Post-functionalization of disubstituted polyacetylenes via click chemistry

TONG Li[1], QIN AnJun[1], ZHANG XiaoA[1], MAO Yu[1], SUN JingZhi[1*] & TANG Ben Zhong[1,2*]

[1]*Institute of Biomedical Macromolecules, MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China*
[2]*Department of Chemistry, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China*

We report a synthetic design and the experimental exploration of preparation of disubstituted polyacetylenes (PAs, **P3**) through 1,3-dipolar cycloaddition of azides with precursor PA bearing alkyne pendants. The precursor PA (**P2**) was derived by desilylation of the pristine PA with trimethylethynylsilane side chains (**P1**). **P1** was obtained by polymerization of a dual-alkyne containing monomer with one of the alkynes end-capping by trimethylsilane (**M**) under the promotion of WCl$_6$-Ph$_4$Sn catalyst. Two synthetic routes, i.e. two-steps (from **P1** to **P3** via precursor **P2**) and one-pot (from **P1** to **P3** without separation and purification of **P2**) were tried and the results indicated that one-pot strategy is more facile and resultant **P3-1** showed higher purity and higher molecular weight than the resultant of **P3-2**. By using the techniques such as GPC, FTIR and ^{1}H NMR spectroscopy the polymerization behavior and the structures of the polymers were well characterized.

disubstituted polyacetylene, click chemistry, one-pot method, selective polymerization

1   Introduction

Polyacetylene (PA) is the prototypic conjugated polymer for its metallic conductive properties, but its intractability and instability greatly limited its scope of practical applications. If appropriate substituents are attached to the polyene backbone, the above-mentioned problems could be solved and meanwhile the substituents might endow it with new functional properties [1–3]. The substituted PAs have been found to show photoconductivity, optical nonlinearity, magnetic susceptibility, photo- and electroluminescence, liquid crystallinity, biocompatibility, chain helicity, and so on [1–26], indicating the bright prospect of the substituted PAs. Generally, disubstituted PAs are superior to their monosubstituted counterparts in performance [15–23]. However, the molecular functionalization of disubstituted PAs is difficult [2, 3]. Up to now, disubstituted acetylenes

with limited types of functional moieties [15–23] have been obtained, and apparently it still remains a daunting challenge to polymerize disubstituted acetylenes bearing reactive groups with active protons or coordinative ligands which would readily deactivate the brittle transition-metal catalysts for acetylene polymerizations. There is no doubt that new synthetic methods need to be explored for preparing the functional disubstituted PAs.

Through the efforts of chemists, many effective methods have been found, and most of them are focused on the synthesis of new monomers or on the exploration of new catalyst systems [3, 24, 25]. But in practice, if the monomers are different, the reaction conditions are often necessary to be explored again, which makes the research rather cumbersome and time-consuming. Alternatively, if we can obtain a precursor of disubstituted PAs, based on which the expected functional disubstituted PAs can be indirectly prepared by post-polymerization modification, the synthesis of functional disubstituted PAs will become more facile and a variety of novel functional disubstituted PAs will come into being.

*Corresponding author (email: sunjz@zju.edu.cn; tangbenz@ust.hk)

Masuda and coworkers, Tang and coworkers have done some contribution in this area [15–23, 26]. However, the exploration has never desisted.

It is well-known that the 1,3-dipolar cycloaddition of azides with alkynes catalyzed by copper(I) complexes under mild conditions, coined as "click reaction", has received extensive attention as a highly efficient and stereoselective reaction coupled with excellent functional group compatibility [27–34]. The click chemistry strategy has been successfully utilized to macromolecular chemistry, affording polymeric materials varying from block copolymers, dendrimers, to complex macromolecular structures. It is a rational consideration that combining the click chemistry with the precursor route to disubstituted PAs renders a great chance to prepare functionalized PAs.

Herein, we demonstrate the design and synthesis of a monomer with two kinds of internal alkynes (trimethyl((4-(pent-1-ynyl)phenyl)ethynyl)silane), and the polymerization of such a monomer by selective opening one alkyne and leaving trimethylsilyl(TMS)-linked alkyne intact. The obtained polymer (P1) bearing TMS-protected alkyne can be used as a precursor. After de-protection, the free alkyne group is potentially allowable for the click reaction with variety of functional blocks with azide group. Thus, a facile route to functional disubstituted PAs is available. For convenience, we have also explored one-pot synthetic route to the post-functionalized disubstituted PAs.

2   Experimental

2.1   General experimental section

All the chemicals used in this study were purchased from Acros or Alfa without otherwise stating. Tetrahedrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen before used. Other solvents were purified by standard methods.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker ADVANCE DMX 500 MHz spectrometer with tetramethylsilane as the internal standard. FTIR spectra were recorded on a Bruker Vector 22 spectrometer. Average molecular weights (M_w) and polydispersity indices (PDI) of the polymers were estimated by a Waters PL-GPC-50 gel permeation chromatography (GPC) system equipped with a Refractive Index (RI) detector, using a set of monodisperse polystyrenes as calibration standards. High-resolution mass spectra (HRMS) were taken on a GCT Premier CAB 048 mass spectrometer operating in MALDI-TOF model.

