by the colour of the resultant mixture. For most PDSAs, the solution appears yellow , while for PMSAs, the colour is usually dark orange to red. The generation of PMSA has been confirmed by infrared and ^1H and ^{13}C NMR spectral data (see the Experimental section and Fig. S5 and S6 in the ESI†). To obtain the expected PDSA, the end alkyne must be protected with a bulky and hydrophobic trialkylsilane unit. In our previous attempt, trimethylsilane 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]

Introducing alkyne into PDSA by the activated ester strategy

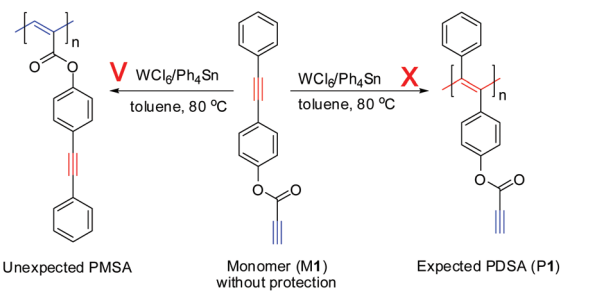
The problems are dissolved by aid of the activated ester strategy. As shown in Scheme 2, the end alkyne functional group can be attached onto the side chains of PDSA through the replacement of pentafluoro-phenol with propargylamine. The precursor PDSA (**P0**) was prepared according to the procedures described elsewhere.[15] The average molecular weight was 14.5 kDa and poly-dispersion index (PDI) was 1.79, as estimated by GPC technique using monodisperse polystyrene samples as the internal calibration.



Scheme 2 Synthetic route to alkyne-functionalized PDSA (**P2**) from precursor (**P0**) and triazole-functionalized PDSA through post-polymerization modification *via* the CuAAC reaction.

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 the precursor (**P0**) and the resultant PDSA (**P2**), 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 **P2**, indicating the full disengagement of the pentafluoro-phenol in **P0** (Fig. 1).

The successful replacement of the activated ester (pentafluoro-phenol) group by propargylamine was also confirmed by the Fourier transition infrared (FTIR) spectra of **P0** and **P2**. For the FTIR spectrum of **P0** (Fig. 2A), the absorption band with a peak at 3060 cm^{-1} is assigned to the stretching vibration of the C–H bond on phenyl. Concomitantly, the absorption bands at around 1605, 1520, 844 and 690 cm^{-1} (not marked) provide proof of the existence of the phenyl group, and the latter two bands are fingerprints of the 1,4-di-substituted and mono-substituted phenyl groups. These bands



Scheme 1 Direct polymerization monomer (**M1**) containing both mono- and di-substituted acetylene moieties under WCl_6-Ph_4Sn catalyst.

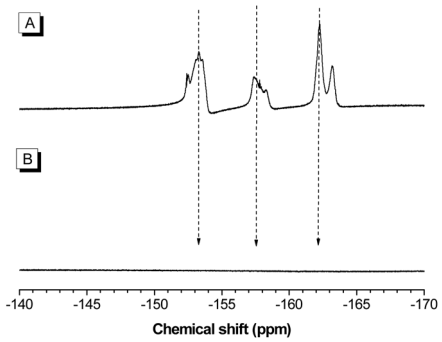


Fig. 1 ^{19}F NMR spectra of (A) the precursor PDSA (**P0**) and (B) the propargylamine modified PDSA (**P2**).

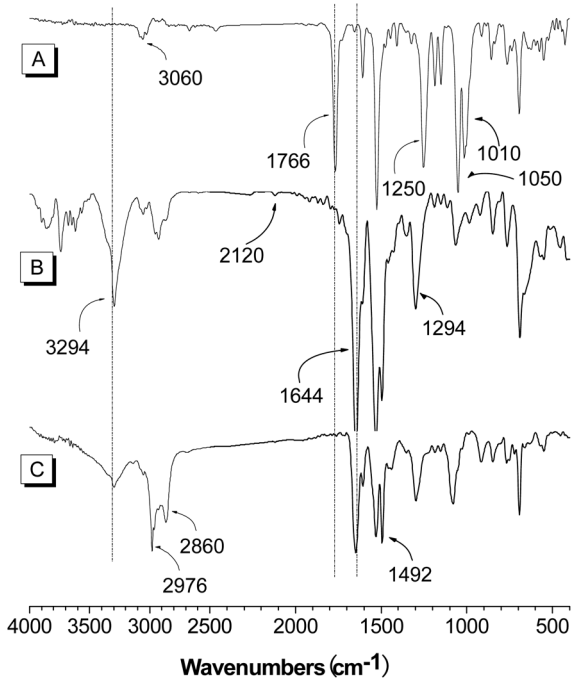


Fig. 2 FTIR spectra of the precursor PDSA (P**0**) and propargylamine modified PDSA (P**2**) and triazole functionalized PDSA (P**3**).

