Polymer Bulletin 51, 263–269 (2004)
DOI 10.1007/s00289-004-0225-9

Polymer Bulletin

Chemical Modification of Novel Alkyne-Containing Polymers Obtained by Radical Polymerization of Conjugated Enynes

Bungo Ochiai,[1,3] Ikuyoshi Tomita (✉),[1] and Takeshi Endo[2,3]

[1]Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta-cho 4259, Midori-ku, Yokohama 226-8502, JAPAN
[2]Chemical Resources Laboratory, Tokyo Institute of Technology, Nagatsuta-cho 4259, Midori-ku, Yokohama 226-8503, JAPAN
[3]Present Address: Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, JAPAN
e-mail: tomita@echem.titech.ac.jp, Fax: +81-45-924-5489, Tel: +81-45-924-5413

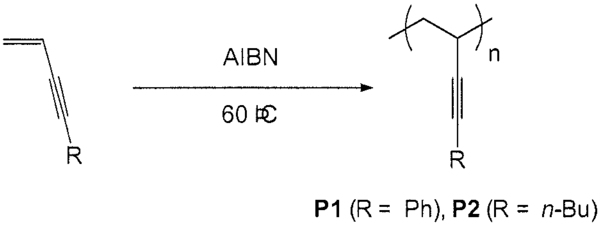
Received: 9 September 2003/Revised version: 16 December 2003/Accepted: 27 December 2003

Summary

Alkyne-containing polymers, obtained by the radical polymerization of 4-substituted conjugated enynes (CH_2=CH—C≡C—R: R— = Ph— and *n*-Bu—), were subjected to polymer reactions through their alkyne moieties. That is, the radical addition of a thiol fragment, the hydrosilylation, and reduction via the hydroalumination were carried out to give polymers bearing alkenyl sulfide, alkenylsilane, and alkene moieties, respectively.

Introduction

Previously, we reported the radical polymerization of 4-substituted 1-buten-3-ynes giving rise to polymers consisting of specific 1,2-polymerized units (i.e., units having alkyne substituents) (Scheme 1) [1–3]. The versatile reactivity of the alkyne derivatives [4-10] may permit applications of the alkyne-containing polymers not only as the thermosetting resins [11] but also as reactive precursors affording many functional materials. Nevertheless, there are only a few reports on the chemical conversions of polymers having alkyne moieties [12, 13]. We herein describe chemical modifications of two kinds of polyenynes (**P1** and **P2**), obtained by the radical polymerization of 4-phenyl-1-buten-3-yne (**1**) and 1-octen-3-yne (**2**), respectively.



Scheme 1

Experimental

Materials and instruments

Polymers (**P1** and **P2**) were prepared by the radical polymerization of **1** and **2**, respectively [1–3]. Triethylsilane was distilled under N_2. Benzene, tetrahydrofuran (THF), and toluene were dried over sodium benzophenone ketyl and distilled under N_2. Other reagents were used as received.

Nuclear magnetic resonance (NMR) spectra were measured on a JEOL EX-400 instrument using tetramethylsilane as an internal standard (400 MHz and 100 MHz for ^{1}H and ^{13}C NMR, respectively). Fourier transform infrared (FT-IR) spectra were measured on a JASCO FT/IR-5300 instrument (thin film cast from $CHCl_3$). Gel permeation chromatography (GPC) measurements were performed on tandem columns of Tosoh TSK-gel G2500HXL and G3000HXL or of G4000HXL and G5000HXL using THF as an eluent at 30 °C. Polystyrene standards were used for calibration.