2.2   Synthesis of the monomer

1-Bromo-4-(pent-1-ynyl)benzene (2)

Into a rounded bottom flask equipped with a stirring bar was placed 3 g (11 mmol) of 1-bromo-4-iodobenzene (**1**). The

flask was put into a glovebox and 75 mg (11 mmol) of dichlorobis(triphenylphosphine)palladium(II), 81 mg (0.4 mmol) of CuI, and 56 mg (0.22 mmol) of triphenylphosphine were added. Afterward, 50 mL anhydrous THF, 60 mL dried triethylamine and 1.36 mL (14.3 mmol) of 1-pentyne were injected into the flask by syringes under stirring respectively. The mixture was stirred at room temperature for 4 h. The formed precipitates were filtered and washed with diethyl ether. The organic solvent was combined and evaporated by vacuum rotary. The crude product was purified by silica gel column chromatography using petroleum ether as eluent. A light yellow liquid was obtained in 85.5% yield. ^{1}H NMR (500 MHz, CDCl$_3$), δ (TMS, ppm): 7.40 (d, 2H), 7.25 (d, 2H), 2.36 (t, 2H), 1.62 (m, 2H), 1.03 (t, 3H) ^{13}C NMR (125 MHz, CDCl$_3$), δ (TMS, ppm): 133.3, 131.6, 123.3, 121.7, 91.8, 79.9, 22.3, 21.6, 13.8.

1-Iodo-4-(pent-1-ynyl)benzene (3)

A two-necked rounded bottom flask equipped with a rubber plug and a stirring bar was evacuated under vacuum and flushed with nitrogen three times. Then 2 g (8.97 mmol) of **2** in 100 mL THF was injected into the flask. The flask was put into acetone bath immediately, stirred, and then poured liquid nitrogen was put into the acetone in order to get low temperature of −78 °C. Under this temperature, 6.17 mL (9.87 mmol) of *n*-BuLi was injected dropwise into the solution and reacted for 1 h. Afterwards, with strong nitrogen flow, the rubber plug was opened to add 3 g (8.97 mmol) of I$_2$ as fast as possible and reacted for another 0.5 h. Then it was admitted to rise to room temperature and continued to react for 1 h or about so. Deionized water was added to end the reaction and was extracted with DCM for 3 times with the followed step that washing the organic solution with Na$_2$S$_2$O$_3$ (aq.) and deionized water respectively. The organic phase was dried over magnesium sulfate and the crude product was condensed under vacuum rotary without further purified. A brown liquid (2 g) was obtained in 83.3% yield. ^{1}H NMR (500 MHz, CDCl$_3$), δ (TMS, ppm): 7.62 (d, 2H), 7.13 (d, 2H), 2.37 (t, 2H), 1.63 (m, 2H), 1.06 (t, 3H).

Trimethyl((4-(pent-1-ynyl)phenyl)ethynyl)silane (M)

The procedure was the similar to synthesis of compound **2**. A yellow liquid was obtained in 58.8%. The synthesis of M would be shown in Scheme 1. ^{1}H NMR (500 MHz, CDCl$_3$), δ (TMS, ppm): 7.36 (d, 2H), 7.30 (d, 2H), 2.38 (t, 2H), 1.63
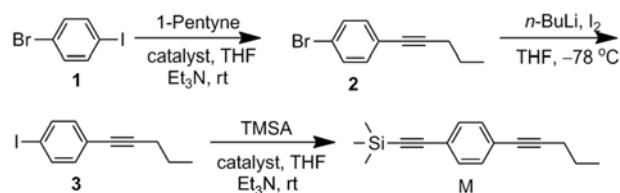

Scheme 1   Synthetic route to the monomer with two alkynes.

(m, 2H), 1.04 (t, 3H), 0.24 (s, 9H) ^{13}C NMR (125 MHz, CDCl$_3$), δ (TMS, ppm): 131.9, 131.5, 124.5, 122.3, 105.0, 95.8, 92.7, 80.7, 22.4, 21.7, 13.8, 0.18. HRMS (MALDI-TOF, *m/z*): (M$^+$) calcd for C$_{16}$H$_{20}$Si, 240.1334; found, 240.1336.

2.3　Polymerization

All the polymer reactions shown in Scheme 2 were carried out under dry nitrogen in a vacuum-line system except for the purification of the polymers, which was done in an open atmosphere. Typical procedures for polymerization are given below.

