Functionalization of Disubstituted Polyacetylenes through Polymer Reactions: Syntheses of Functional Poly(1-phenyl-1-alkyne)s

Zhen Li,[†] Yongqiang Dong,[†,§] Anjun Qin,[†] Jacky W. Y. Lam,[†] Yuping Dong,[†] Wangzhang Yuan,[§] Jingzhi Sun,[§] Jianli Hua,[†] Kam Sing Wong,[‡] and Ben Zhong Tang*,[†,§]

Departments of Chemistry and Physics, The Hong Kong University of Science & Technology,
Clear Water Bay, Kowloon, Hong Kong, and Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

Received August 31, 2005
Revised Manuscript Received December 1, 2005

Polyacetylene (PA) is the best-known conjugated polymer, but its intractability and instability have greatly limited its scope of practical applications.[1] Attachments of appropriate substituents or pendants to the polyene backbone can help improve its processability and stability as well as endow it with new functional properties.[2,3] We have been interested in functionalizing PA at the molecular level and have successfully polymerized hundreds of monosubstituted acetylenes containing a variety of functional groups.[3] Disubstituted PAs are generally superior to their monosubstituted counterparts in performance: for example, poly(1-phenyl-1-octyne), a disubstituted PA, strongly resists thermal decomposition (no molecular weight change detectable after annealing in air at 120 °C for 20 h) and efficiently emits blue light (with a fluorescence quantum yield Φ_F of 43%),[4] while poly(phenylacetylene), a monosubstituted PA, readily degrades and emits weakly.[5] It is envisioned that introduction of functional groups to the disubstituted PAs will confer new functionalities on the polymers, hence yielding new materials with better performances. Molecular functionalization of disubstituted PAs has, however, been difficult.[3]

Our research efforts have so far enabled us to polymerize disubstituted acetylenes containing limited types of functional moieties.[6−9] It remains challenging to polymerize disubstituted acetylenes carrying functional groups with active protons (e.g., amide) and coordinative ligands (e.g., pyridine) because they readily deactivate the transition-metal catalysts for acetylene polymerizations. Our recent success in the synthesis of hyperbranched polyynes[10] promoted us to attach ethynyl units to PA backbones as pendant groups because the triple bonds may make the linear polyenes thermally curable, metal coordinative, and photonically responsive. We polymerized a 1-phenyl-1-alkyne containing the diphenylacetylene moiety but found that the diphenylacetylene unit was also polymerized and that the product was thus a cross-linked polymer.[11] Clearly, new synthetic routes need to be explored for preparing the functional PAs that are inaccessible by the polymerizations of their monomers. In this report, we present such a new approach. We developed a polymer reaction route that offered ready access to soluble functional disubstituted PAs containing reactive diarylethynyl and polar pryridyl and amido units (**5**−**7**; Scheme 1), none of which, as discussed above, could be obtained from the polymerizations of their corresponding monomers without synthetic difficulties and structural complications.

Our initially designed synthetic route was to prepare **4** by directly polymerizing its monomer **2** and then subject the polymer intermediate **4** to the reactions with desired functional groups. Our attempted polymerization of **2**, however, failed. We thus took an alternative approach: we polymerized **1** and then transformed polymer **3** to polymer **4** by the reaction with 4-iodophenol in the presence of KI under basic conditions. While **4** can react with various functional groups via different chemical processes, its coupling reactions with arylacetylenes were studied in this work as a demonstration of its usefulness and versatility.

The results of the polymerization and postpolymerization reactions are summarized in Table 1. The polymerization of **1** is effected by the tungsten-based metathesis catalyst, producing polymer **3** with a high molecular weight and a low polydispersity index in a high yield. The chlorine atom of **3** is readily replaced by the 4-iodophenoxy group via the base-catalyzed polymer reaction. The couplings of **4** with the three arylacetylenes all proceed to completion in the presence of the palladium catalyst, resulting in the quantitative formation of the desired products **5**−**7**.

The reaction products were characterized by spectroscopic analyses, and all the polymers (**3**−**7**) gave satisfactory data corresponding to their expected molecular structures (see Supporting Information for details). The ^{13}C NMR spectra of the polymers are given in Figure 1 as examples, with that of monomer **1** shown in the same figure for comparison. While the acetylene carbon atoms of monomer **1** resonate at δ 88.3 and 81.6, these peaks are absent in the spectrum of its polymer **3**. A new broad peak due to double-bond resonance appears at $\delta \sim 140$ (Figure 1B), confirming that the triple bond of **1** has been transformed to the double bond of **3** by the acetylene polymerization. After reacting with 4-iodophenol, the resonance peak of CH_2Cl unit at δ 46.2 completely disappears. In replacement, new peaks due to the resonances of the phenyl carbon atoms ($C_{Ph}{-}O$ and $C_{Ph}{-}I$) and the methylene carbon atom (CH_2O) appear at δ 158.9, 82.9, and 68.1, respectively (Figure 1C). The elemental analysis data of **4** agree well with its theoretic contents, further verifying that the chlorine atoms have been quantitatively substituted by the iodophenoxy groups.