*Radical addition of dodecanethiol to **P1***

A benzene (1.0 mL) solution of **P1** (131 mg, 1.0 mmol unit), dodecanethiol (202 mg, 1.0 mmol), and 2,2'-azobis(isobutyronitrole) (AIBN, 5 mg, 0.03 mmol) was heated at 60 °C for 1 day in a degassed sealed tube. The resulting solution was poured into methanol and the precipitated product was collected by filtration and dried under vacuum to give a polymer in 97% (174 mg). ^{1}H NMR ($CDCl_3$) δ 0.7–4.5 (CH_3—, —CH_2—, —CH—), 5.7–8.0 (C_6H_5—, >C=CH—) ppm; ^{13}C NMR ($CDCl_3$) δ 14.0–14.3 (CH_3—), 22.5–22.7 (CH_3CH_2—), 26.6–51.2 (—CH_2CH—), 28.3–29.6 ($CH_3CH_2(CH_2)_{10}CH_2$—), 31.7–31.9 (—CH_2S—), 79.6–83.6 (—C≡C—Ph), 88.2–96.3 (—C≡C—Ph), 121.5–132.6 (C_6H_5—), 134.8–145.0 (>C=C<) ppm; IR 3056, 3023, 2926, 2853, 2230, 1946, 1878, 1803, 1671, 1599, 1574, 1491, 1443, 1306, 1177, 1155, 1071, 1030, 910, 843 ,754, 735, 694 cm^{-1}.

*Radical addition of dodecanethiol to **P2***

Likewise, the reaction of **P2** (113 mg, 1.1 mmol unit) and the subsequent precipitation into methanol-water (v/v = 5/1) provided a polymer in 88% (214 mg). ^{1}H NMR ($CDCl_3$) δ 0.8–1.0 (CH_3—), 1.1–1.9 (—CH_2—), 2.0–2.4 (—CH—), 2.4–2.8 (—SCH_2—), 4.8–5.8 (>C=CH—) ppm; ^{13}C NMR ($CDCl_3$) δ 13.3–14.2 (CH_3—), 18.3–18.7 ($CH_3CH_2(CH_2)_2C≡C$—), 20.8–23.5 ($CH_3CH_2(CH_2)_{10}$—, $CH_3CH_2CH_2CH_2C≡C$—), 26.0–50.1 (—CH_2CH—), 27.5–32.0 ($CH_3CH_2(CH_2)_{10}CH_2$—, —$CH_2C≡C$—, —CH_2S—), 79.9–82.0 (—C≡C—Bu^n), 82.0–83.8 (—C≡C—Bu^n), 130.0-139.4 (>C=C<) ppm; IR 2926, 2855, 2733, 2673, 2234, 2033, 1734, 1620, 1464, 1377, 1300, 1262, 1233, 1157, 1103, 1026, 932, 860, 804, 723 cm^{-1}.

*Hydrosilylation of **P1***

To a toluene (1.0 mL) solution of **P1** (127 mg, 1.0 mmol unit) were added triethylsilane (216 mg, 2.0 mmol) and a THF solution of H_2PtCl_6 (0.05M, 0.02 mL, 0.001 mmol) and the mixture was heated at 100 °C for 12 h under N_2. The resulting solution was then poured into methanol and the precipitated product was collected by filtration and dried under vacuum to give a polymer in 92% (153 mg). ^{1}H NMR ($CDCl_3$) δ –0.8–4.5 (CH_3—, —CH_2—, —CH—), 5.0–5.8 (Ph—C=CH—), 6.2–8.5 (C_6H_5—) ppm; ^{13}C NMR ($CDCl_3$) δ 2.2–3.0 ($(CH_3CH_2)_3Si$—), 6.6–7.3 (CH_3CH_2Si—), 24.2–48.5 (—CH_2—, —CH—), 80.0–85.2 (—C≡C—Ph), 88.5–97.5 (—C≡C—Ph), 121.3–133.1 ($C_6\mathrm{H}_5$—), 137.6–143.2 (>C=C<) ppm; IR 3056, 3021, 2953, 2874, 2731, 2227, 1944, 1878, 1802, 1748, 1597, 1574, 1541, 1491, 1443, 1418, 1377, 1217, 1179, 1155, 1071, 1007, 964, 914, 887, 754, 694 cm^{-1}.