Into a 10 mL Schlenk tube with a side arm was added 294 mg (1.2 mmol) of the monomer (M). The tube was evacuated under vacuum and flushed with dry nitrogen three times before injecting 2 mL of toluene. The catalyst solution was prepared in another tube by dissolving 24 mg (0.06 mmol) of tungsten chloride (WCl$_6$) and 26 mg (0.06 mmol) of tetraphenyltin (Ph$_4$Sn) in 2 mL of toluene. After aging for 15 min at room temperature, the monomer solution was transferred to this tube using a hypodermic syringe. The reaction mixture was stirred at 80 °C for 24 h. Diluted with 4 mL CHCl$_3$, the crude product was added dropwise to 300 mL methanol through a cotton filter under stirring. The precipitate was allowed to stand over night and then filtered with a Gooch crucible, washing with methanol for 3 times.
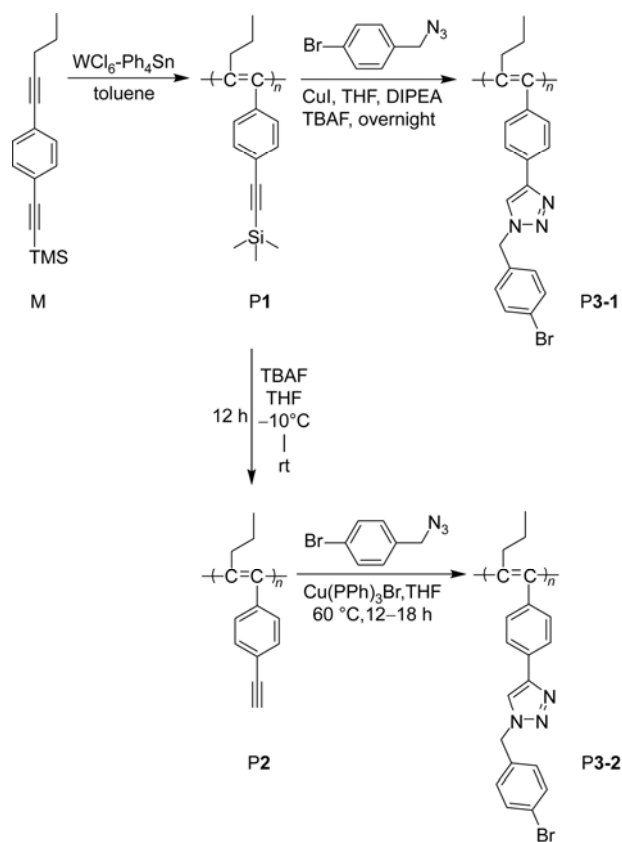
Scheme 2　Two post-function methods for the preparation of disubstituted PAs via click reaction.

The polymer which was dried in an open atmosphere to a constant weight was isolated as a green-yellow solid. IR (thin film), ν (cm^{-1}): 2157(C≡C), 1658(C=C). ^{1}H NMR (500 MHz, CDCl$_3$), δ (TMS, ppm): 7.4–6.9 (aromatic protons), 2.38, 1.62, 1.04 (pentyne), 0.26 (protons in TMS groups) ^{13}C NMR (125 MHz, CDCl$_3$), δ (TMS, ppm): 142.0 (C=C), 133.2, 131.2, 121.2 (aromatic carbons), 105.7, 94.62 (internal alkyne linking to protection TMS group), 37.9, 22.4, 14.6 (carbons belonging to pentyne), 0.27 (carbons in TMS groups).

2.4　Desilylation of the polymer

Into a 10 mL Schlenk tube was added 87 mg (0.36 mmol) of polymer P**1**. After the tube being evacuated under vacuum and flushed with dry nitrogen for 3 times, 3.5 mL of fresh distilled THF was injected. When the polymer P**1** was dissolved completely, the tube was put into ice-salt (NaCl) bath to reach −10 °C, and 0.9 mL of 1 M TBAF (tetrabutylammonium fluoride) solution in THF was added dropwise, stirring. Then the mixture was allowed to warm up to ambient temperature and reacted overnight. The following step was the same as shown in the polymerization part. IR (thin film), ν (cm^{-1}): 3312 (HC≡), 2104(C≡C), 1605 (C=C).

2.5　Click reaction

1-(Azidomethyl)-4-bromobenzene (N$_3$-R)

A rounded bottom flask was equipped with a stirring bar, 2 g (8 mmol) of 1-bromo-4-(bromomethyl)benzene and 0.63 g (9.6 mmol) of NaN$_3$ was placed. Then, 50 mL DMSO was added and the mixture was stirred at 30 °C overnight. Followed by ending the reaction with deionized water was extracting the mixture with diethyl ether for 6 times or more. All the organic solvent was condensed and purified by a silica gel column chromatography using petroleum ether as eluent. A transparent liquid was obtained in 60% yield. ^{1}H NMR (500 MHz, CDCl$_3$), δ (TMS, ppm): 7.50 (m, 2H), 7.18 (d, 2H), 4.30 (s, 2H). ^{13}C NMR (125 MHz, CDCl$_3$), δ (TMS, ppm): 134.6, 132.2, 130.0, 122.5, 54.3.