Polymer **5** exhibits resonance peaks associated with the acetylenic triple bonds at δ 93 and 87 but no peaks of the $C_{Ph}{-}I$ moiety at δ 82.9 (Figure 1D), confirming the quantitative completion of the coupling reaction: all the iodine atoms in **4** have been replaced by the phenylethynyl groups. Similar changes in chemical shifts are observed in the spectra of **6** and **7**. The resonances of the carboxy (CO_2) and amido (CONH) units in the downfield region of the spectrum of **7** (Figure 1F) validate the integration of the polar functional groups into the polymer structure.

The molecular structures of the reaction products are further substantiated by their ^{1}H NMR and IR analysis data. As can be seen from the ^{1}H NMR spectra shown in Figure S1 (Supporting Information), the reaction of **3** with 4-iodophenol duly shifts the resonance peak from δ 3.18 (CH_2Cl) to 3.49 (CH_2O). Polymers **5**−**7** all show expected resonance peaks (Figure S2). The peak of the proton ortho to the nitrogen atom in the pyridyl unit in **6** is clearly seen at δ 8.59. The triple bonds in **5**−**7**

---

* Corresponding author: Ph +852-2358-7375; Fax +852-2358-1594; e-mail tangbenz@ust.hk.

[†] Department of Chemistry, The Hong Kong University of Science & Technology.

[‡] Department of Physics, The Hong Kong University of Science & Technology.

[§] Zhejiang University.

10.1021/ma051907q CCC: $33.50

Scheme 1

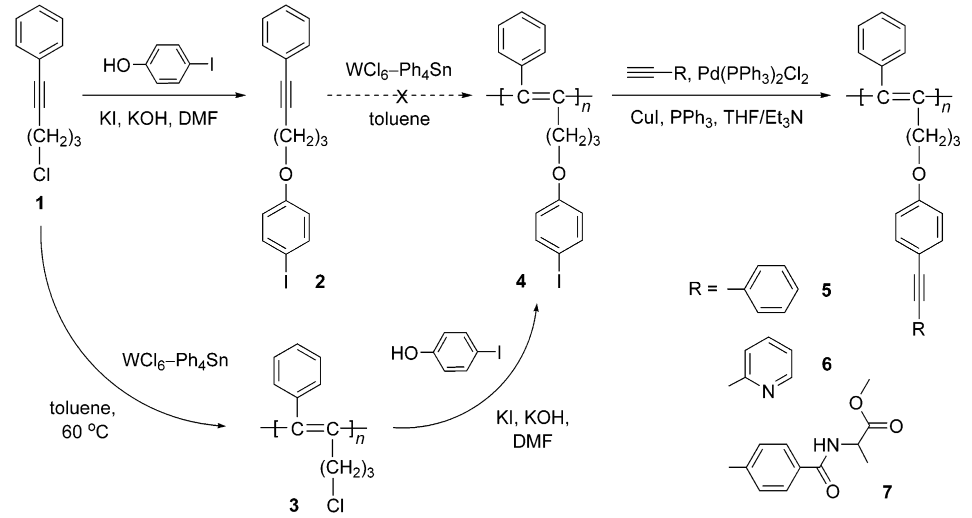

Table 1. Syntheses and Optical Properties of the Functionalized Disubstituted Polyacetylenes

						fluorescence decay[d]			
no.	yield (%)	M_w [a]	M_w/M_n [a]	λ_{max} [b] (nm)	Φ_F[c] (%)	A_1	A_2	τ_1	τ_2
3	74	23 700	1.74	460	10	36	64	0.22	1.42
4	71	29 400	2.54	454	16		100		1.05
5	100	30 100	2.65	451	25	14	86	0.16	1.13
6	100	24 800	2.57	452	45	26	74	0.18	1.10
7	100	33 200	1.97	435	12	6	94	0.11	1.40

[a] Determined by GPC in THF on the basis of a polystyrene calibration. [b] Maximum wavelength of emission spectrum of polymer solution in THF; concentration: 6×10^{-3} mg/mL; excitation wavelength: 329 nm. [c] Fluorescence quantum yield in THF using 9,10-diphenylanthracene in cyclohexane (Φ_F = 90%) as standard. [d] Fraction (A, %) and lifetime (τ, ns) of shorter (1) or longer lived species (2).