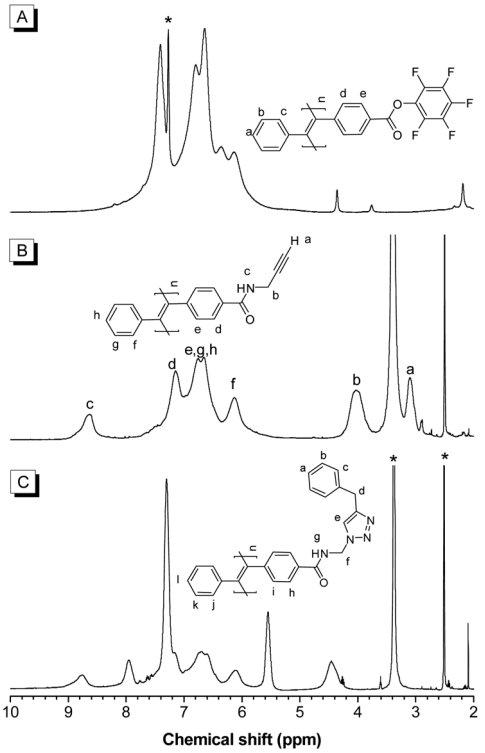


Fig. 3 ^{1}H NMR spectra of (A) the matrix polymer, (B) the alkyne modified and (C) the triazole functionalized PDSAs. The solvent peaks are marked as asterisks.

show up in all of the PDSAs' spectra in this work (Fig. 2, S1 and S4†). The absorption band at 1766 cm^{-1} originates 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 the 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 the ester to the amide group. The absorption band at 1294 cm^{-1} is an ancillary 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 the C–H bond on alkyne. In principle, this band should be the sharp one. The broadening observed here is ascribed to the overlapping with the stretching mode of the N–H bond in the 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 the C–H bond of the methylene group. Incidentally, the band for the bending mode of C–H bonds in the methylene group appears at around 1492 cm^{-1}. The simultaneous appearance of these bands clearly proves the presence of propargyl-groups in P**2** and the transformation of the ester to the amine group. It is noteworthy that the absorption band of the 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.

^{1}H NMR spectra provide further evidence 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, respectively. 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

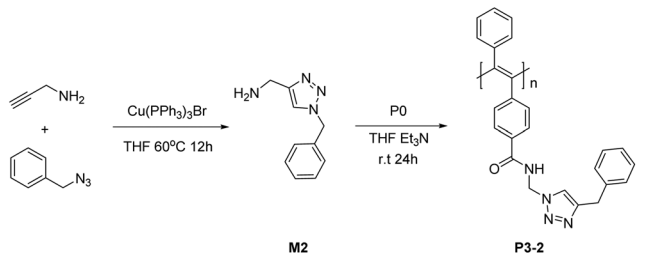
Based on the propargyl group, Cu(I) catalyzed azide–alkyne cycloaddition (CuAAC) reaction can be carried out to furnish P**2** with different functionalities. As shown in Scheme 2, benzyl azide was used as a simple model compound to modify P**2** through the CuAAC click reaction with the propargyl group and the triazole-functionalized PDSA (P**3**) was derived. The average molecular weight, Mw, and PDI of P**3** were measured to be 9.6 kDa and 1.23, respectively. The lowered molecular weight does not mean that the polymer degradation is induced by post-polymerization modification. Because, on the 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 adjunctive

phenyl groups on the pendents of P3 may have stronger interactions with PS and result in a longer retention time. On the other hand, from the chemical point of view, the CuAAC reaction proceeded under mild conditions that are harmless to the polymer structure. The transformation of P2 to P3 has also been confirmed by ^{1}H NMR spectroscopic evidence. For P2, the chemical shifts of the proton on propargyl appears at 3.09 ppm, corresponding to H^a in Fig. 3B. After the modification reaction, this peak totally disappears and a new peak appears at around 7.95 ppm, which corresponds to the transition from the proton on alkyne to the one on the 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 a much lower field. The chemical shift for the methylene protons on the propargyl group of P2 is about 4.04 ppm; it shifts to about 4.45 ppm in P3. 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 a relatively lower field when compared with the protons on normal methylene groups because of the mutual interaction of the triazole and phenyl rings.