*Hydrosilylation of **P2***

Similar to the case of **P1**, the reaction of **P2** (121 mg, 1.1 mmol unit) and the subsequent precipitation into methanol-water (v/v = 5/1) gave a polymer in 77% (193 mg). ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.4–0.8 ($\mathrm{C}H_3(\mathrm{CH_2})_3$—, ($\mathrm{CH_3C}H_2)_3\mathrm{Si}$—), 0.8–1.0 ($\mathrm{CH_3C}H_2\mathrm{CH_2}$—), ($\mathrm{C}H_3\mathrm{CH_2})_3\mathrm{Si}$—), 1.1–1.8 ($\mathrm{CH_3CH_2C}H_2$—), 1.8-2.4 (>C=C—$\mathrm{C}H_2$—), 2.4-2.8 (—C$H$—), 5.2-5.8 (>C=C$H$—) ppm; ^{13}C NMR ($\mathrm{CDCl_3}$) δ 2.7–6.4 (($\mathrm{CH_3}C\mathrm{H_2})_3\mathrm{Si}$—), 6.7–7.9 ($C\mathrm{H_3CH_2Si}$—), 13.8–14.2 ($C\mathrm{H_3CH_2CH_2}$—), 22.3–22.9 ($\mathrm{CH_3}C\mathrm{H_2CH_2}$—), 22.9–23.5 ($\mathrm{CH_3CH_2}C\mathrm{H_2}$—), 26.7–47.3 (—$C\mathrm{H_2}C\mathrm{H}$—), 28.5–32.3 (>C=$\mathrm{C}C\mathrm{H_2}$—), 129.7–130.3, 135.8–138.0, 140.0–142.9, 142.9–149.0 (>C=C<) ppm; IR 2955, 2930, 2874, 2731, 1605, 1460, 1418, 1377, 1262, 1236, 1096, 1017, 968, 804, 720, 673 cm^{-1}.

*Reduction of **P1** via hydroalumination (at 40 °C)*

To a toluene solution (1.0 mL) of **P1** (134 mg, 1.0 mmol unit) was added a toluene solution of diisobutylaluminium hydride (DIBAL-H) (1 M, 1.5 mL, 1.5 mmol) and the mixture was heated at 40 °C for 12 h under $\mathrm{N_2}$. The resulting solution was poured into a mixture of benzene and water (40 mL each) under $\mathrm{N_2}$ and the insoluble part was removed by filtration. The organic layer was washed twice with brine, concentrated under vacuum, and poured into methanol. The precipitate was collected by filtration and dried under vacuum to give a polymer in 92% (122 mg). ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.2–4.4 (—$\mathrm{C}H_2$—, —CH—), 4.8–5.6 (>C=CH—), 5.6–8.0 ($\mathrm{C_6}H_5$—) ppm; ^{13}C NMR ($\mathrm{CDCl_3}$) δ 27.5–53.5 (—$C\mathrm{H_2}$—, —CH—), 80.2–84.5 (—C≡C—Ph), 90.0–96.3 (—C≡C—Ph), 123.5–150.6 ($C_6\mathrm{H}_5$—, >C=C<) ppm; IR 3077, 3056, 3021, 2924, 2853, 2402, 2226, 1948, 1881, 1806, 1723, 1640, 1597, 1574, 1491, 1445, 1408, 1327, 1262, 1217, 1179, 1157, 1073, 1028, 982, 914, 799, 758, 673 cm^{-1}.

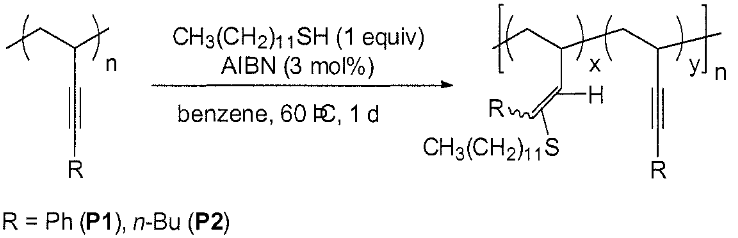
*Reduction of **P1** via hydroalumination (at 80 °C)*

The same reaction was also carried out at 80 °C for 12 h using **P1** (259 mg, 2.0 mmol unit) to give a polymer in 81% (213 mg). ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.2–4.4 (—$\mathrm{C}H_2$—, —CH—), 4.8–5.6 (>C=CH—), 5.6–8.0 ($\mathrm{C_6}H_5$—) ppm; ^{13}C NMR ($\mathrm{CDCl_3}$) δ 25.0–53.2 (—$C\mathrm{H_2}$—, —CH—), 119.1–149.0 ($C_6\mathrm{H}_5$—, >C=C<) ppm; IR 3056, 3023, 2922, 2855, 2361, 1944, 1885, 1802, 1638, 1599, 1574, 1493, 1445, 1327, 1262, 1217, 1179, 1155, 1073, 1028, 966, 914, 843, 799, 758 cm^{-1}.