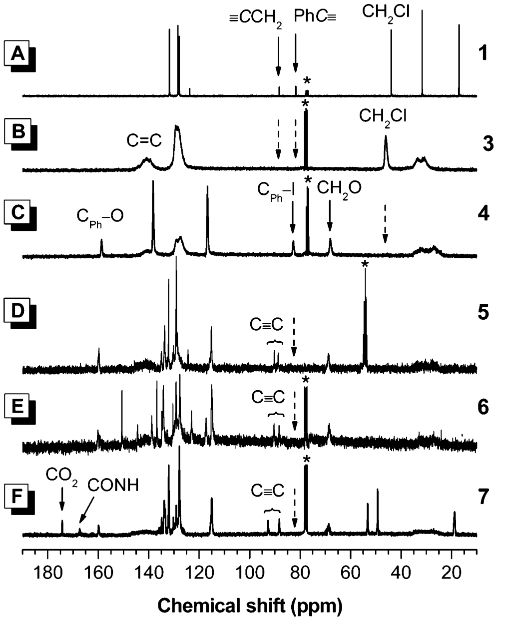

Figure 1. ^{13}C NMR spectra of (A) **1**, (B) **3**, (C) **4**, (E) **6**, (F) **7** (all in chloroform-*d*), and (D) **5** (in dichloromethane-d_2). The solvent peaks are marked with asterisks.

display their diagnostic stretching bands at 2216−2205 cm^{-1} in the IR spectra of the polymers. The NH band at 3340 cm^{-1} and C=O bands at 1746 and 1642 cm^{-1} (Figure S3E) certify the incorporation of the amide and ester groups into the molecular structure of polymer **7**.

The aromatic rings of polymer **4** absorb at ~240 nm (K band) and ~280 nm (B band), while its polyene backbone absorbs in the wavelengths longer than 300 nm (Figure S4, Supporting Information). Strong absorption peaks are observed at ~300 nm in the UV spectra of **5**−**7** due to the electronic transitions of their diarylacetylene chromophores.[12] Upon photoexcitation, **4** emits a blue light (Figure S4), whose λ_{max} is close to that of its precursor **3** (Table 1) and those of its nonfunctionalized poly(1-phenyl-1-alkyne) parents,[3] indicating that the light emission is from its poly(1-phenyl-1-pentyne) skeleton. The introduction of the phenylethynyl unit does not affect the emission color but enhances the luminescence efficiency. This effect is more pronounced in the case of **6**: the attachment of the pyridylethynyl group boosts the Φ_F value of **6** to as high as 45%, nearly 3-fold higher than that of its parent form (**4**). The incorporation of the amido and carboxy groups, on the other hand, blue-shifts λ_{max} and decreases Φ_F, demonstrating that the light-emitting process can be tuned by introducing different functional groups to the polymer structure through the polymer reaction. The fluorescence decay varies with the molecular structure (Table 1), but the picture seems complicated. Further studies are under way in collaboration of our physicist colleagues to decipher the involved photodynamic mechanisms.

In our study on hyperbranched polyynes, we have found that the acetylenic triple bonds embedded in the scaffolds of the polymers have enabled them to be thermally cured, photonically cross-linked, and coordinatively metallized.[10] We checked whether the acetylenic triple bonds inserted into the pendants of the linear polyenes **5**−**7** could also endow them with similar properties. Compared to their precursors **3** and **4** (without triple bonds), polymers **5**−**7** (with triple bonds) yield larger amounts of weight residues when pyrolyzed at >500 °C (Figure S5, Supporting Information). These higher pyrolysis yields must be associated with the facile thermolytic curing of the triple bonds at the high temperatures.[10,13] Exposure of polymer **6** to a UV light followed by development results in the formation of a negative photoresist pattern (Figure 2A). Clearly **6** is photo-cross-linkable.[14] When the pattern is shone with a handheld UV

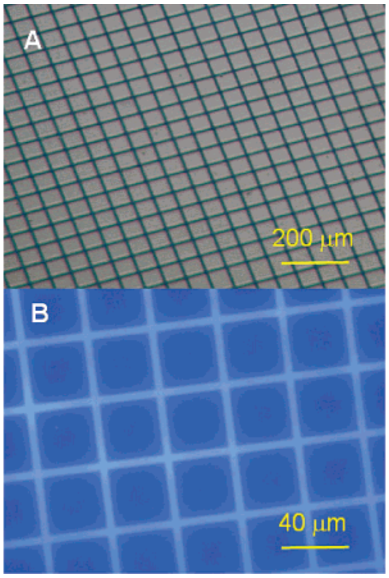

Figure 2. Photoresist patterns of **6** taken under (A) normal room lighting and (B) UV lamp illumination.