The transition from P2 to P3 has also been confirmed by the changes in their FTIR spectra (Fig. 2, spectra B and C). For P2, 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 the C–H bond on alkyne and the stretching band of the N–H bond on the imide group. For P3, 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 evidently stronger in P3 than that in P2. Meanwhile, the band splits into two groups of sub-bands because the methylene groups are in two different chemical atmospheres, one lies between the amide and triazole and the other between the triazole and phenyl groups.

Preparation of PDSA by an alternative combination of activated ester with CuAAC strategy

P3 can be derived from an alternative combination of the activated ester with the 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 the triazole moiety. Afterwards, the triazole moieties are grafted onto the P0 from the primary amine functionalized triazole intermediate *via* the activated ester strategy. The average molecular weight of Mw and PDI are 10.2 kDa and 1.36 respectively, which are comparable to the resultant P3 derived from Scheme 2. The ^{1}H NMR spectrum is quite similar to that recorded for the resultant P3 from Scheme 2 (Fig. S8†), indicating that the same polymer derived from different synthetic routes.



Scheme 3 Synthetic route to the triazole functionalized PDSA (P3) from P0 through post-polymerization modification *via* the activated ester strategy.

In summary, we have shown an improved preparation method of functional PDSAs through the synthetic route of combining an 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 confirming the accessibility of the pre-designed synthetic route. In comparison with the widely used activated ester strategy, the combination with the CuAAC reaction offers the possibility of modification of the precursor PDSA with azide-containing compounds, thus expanding the platform of functional PDSAs. In comparison with the previously reported route, which used the end-alkyne-containing PDSA as the 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 in fabricating 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. Propargylamine and benzyl azide were purchased from Acros. DMAP and TsOH were 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 °C) were purchased from Sinopharm Co. Ltd. They were of analytical grade and directly used as received without further purification.

Instruments

^{1}H and ^{19}F NMR spectra were recorded on a Bruker ARX 500 NMR spectrometer using tetramethylsilane (TMS; δ = 0 ppm) as an internal standard. FTIR spectrum was recorded on a

Perkin Elmer 16 PC FT-IR spectrophotometer. High-resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in a MALDI-TOF mode. Molecular weights (M_w and M_n) and polydispersity indices (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 the molecular weight range of 10^3–10^7 were used for molecular weight calibration.

Polymer synthesis

Preparation of monomer 1 (M1). The synthesis method of the monomer is 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 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 were injected into the flask. The mixture was stirred at room temperature for 24 h. The filtrate was removed and the solution was concentrated by rotatory evaporator. After extraction with DCM several times, the crude product was purified by column gel using PE : ethyl acetate = 30 : 1 (by volume). Finally, a 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 were added into the flask. 100 mL freshly distilled DCM was poured into the system as a solvent. Lastly, 0.7 g (10 mmol) propargylamine was added. The solution color turned out to be dark brown. After two days 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), a white solid was obtained with a 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 a side arm was added 144 mg (0.5 mmol) M**1** and flushed with nitrogen 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 Schlenk tubes were injected with 1 mL freshly distilled toluene. After being aged at 80 °C for 15 min, the monomer solution was transferred to the catalyst solution immediately, and polymerized at 80 °C for 24 h. The polymerization solution was poured into 180 mL hexane/$CHCl_3$ (5 : 1 by volume) and filtered. Finally a 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: M_w = 9500, M_w/M_n = 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 a 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 the 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 a vacuum oven at 60 °C overnight, 65 mg yellowish-green solid (P**3**) was obtained 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 the 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 a 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 of the target product was obtained with a 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 the last step) and 38.9 mg (0.1 mmol) P**0** were 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 obtained 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 the amido group), 4.50 (2H, methylene linked to the triazole group).

Acknowledgements

This work was partially supported by the National Science Foundation of China (21490571); the Research Grants Council

of Hong Kong (N_HKUST604/14 and N_HKUST620/11), J. Z. Sun thanks the support from Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application (Soochow University). B. Z. Tang and A. Qin thank the support of the Guangdong Innovative Research Team Program of China (20110C0105067115).

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