General procedures of P2's click reaction

24 mg (0.14 mmol) of P**2** and 3 mg (0.0029 mmol) of Cu(PPh$_3$)$_3$Br were added into a 10 mL Schlenk tube, which was evacuated and flushed with dry nitrogen for three times then 2 mL of fresh distilled THF being injected. N$_3$-R then was injected and the mixture was stirred at 60 °C for 12 h. The successive procedures were similar to the procedures as shown before. The product P**3** was isolated as a black solid in yield of 59.1%. ^{1}H NMR (500 MHz, CDCl$_3$), δ (TMS, ppm): 8.1–6.7 (aromatic protons), 5.5 (protons attached to phenyl and triazole), 2.34, 1.67, 1.02 (pentyne).

Procedures of one-pot method

Into a 10 mL Schlenk tube was added stirring bar and 69 mg (0.29 mmol) of P**1**. The tube was put in glove box and 11 mg (0.058 mmol) CuI was added. Then 3.5 mL fresh distilled THF, 0.24 mL (1.45 mmol) DIPEA was injected before 0.12 mL 1 M TBAF in THF being injected dropwise. The mixture was stirred at 50 °C for 12 h. The successive procedures were the same as before. A black solid P**3** was obtained in yield of 83.3%. ^{1}H NMR (500 MHz, CDCl$_3$), δ (TMS, ppm): 9.0–5.9 (aromatic protons), 5.5 (protons on phenyl and triazole), 2.32, 1.59, 1.01 (protons of pentyne).

3 Results and discussion

The synthesis of monomer containing two alkyne moieties is a key step to the target polymer. In principle, M can be obtained by direct substitution of the bromide of compound **2** by trimethylethynylsilane. But in experiment, the separation of **2** and M was unexpectedly difficult. Fortunately, this problem was solved by introducing one more step, as shown in the Scheme 1 [4, 34]. We finally got the monomer in high purity by transformation of **2** to **3**, which was confirmed by the ^{1}H and ^{13}C NMR spectra as well as HR-MS analysis.

The experimental results of the disubstituted PA (P**1**) were summarized in Table 1. In previous studies, the yield and M_w of disubstituted polyacetylenes could not meet demands simultaneously [3, 26]. But our present results are different, the yield can be over 30% and the M_w has reached 10^4 Da with relatively narrow polydispersity. Besides, the solubility of the disubstituted polymer P**1** was also checked and to our delight, P**1** could dissolve well in CHCl$_3$ (at least 120 mg/mL), THF, CH$_2$Cl$_2$ and acetone.

In addition, successful selective consumption of alkyne group was confirmed by [13]C (Figure 1) and FTIR measurement (Figures 1 and 2). For example, in Figure 1(a), the resonance peaks at $\delta = 92$ and 81 ppm (denoted as peaks e and f) are corresponding to the penta-1-ynyl. They disappeared after polymerization (Figure 1(b)); while, the peaks for g and h are still in presence. The characteristic signal at $\delta = 140$ ppm in Figure 1(b) can be assigned to the carbons in PAs' backbone. These data validate that the selective polymerization of internal alkyne has been achieved.

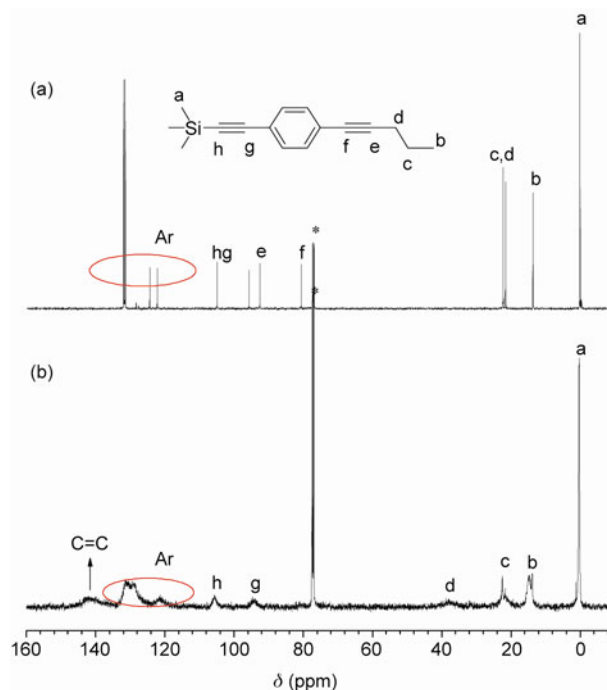FTIR spectra give more information. As shown in Figure 2, Figure 2(a) displays the IR absorption features of M, the

Table 1 Results of polymerization for P**1**[a)]

No.	Temperature (°C)	Yield (%)	M_w	PDI
1	80	33.2	17000	2.00
2	80–95 [b)]	24.1	38000	3.17

a) Catalyzed by WCl$_6$-Ph$_4$Sn in toluene under nitrogen for 24 h; [M]$_o$ = 1 M, [WCl$_6$] = [Ph$_4$Sn] = 0.05 M. Determined by GPC in THF on the basis of a linear polystyrene calibration; b) the temperature was kept at 95 °C for about 2 h then cooled to 80 °C.