lamp, it emits bright blue light. The light-emitting photoresist may find applications in fluorescence imaging, information storage, and LCD backlighting. The acetylene triple bonds of the polymers readily coordinate with transition metals: for example, polymer **6** is metallized by simply stirring its mixture with $Co_2(CO)_8$ in THF at room temperature for a short while, as evidenced by the characteristic cobalt−carbonyl stretching band at ∼2000 cm^{-1} in the IR spectrum of the resultant polymer−cobalt complex (Figure S6).[10,15]

In summary, in this study, we developed a polymer reaction route for molecular functionalization of disubstituted PAs. The structural functionalization confers unique functional properties on the PAs: the polymers become curable, patternable, and metallizable. Our approach enjoys a few notable advantages: the reaction is straightforward, the catalyst is functionality-tolerant, and the procedure is simple. It is anticipated that many other functional groups can be incorporated into the molecular structures of the disubstituted PAs by this versatile polymer reaction strategy. Our work thus opens a new avenue to functionalization of disubstituted PAs, which will facilitate the generation of new functionalized PAs with novel materials properties.

Acknowledgment. This project was partially supported by the Research Grants Council of Hong Kong (603505, 603304, 604903, and 6085/02P) and the National Natural Science Foundation of China (N_HKUST606_03).

Supporting Information Available: Detailed synthetic procedures and characterization data for the monomers and polymers; ^{1}H NMR, FT-IR, and UV/PL spectra and TGA thermograms of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Safir, A. L.; Novak, B. M. *Macromolecules* **1993**, *26*, 4072. (b) Swager, T.; Dougherty, D.; Grubbs, R. *J. Am. Chem. Soc.* **1988**, *110*, 2973. (c) Edwards, J.; Feast, W.; Bott, D. *Polymer* **1984**, *22*, 395.

(2) Aoki, T.; Kaneko, T. *Polym. J.* **2005**, *37*, 717. (b) Kwak, G.; Fujiki, M.; Sakaguchi, T.; Masuda, T. *Macromolecules*, in press. (c) Yashima, E.; Maeda, K.; Nishimura, T. *Chem.*—*Eur. J.* **2004**, *10*, 43. (d) Masuda, T.; Sanda, F. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, 2003; Chapter 3.11. (e) Sedlacek, J.; Vohlidal, J. *Collect. Czech. Chem. Commun.* **2003**, *68*, 1745. (f) Schenning, A. P. H. J.; Fransen, M.; Meijer, E. W. *Macromol. Rapid Commun.* **2002**, *23*, 266. (g) Choi, S. K.; Cal, Y. S.; Jin, S. H.; Kim, H. K. *Chem. Rev.* **2000**, *100*, 1645. (h) Koltzenburg, S.; Stelzer, F.; Nuyken, O. *Macromol. Chem. Phys.* **1999**, *200*, 821. (i) D'Amato, R.; Sone, T.; Tabata, M.; Sadahiro, Y.; Russo, M. V.; Furlani, A. *Macromolecules* **1998**, *31*, 8660. (j) Akagi, K.; Piao, G.; Kaneko, S.; Sakamaki, K.; Shirakawa, H.; Kyotani, M. *Science* **1998**, *282*, 1683. (k) Ginsburg, E. J.; Gorman, C. B.; Grubbs, R. H. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: Weinheim, 1995; Chapter 10. (l) Saunders, R. S.; Cohen, R. E.; Schrock, R. R. *Acta Polym. Sci.* **1987**, *81*, 121. (m) Simionescu, C. I.; Percec, V.; Dumitrescu, S. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2497.

(3) Lam, J. W. Y.; Tang, B. Z. *Acc. Chem. Res.* **2005**, *38*, 745. (b) Lam, J. W. Y.; Tang, B. Z. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2607. (c) Cheuk, K. K. L.; Li, B. S.; Tang, B. Z. *Curr. Trends Polym. Sci.* **2002**, *7*, 41. (d) Tang, B. Z. *Polym. News* **2001**, *26*, 262.

(4) Lam, J. W. Y.; Dong, Y.; Cheuk, K. K. L.; Luo, J.; Xie, Z.; Kwok, H. S.; Mo, Z.; Tang, B. Z. *Macromolecules* **2002**, *35*, 1229.