Results and discussion

Radical addition of dodecanethiol to polyenynes

Additions of thiols to alkyne derivatives proceed via the radical [8] or the ionic mechanism [9] to give alkenyl sulfides and/or bis(alkylmercapto)alkanes whose further reactions can give rise to versatile sulfur-containing materials. Thus the radical addition of dodecanethiol to the polyenynes (**P1** and **P2**) was carried out to demonstrate this possibility. The reaction of the polymers with dodecanethiol (1 equiv to the C≡C moieties) was carried out at 60 °C for 1 day in a degassed sealed tube using AIBN (3 mol%) as a radical source (Scheme 2, Table 1). Consequently, polymers having alkenyl sulfide moieties were produced effectively [14]. Under the examined conditions, side reactions that involve the crosslinking did not occur judging from the molecular weight of the polymers obtained after the polymer reaction. The unit ratios (x/y) of the polymers obtained from **P1** and **P2** were determined by their ^{1}H NMR spectra. For example, the polymer obtained from **P1** exhibits broad peaks for aromatic and olefinic protons at 5.7-8.0 ppm and for aliphatic protons in the main chain and the dodecyl moieties at 0.7-4.5 ppm in the ^{1}H NMR spectrum (Figure 1). On the basis of the peak intensity ratio, the composition of the polymer was estimated to be x:y = 23:77. Likewise, the unit ratio of the polymer produced from **P2** was found be x:y = 64:36. The higher conversion of the alkyne moieties in **P2** is probably due to the less sterically demanding *n*-butyl substituent.



Scheme 2

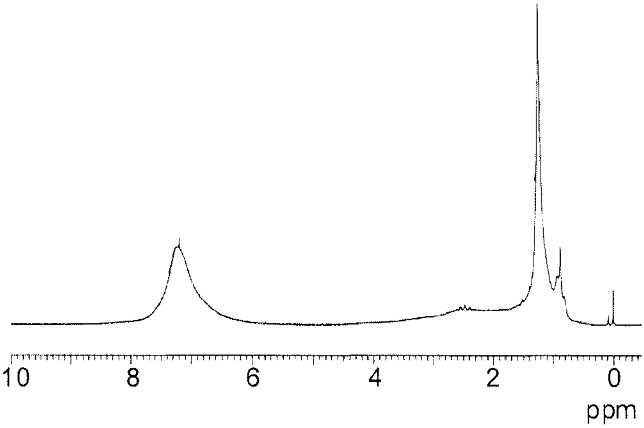


Figure 1. ^{1}H NMR spectrum of the polymer obtained by the radical addition of dodecanethiol to **P1**.

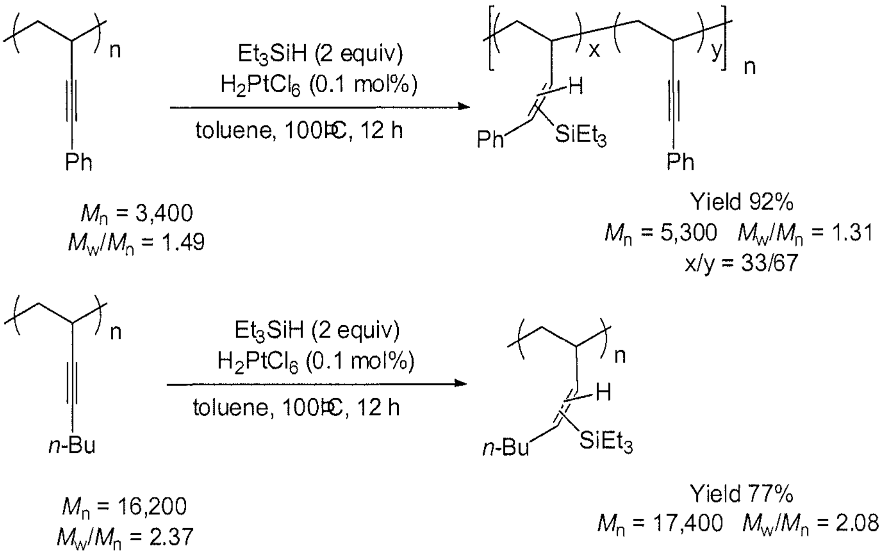
Table 1. Radical addition of dodecanethiol to polyenynes (**P1** and **P2**)[a]