Figure 1 ^{13}C NMR spectra of the monomer (a) and its polymer P**1** (b) in CDCl$_3$. The solvent peak is marked with an asterisk.

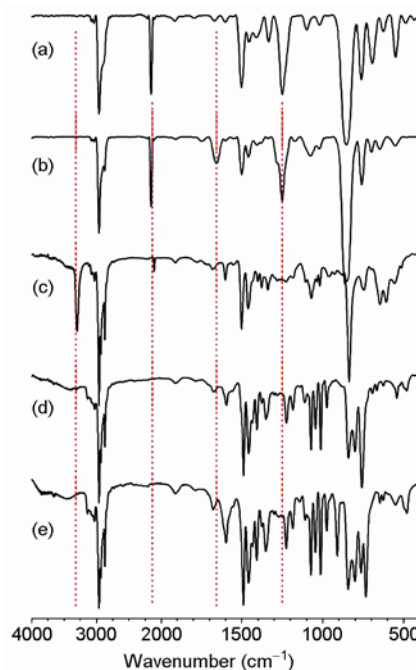**Figure 2** IR spectra of the monomer M (a), its polymer P**1** (b), P**2** (c), P**3-2** (d) and P**3-1** (e).

stretching band of C≡C is clearly shown at wavenumber of 2157 and 1520 cm^{-1}, indicating the existence of pristine C≡C bonds. After the polymerization reaction catalyzed by WCl$_6$-Ph$_4$Sn system, these two bands are still in presence, suggesting that only partial alkynes have been consumed. In

other words, the WCl_6-Ph_4Sn catalyst system can only polymerize one of the two kinds of internal alkyne groups. The selective polymerization of alkyne is attributed to the steric and electronic effect of the protected groups (TMS) [33].

It's well known that 1,3-dipolar cycloadditions between terminal alkynes and azides proceeds efficiently in mild condition. To make use of this facile synthetic strategy, the desilylation of P1 was firstly carried out (Scheme 2). The characterization data of the resultant polymer (P2) are list in Table 2; and the FTIR spectrum is shown in Figure 2. Figure 2(c) displays the IR absorption features of P2, the absorption band at a wavenumber of 2144 cm^{-1} is assigned to the stretching mood of $C \equiv C$. In addition, a new band at a wavenumber of 3312 cm^{-1} emerges (in comparison with Figure 2(b)). This band is associated with C—H stretching mood of the $C \equiv C$—H entity. These two bands at 2144 and 3312 cm^{-1} indicate the releasing of external alkyne in P2.

The existence of free external alkyne group allows us to implement the post-modification of P2 by clicking alkyne with azide compounds bearing functionalities. To validate this idea, we conducted a click reaction of P2 with 1-(azidomethyl)-4-bromobenzene. Delightfully, the reaction went on smoothly, and P3 was obtained in a mild condition, i.e. just stirring at 60 °C for 12–18 h in the presence of Cu(I) catalyst. To characterize the structure of the resulted polymer, both FTIR and ^{1}H NMR spectroscopic techniques were used. As shown by Figure 2D, the IR absorption bands at 2144 and 3312 cm^{-1} both disappeared completely, indicating that the $C \equiv C$—H moieties had been consumed thoroughly. Meanwhile, in the finger-print region, the bands at around 1050–1100 cm^{-1} can be assigned to the bending mood of polar $C = N$ bonds. The emergence of these bands implies the formation of triazole moieties in the click reaction process.

^{1}H NMR spectra disclose further information about the post-polymerization reaction (see Figure 3). In Figure 3(a), the resonance peaks showing in the high-field region ($\delta < 3$) are assigned to the chemical shifts of the propanyl attaching to polymer backbone and the methyls in TMS, and the broad band showing around 7.2 ppm are caused by the protons on the phenyl group. After click reaction, the resonance

Figure 3 ^{1}H NMR spectra of P1 (a), click reaction product P3-2 (b) and P3-1 in CDCl$_3$ (c). The solvent peaks are marked with asterisks.