(5) Lee, C. W.; Wong, K. S.; Lam, W. Y.; Tang, B. Z. *Chem. Phys. Lett.* **1999**, *307*, 67.

(6) Dong, Y. P.; Lam, J. W. Y.; Peng, H.; Cheuk, K. K. L.; Kwok, H. S.; Tang, B. Z. *Macromolecules* **2004**, *37*, 6408. (b) Lam, J. W. Y.; Dong, Y. P.; Cheuk, K. K. L.; Law, C. C. W.; Lai, L. M.; Tang, B. Z. *Macromolecules* **2004**, *37*, 6695. (c) Lam, J. W. Y.; Dong, Y. P.; Cheuk, K. K. L.; Tang, B. Z. *Macromolecules* **2003**, *36*, 7927. (d) Lam, J. W. Y.; Luo, J. D.; Dong, Y. P.; Cheuk, K. K. L.; Tang, B. Z. *Macromolecules* **2002**, *35*, 8288. (e) Lam, J. W. Y.; Dong, Y. P.; Cheuk, K. K. L.; Luo, J. D.; Xie, Z. L.; Kwok, H. S.; Mo, Z. S.; Tang, B. Z. *Macromolecules* **2002**, *35*, 1229. (f) Lam, J. W. Y.; Kong, X.; Dong, Y. P.; Cheuk, K. K. L.; Xu, K.; Tang, B. Z. *Macromolecules* **2000**, *33*, 5027. (g) Huang, Y. M.; Ge, W.; Lam, J. W. Y.; Tang, B. Z. *Appl. Phys. Lett.* **1999**, *75*, 4094.

(7) Huang, Y. M.; Ge, W.; Lam, J. W. Y.; Tang, B. Z. *Appl. Phys. Lett.* **2001**, *78*, 1652. (b) Huang, Y. M.; Lam, J. W. Y.; Cheuk, K. K. L.; Ge, W.; Tang, B. Z. *Macromolecules* **1999**, *32*, 5976.

(8) Hua, J. L.; Li, Z.; Lam, J. W. Y.; Xu, H. P.; Sun, J. Z.; Dong, Y. P.; Dong, Y. Q.; Qin, A. J.; Yuan, W. Z.; Chen, H. Z.; Wang, M.; Tang, B. Z. *Macromolecules* **2005**, *38*, 8127.

(9) Hua, J. L.; Lam, J. W. Y.; Dong, H.; Wu, L.; Wong, K. S.; Tang, B. Z. *Polymer*, in press.

(10) Häussler, M.; Zheng, R.; Lam, J. W. Y.; Tong, H.; Dong, H.; Tang, B. Z. *J. Phys. Chem. B* **2004**, *108*, 10645−10650. (b) Lam, J. W. Y.; Peng, H.; Häussler, M.; Zheng, R.; Tang, B. Z. *Mol. Cryst. Liq. Cryst.* **2004**, *415*, 43. (c) Häussler, M.; Dong, H. C.; Lam, J. W. Y.; Zheng, R.; Qin, A.; Tang, B. Z. *Chin. J. Polym. Sci.* **2005**, *23*, 567.

(11) Lam, J. W. Y.; Dong, Y. P.; Law, C. C. W.; Dong, Y. Q.; Cheuk, K. K. L.; Lai, L. M.; Li, Z.; Sun, J.; Chen, H.; Zheng, Q.; Kwok, H. S.; Wang, M.; Feng, X.; Shen, J.; Tang, B. Z. *Macromolecules* **2005**, *38*, 3290.

(12) Rosseto, R.; Torres, J. C.; Nero, J. D. *Mater. Res.* **2003**, *6*, 341.

(13) Gavrin, A. J.; Douglas, E. P. *Macromolecules* **2001**, *34*, 5876. (b) Barentsen, H. M.; van Dijk, M.; Kimkes, P.; Zuilhof, H.; Sudholter, E. J. R. *Macromolecules* **1999**, *32*, 1753.

(14) Badarau, C.; Wang, Z. Y. *Macromolecules* **2003**, *36*, 6959.

(15) Clendenning, S. B.; Liu, K.; Manners, I.; Aouba, S.; Ruda, H. E. *Macromolecules* **2005**, *38*, 2023. (b) Scholz, S.; Leech, P. J.; Englert, B. C.; Sommer, W.; Weck, M.; Bunz, U. H. F. *Adv. Mater.* **2005**, *17*, 1052.

MA051907Q