Run	R (M_n, M_w/M_n)[b]	Yield (%)	M_n[b]	M_w/M_n[b]	x/y[c]
1	Ph (3500, 1.51)	98[d]	3800	1.42	23/77
2	*n*-Bu (16200, 2.37)	88[e]	17200	2.11	64/36

[a] Reaction conditions: polymer (1.0 mmol), dodecanethiol (1.0 mmol), AIBN (3 mol%), benzene (1.0 mL), at 60 °C for 1 day. [b] Estimated by GPC (polystyrene standards, THF).
[c] Determined by ^{1}H NMR. [d] Isolated yield after precipitation into methanol.
[e] Isolated yield after precipitation into methanol–water (v/v = 5/1).

Hydrosilylation of polyenynes

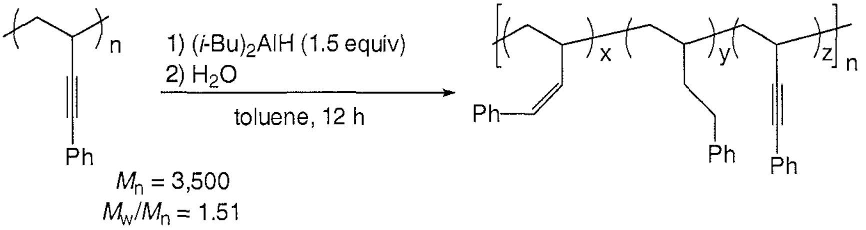
The transition metal-catalyzed hydrosilylation of alkynes proceeds under mild conditions and alkenylsilanes, which are useful synthetic precursors of various alkenes by subsequent electrophilic substitutions, are produced with high geometrical selectivity and regioselectivity [15,16]. Thus, the hydrosilylation of the polyenynes was carried out with H_2PtCl_6 catalyst. Polymers having alkenylsilane moieties were obtained by the reaction of **P1** or **P2** with triethylsilane (2 equiv) in the presence of H_2PtCl_6 (0.1 mol%) in toluene at 100 °C for 12 hours (Scheme 3). The hydrosilylation of **P2** proceeded smoothly to afford a polymer with a quantitative alkenylsilane content, while that of **P1** did not take place completely (incorporation efficiency; 33%). The lower efficiency in the case of **P1** may be due to the steric bulkiness of the substituents that is a major factor in the hydrosilylation of alkynes (i.e., the less sterically demanding *n*-butyl group is more preferable than the phenyl group). The addition of the Si-H moieties is supposed to take place in a *syn*-selective fashion as reported for the hydrosilylation of many alkyne derivatives using H_2PtCl_6 [15]. The regioselectivity between $R(Et_3Si)C{=}CH$— and $RHC{=}C(Et_3Si)$— for **P1** (R = Ph) and **P2** (R = *n*-Bu) was supposed to be approximately 10/0 and 6/4, respectively [17].



Scheme 3

Reduction of polyenynes via hydroalumination

Reduction of alkyne moieties in **P1** was also performed via the hydroalumination using DIBAL-H [18] followed by hydrolysis (Scheme 4, Table 2). For example, the reaction of **P1** and DIBAL-H (1.5 equiv to the $C\equiv C$ moieties) at 40 °C for 12 hours provided a polymer containing a phenyethenyl group by means of the reduction of the $C\equiv C$ moieties accompanied by the un-reduced phenyethynyl group (x and z units, respectively, x/z = 70/30). Under a little more forced conditions (i.e., at 80 °C), the conversion of the $C\equiv C$ moieties took place in a quantitative manner, but a polymer was found to be contaminated with a saturated phenylethyl substituted unit (y unit, x/y = 86/14) as a result of dihydroalumination process. In both cases, the polymers were found to consist of *cis*-double bond moieties as expected from the *syn*-addition of the Al—H to the $C\equiv C$ moieties. Attempts to employ **P2** for the reduction was not successful and a polymer with poor solubility was obtained probably due to crosslinking reactions such as the multiple addition of the alkenylaluminum to the alkyne moieties [19]. The analogous reaction did not occur in the case of **P1**, judging from the molecular weight of the reduced polymers.