peak for TMS vanished totally, suggesting that the desilylation was well proceeded. The resonance peaks for propanyl groups shifted to low field slightly and became broader. The resonance peaks at field lower than 7.0 ppm show some new features in Figure 3(b). On one hand, they are split, which is reasonable because the click reaction has introduced a bromophenyl group into the resulted polymer. On the other hand, the chemical shifts appear in lower field; this is also reasonable because both bromo- and triazolyl-moieties are electron withdrawing functionalities. More significantly, a new peak at around $\delta = 5.46$ ppm is observed in Figure 3(b), which is assigned to the protons on the methyl group linking the end phenyl with triazole moiety. These observations evidently confirm the successful transformation of P2 to expected functional disubstituted PA, or P3 through the click chemistry strategy. Moreover, the peak attributed to the $C \equiv C$—H proton at around $\delta = 3$ ppm could hardly be seen in Figure 3(b). It implies that the efficiency of the grafting is higher than the upper limitation of NMR spectroscopy (97%).

In our experiment, we encountered the difficulty of low throughput due the low solubility of P2 in the solvents that suitable for click reaction of P2 with azides. The data in Table 2 reveal that the final polymer (P3-2) has an evident lower molecular weight than its precursor polymer P2, although the molecular weight of the repeat unit of P3 is higher than that of P2. Besides the systematic error in molecular weight measurement caused by different experimental batches, this observation can be explained as following. After purification and drying in vacuum, the collected P2 can be

Table 2 Experimental results of P2, P3-1 and P3-2[a]

Polymer	Yield (%)	Solubility	M_w	PDI
P2	54.5	L[b]	30000	1.9
P3-1	83.3	A[c]	27000	1.9
P3-2	59.1	A[c]	12000	1.7

a) P3-1 and P3-2 stand for the target polymer P3 obtained by one-pot and two-step methods, respectively; b) the solubility was very low in organic solvents; c) the solubility in some organic solvents is acceptable. Molecular weight was determined by GPC in THF on the basis of a linear polystyrene calibration.
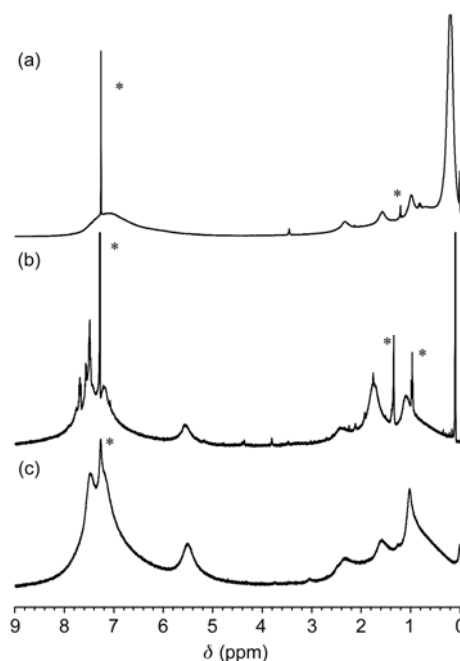
dissolved partially in proper solvents. It means that only the fraction with low molecular weight has gone through with the click reaction. Consequently, the finally obtained polymer has a lower molecular weight. Considering that the click reaction is highly efficient, we tried to prepare P**3** through a one-pot scheme (see Scheme 2). Fortunately, resultant showing the same aspect as P**3-2** was obtained and it was denoted as P**3-1**. To make it doubtless that the resultant has the same intrinsic structure as P**3-1** rather than the untouched precursor P**2**, both FTIR and ^{1}H NMR characterizations were carried out on the resultant, and the recorded data are demonstrated in Figure 2 (curve (e)) and (curve (c)), respectively.

It is obvious that spectral features of curve E seems identical to that of D. Specifically, the disappearance of the absorption band at 2144 and 3312 cm^{-1} indicates the C≡C bonds have been transformed, and the appearance of the bands at around 1000–1100 cm^{-1} indicates the formation of triazole group. Moreover, curve (c) in Figure 3 shows similar characteristics of curve (b). The most significant one is the emergence of a δ at around 5.54 ppm, which is an indication of the triazole moiety. Therefore, both FTIR and NMR spectra clearly validate that the obtained polymer is the expected resultant.

There are two noteworthy essences in the one-pot route. One is revealed by the comparison between curve (b) and (c) in Figure 3. The resonance peaks at 0.88 and 1.26 ppm in curve (b) are assigned to the hexane, which was used for precipitation of the resultant mixture and encapsulated in polymer matrix. Both of them are invisible in curve (c) due to the saving of the middle separation and purification steps. The other is that the molecular weight of P**3-1** (27000) is evidently higher than that of P**3-2** (12000). These data suggest that the one-pot strategy can give rise to expected disubstituted functional PAs with higher purity and higher molecular weight.