Scheme 4

Table 2. Reduction of **P1** by hydroalumination with DIBAL-H

Run	Temperature (°C)	M_n[b]	M_w/M_n[b]	Yield (%) [c]	x/y/z[d]
1	40	2200	1.55	92	70/0/30
2	80	2600	1.62	81	86/14/0

[a] Reaction conditions: **P1** (1.0 mmol), DIBAL-H (1.5 mmol, 1.0 M in toluene), for 12 hours under N_2. [b] Estimated by GPC (polystyrene standards, THF). [c] Isolated yield after precipitation into methanol. [d] Determined by ^{1}H NMR.

Conclusions

Alkyne-containing polymers, obtained by the radical polymerization of 4-substituted conjugated enynes (CH_2=CH—C≡C—R: R— = Ph— and *n*-Bu—), were subjected to the chemical modifications of their alkyne moieties. The radical addition of a thiol fragment, the hydrosilylation, and the hydroalumination afforded the polymers bearing alkenyl sulfide, alkenylsilane, and alkene moieties in the side chain, respectively. Since the resulting polymers are not obtainable by the polymerization of the corresponding butadiene derivatives, polyenynes are also potentially useful prepolymers for the synthesis of 1,2-polybutadiene derivatives.

Acknowledgements. This research was partially supported by the Ministry of Education, Science, Sports, and Culture, Grant-in Aid for Encouragement of Young Scientists, 10750631, 1998. Financial support from Japan Society for the Promotion of Science to B.O. is gratefully acknowledged.

References

1. Ochiai B, Tomita I, Endo T (1998) Chem Lett 563
2. Ochiai B, Tomita I, Endo T (2001) Macromolecules 34: 1634
3. Ochiai B, Tomita I, Endo T (2001) Macromol Chem Phys 202: 3099
4. (a) Siegel S (1991) In: Trost BM, Fleming I (eds) Comprehensive Organic Synthesis. Pergamon, Oxford (Vol 8, pp 417) (b) Takaya H, Noyori R (1991) In: Trost BM, Fleming I (eds) Comprehensive Organic Synthesis. Pergamon, Oxford (Vol 8, pp 443)
5. Yusybov MS, Filimonov VD (1991) Synthesis 131
6. Fuks R, Viehe HG (1969) In: Viehe HG (ed) Chemistry of Acetylenes. Marcell Dekker, New York (pp 425)
7. Schuster M, Blechert S (1997) Angew Chem Int Ed Engl 36: 2037

8. Stacey FW, Harris JF (1963) Org React 13: 150
9. Dickstein JI, Miller SI (1978) In: Patai S (ed) The Chemistry of Carbon-Carbon Triple Bond. Wiley, Chichester (Part 2, pp 813)
10. Schmid GH (1978) In: Patai S (ed) The Chemistry of Carbon-Carbon Triple Bond. Wiley, Chichester (Part 1, pp 275)
11. Ochiai B, Tomita I, Endo T (2001) Polymer 42: 8581
12. D'alelio GF, Evers RC (1967) J Polym Sci Part A-1 Polym Chem 5: 999
13. Xu W, Alper H (1996) Macromolecules 29: 6695
14. Bis(alkylmercapto)alkane moieties, produced by the further addition of dodecanethiol to the resulting alkenyl sulfide moieties, were not observable in the ^{1}H NMR, ^{13}C NMR, and IR spectra.
15. Hiyama T, Kusumoto T (1991) In: Trost BM, Fleming I (eds) Comprehensive Organic Synthesis. Pergamon, Oxford (Vol. 8, pp 763)
16. Lewis LN, Sy KG, Donahue PE (1992) J Organomet Chem 427: 165
17 These ratios might involve some errors because they were determined by the rather broad peaks observed in their ^{1}H NMR spectra.
18. Hudrlik PF, Hudrlik AM (1978) In: The Chemistry of Carbon-Carbon Triple Bond. Wiley, Chichester (Part 1, pp 199)
19. The alkenylaluminium intermediates produced by the hydroalumination of sterically less hindered alkynes are often susceptible to the further addition toward the alkynes leading to the oligomerization of the alkyne moieties. See ref (20).
20. Eisch JJ, Kaska WC (1966) J Am Chem Soc 88: 2213