4 Conclusions

In summary, we have demonstrated that functional disubstituted PAs can be successfully prepared by click chemistry strategy. By rational design, a dual-alkyne containing monomer with one of the alkynes end-capping by trimethylsilane (TMS) was synthesized. This monomer can be selectively polymerized and P**1** has been derived by using WCl$_6$-Ph$_4$Sn catalyst, leaving the TMS end-capped alkyne group untouched and the other completely consumed in polymerization reaction. After desilylation of P**1**, the precursor polymer P**2** was derived, the presence of free external alkynes was confirmed by FTIR, and ^{1}H NMR spectroscopy. The click reaction between P**2** and functional azides was tried and expected polymer P**3** was obtained. To find a more facile synthetic route, both one-pot and two-steps methods have been explored, and the experimental results revealed

that one-pot method gave rise to resultant polymer with higher purity and higher molecular weight. All these remarks have been supported by experimental and spectral data.

1   Aoki T, Kaneko T. New macromolecular architectures for permselective membranes-gas permselective membrane from dendrimers and enantioselectively permeable membrane from one-handed helical polymers. *Polym J*, 2005, 37: 717–735

2   Masuda T, Sanda F. *In Handbook of Metathesis*. Ed: Grubbs RH. Weinheim: Wiley-VCH, 2003, Charpter 3. 11

3   Lam JWY, Tang BZ. Functional polyacetylenes. *Acc Chem Res*, 2005, 38: 745–754

4   Masuda T, Higashimura T. Synthesis of polymers from substituted acetylenes: Exploitation of molybdenum-and tungsten-based catalyst. *Acc Chem Res*, 1984, 17: 51–56

5   Lam JWY, Tang BZ. Liquid-crystalline and light-emitting polyacetyenes. *J Polym Sci A: Polym Chem*, 2003, 41: 2607–2629

6   Tang BZ, Chen HZ, Xu RS, Lam JWY, Cheuk KKL, Wong HNC, Wang M. Structure-property relationships for photoconduction in substituted polyacetylenes. *Chem Mater*, 2000, 12: 213–221

7   Kong X, Tang BZ. Synthesis and novel mesomorphic properties of the side-chain liquid crystalline polyacetylenes containing phenyl benzoate mesogens with cyano and methoxy tails. *Chem Mater*, 1998, 10: 3352–3363

8   Okoshi K, Sakajiri K, Kumaki J, Yashima E. Well-defined lyotropic liquid crystalline properties of rigid-rod helical polyacetylene. *Macromolecules*, 2005, 38: 4061–4064

9   Cheuk KKL, Lam JWY, Li BS, Xie Y, Tang BZ. Synthesis, photophysical, and electroluminescent properties of arylenevinylenes-*co*-pyrrolenevinylenes derived from divinylaryl bridged bispyrroles. *Macromolecules*, 2007, 40: 2657–2665

10 Sanda F, Araki H, Masuda T. Synthesis and properties of serine and threonine-based helical polyacetylenes. *Macromolecules*, 2004, 37: 8510–8516

11 Morino K, Maeda K, Yashima E. Helix-sense inversion of poly(phenylacetylene) derivatives bearing an optically active substituent induced by external chiral and achiral stimuli. *Macromolecules*, 2003, 36: 1480–1486

12 Goto H, Zhang HQ, Yashima E. Chiral stimuli-responsive gels: Helicity induction in poly(phenylacetylene) gels bearing a carboxyl group with chiral amines. *J Am Chem Soc*, 2003, 125: 2516–2523

13 Dong YP, Lam JWY, Peng H, Cheuk KKL, Kwok HS, Tang BZ. Syntheses and mesomorphic and luminescent properties of disubstituted polyacetylenes bearing biphenyl pendants. *Macromolecules*, 2004, 37: 6408–6417

14 Lam JWY, Dong YP, Cheuk KKL, Law CCW, Lai LM, Tang BZ. Helical conjugated polymers: Synthesis, stability, and chiroptical properties of poly(alkyl phenylpropiolate)s bearing stereogenic pendants. *Macromolecules*, 2004, 37: 6695–6704

15 Lam JWY, Dong YP, Cheuk KKL, Tang BZ. Helical disubstituted polyacetylenes: Synthesis and chiroptical properties of poly(phenylpropiolate)s. *Macromolecules*, 2003, 36: 7927–7938

16 Yang WZ, Qin A, Lam JWY, Sun JZ, Dong Y, Haussler M, Liu J, Xu HP, Zheng Q, Tang BZ. Disubstituted polyacetylenes containing photopolymerizable vinyl groups and polar ester functionality: Polymer synthesis, aggregation-enhanced emission, and fluorescent pattern formation. *Macromolecules*, 2007, 40: 3159–3166

17 Shida Y, Sakaguchi T, Shiotsuki M, Sanda F, Freeman BD, Masuda

T. Synthesis and properties of poly(diphenylacetylenes) having hydroxyl groups. *Macromolecules*, 2005, 38: 4096–4102

18 Zeng Q, Li ZA, Li Z, Ye C, Qin J, Tang BZ. Convenient attachment of highly polar azo chromophore moieties to disubstituted polyacetylene through polymer reactions by using "click" chemistry. *Macromolecules*, 2007, 40: 5634–5637

19 Li Z, Dong Y, Qin A, Lam JWY, Dong Y, Yuan W, Sun J, Hua J, Wong KS, Tang BZ. Functionalization of disubstituted polyacetylenes through polymer reactions: Syntheses of functional poly(1-phenyl-1-alkyne)s, *Macromolecules*, 2006, 39: 467–469

20 Hua JL, Li Z, Lam JWY, Xu HP, Sun JZ, Dong YP, Dong YQ, Qin AJ, Yuan WZ, Chen HZ, Wang M, Tang BZ. Induced chain alignment, efficient energy transfer, and enhanced light emission in functional polyacetylene-perovskite hybrids. *Macromolecules*, 2005, 38: 8127–8130

21 Xu HP, Sun JZ, Qin A, Hua JL, Li Z, Dong YQ, Xu H, Yuan WZ, Ma YG., Wang M, Tang BZ. Functional perovskite hybrid of polyacetylene ammonium and lead bromide: Synthesis, light emission, and fluorescence imagining, *J Phys Chem B*, 2006, 110: 21701–21709

22 Yuan WZ, Zhao H, Xu HP, Sun JZ, Lam JWY, Mao Y, Jin JK, Zhang S., Zheng, Q, Tang BZ. Improvement of the solubility of multiwalled carbon nanotubes with disubstituted polyacetylenes bearing different side chains, *Acta Polym Sinica*, 2007, 10: 901–904

23 Mao Y, Xu HP, Zhao H, Yuan WZ, Qin A, Yu Y, Faisal M, Zhang XA, Sun JZ, Tang BZ. Composites of quaternized poly(pyridylacetylene) and Ag nanoparticles: Nanocomposite preparation, conductivity and photoinduced patterning. *J Mater Chem,* 2011, 21: 13627–13633

24 Xu HP, Mao Y, Wang J, Xie BY, Jin JK, Sun JZ, Yuan WZ, Qin A, Wang M, Tang BZ. Thermally induced transfiguration of polymer nanowires under irradiation of electron beams. *J Phys Chem C*, 2009, 113: 14623–14627

25 Xu K, Peng H, Lam WY, Dong Y, Sun Q, Salhi F, Tang BZ. Transi-

tion metal carbonyl catalysts for polymerizations of substituted acetylenes. *Macromolecules*, 2000, 33: 6918–6924

26 Liu JZ, Lam JWY, Tang BZ. Acetylenic polymers: Syntheses, structures, and functions. *Chem Rev*, 2009, 109: 5799–5867

27 Rostovtsev VV, Green LG, Fokin VV, Sharpless KB. A stepwise Huisgen cycloaddition process: Copper(I)-catalyzed regioselective "ligation" of azides and terminal alkynes. *Angew Chem Int Ed*, 2002, 41: 2596–2599

28 Bock VD, Hiemstra H, Van Maarseveen JH. Amino-phosphanes in Rh[1]-catalyzed hydroformylation: Hemilabile behavior of P-N ligands under high CO pressure and properties. *Eur J Org Chem*, 2006, 51–61

29 Altintas O, Hizal G, T unca U. ABC-type hetero-arm star terpolymers through "click" chemistry. *J Polym Sci Part A: Polym Chem*, 2006, 44: 5699–5707

30 Lutz JF. 1,3-Dipolar cycloadditions of azides and alkynes: A universal ligation tool in polymer and materials science. *Angew Chem Int Ed*, 2007, 46: 1018–1025

31 Bindr WH, Sachsenhofer R. 'Click chemistry' in polymer and materials science. *Macromol Rapid Commun*, 2007, 28: 15–54

32 Tornoe CW, Christensen C, Meldal M. Peptidotriazoles on solid phase: [1,2,3]-Triazoles by regiospecific copper(I)-catalyzed 1,3-dipolar cycloadditions of terminal alkynes to azides. *J Org Chem*, 2002, 67: 3057–3064

33 Aizpurua JM, Azcune I, Fratila RM, Balentova E, Sagartzazu-Aizpurua M, Miranda JI. "Click" synthesis of nonsymmetrical bis(1,2,3-triazoles). *Org Lett*, 2010, 12(7): 1584–1587

34 Liu JZ, Zheng RH, Tang YH, Lam JWY, Qin AJ, Ye MX, Hong YN, Gao P, Tang BZ. Hyperbranched poly(silylenephenylenes) from polycyclotrimerization of A2-type diyne monomers: Synthesis, characterization, structural modeling, thermal stability, and fluorescent patterning. *Macromolecules*, 2007, 40: 7473–7486