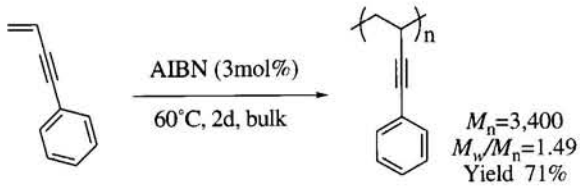
Selective Radical Vinyl Polymerization of 4-Phenyl-1-buten-3-yne: Synthesis of a Novel Acetylene-Containing Polymer

Bungo Ochiai, Ikuyoshi Tomita,† and Takeshi Endo*
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama 226-8503
†Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama 226-8502

(Received February 24, 1998; CL-980135)

The radical polymerization of 4-phenyl-1-buten-3-yne (**1**) was carried out to obtain a polymer having acetylene moieties in the side chain. The polymer prepared at 60 °C was consisted of specific 1,2-polymerized unit. The *Q-e* value of **1** was estimated from the copolymerization with methyl methacrylate to demonstrate a fully delocalized character of the propagating radical.

The polymerizations of monomers with higher degree of unsaturation such as allenes,[1] butadienes,[2] and acetylenes[3] are known to give polymers having unsaturated bonds, which have been applied as reactive or functional polymers. Substituted enynes are also attractive candidates to provide unsaturated polymers containing acetylene, diene, and allene moieties by 1,2-, 3,4-, and 1,4-polymerizations, respectively. Although a few examples of the polymerizations of some substituted enynes have been reported,[4,5] most of which do not give sufficient information on the polymerization behavior and the polymer structure except for the anionic polymerization of 1-buten-3-yne and 2-methyl-1-buten-3-yne by an excess amount of *n*-butyllithium.[6] The radical polymerization of some enyne derivatives has been reported,[7] in which, however, polymers were not obtained sufficiently or were not fully characterized. Herein, we wish to report the selective radical 1,2-polymerization of an aromatic enyne to provide a novel acetylene-containing polymer (Scheme 1).



Scheme 1.

The radical polymerization of 4-phenyl-1-buten-3-yne (**1**)[8] was carried out at 60 °C in bulk for 2 days using 3 mol% of α-α'-azobisisobutyronitrile (AIBN) as an initiator to give an orange-colored glassy polymer (M_n=3,400, M_w/M_n=1.49) in 71% yield.[9] The polymer obtained is soluble in common organic solvents such as chloroform, ethyl acetate, and benzene, but insoluble in alcohols and hexane. From the structural elucidation by ^{1}H-NMR, ^{13}C-NMR, and IR spectra, the polymer was found to be consisted of a specific 1,2-polymerized unit (i.e., the unit having acetylene moiety in the side chain). The polymerization of **1** was also carried out at higher temperatures (80 and 120 °C) only to result in the contamination of the structural units.[10]

Thermal properties of the polymer were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). From the TGA of the polymer, the decomposition temperature (T_d) and the 10% weight loss temperature (T_{d10}) were observed at 376 °C and 383 °C, respectively (under N_2, scan rate: 10 °C/min). The DSC analysis of the polymer shows the glass transition temperature (T_g) at 157 °C and an exothermic peak at ca. 200 °C, which were not detected in the second scan. Since the polymer became insoluble and the peak at 2226 cm^{-1} in the IR spectrum decreased extremely after the measurement, this peak is attributable to the thermal crosslinking reaction of triple bond moieties in the side chain.[11]

The radical copolymerization of **1** with methyl methacrylate (MMA) was carried out to obtain a corresponding copolymer.[12] Accordingly, the monomer reactivity ratios were estimated from the copolymerization system with MMA at the initial stage (i.e., conversion<5%). The estimated monomer reactivity ratios are r_1=3.46, r_2=0.12, and r_1r_2=0.43, indicating that **1** is more reactive than MMA towards the radical growing species (Figure 1.). The *Q-e* value was also estimated from the monomer reactivity ratios to be Q=4.13 and e=-0.52. Compared with other conjugated vinyl monomers (e.g., styrene: Q=1.00, e=-0.80, butadiene: Q=2.39, e=-1.05,[13] and 1-phenyl-1,3-butadiene: Q=1.49, e=-0.79[14]), **1** has a higher Q value which may suggest that the radical polymerization of **1** proceeds through a fully conjugated and stabilized propagating radical.

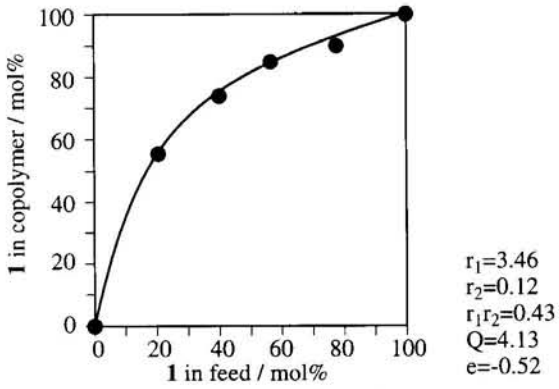


Figure 1. Composition curve of copolymer vs. monomer.

Since the polymer described in this paper has triple bond moieties in the side chain, it may be applied as a reactive polymer revealing new reactivities. The polymer reactions are now in progress.

References and Notes

1 a) I. Tomita, Y. Kondo, K. Takagi, and T. Endo, *Macromolecules*, **27**, 4413 (1994). b) I. Tomita, Y. Kondo, K. Takagi, and T. Endo, *Acta Polymer.*, **46**, 432 (1995). c) K. Takagi, I. Tomita, and T. Endo, *Macromolecules*, **30**, 7386 (1997). d) T. Endo, K. Takagi, and I. Tomita, *Tetrahedron*, **53**, 15187 (1997).

2 J. Porri, and A. Giarrusso, in "Comprehensive Polymer Science", ed by G. Eastmond, A. Ledwith, S. Russo, and P. Sigwalt, Pergamon, Oxford (1989), Vol. 4., p. 53.

3 G. Costa, in "Comprehensive Polymer Science", ed by G. Eastmond, A. Ledwith, S. Russo, and P. Sigwalt, Pergamon, Oxford (1989), Vol. 4, p. 155.

4 E. I. Brodskaya, Yu. G. Krayazhev, Yu. L. Frolov, I. D. Kalikhman, and T. I. Yushmanova, *Vysokomol. Soyed.*, **A11**, 655 (1969).

5 S. G. Grigoryan, A. M. Arzumanyan, A. M. Gromov, G. V. Martirosyan, and A. A. Matnishyan, *Vysokomol. Soyed.*, **27**, 1681 (1985).

6 a) A. Mavinkurve, S. Visser, W. Broek, and A. J. Pennings, *J. Polym. Sci., Part A: Polym. Chem.*, **34**, 985 (1996). b) W. Xu and H. Alper, *Macromolecules*, **29**, 6695 (1996).

7 a) T. I. Vakul'skaya and Yu. G. Krayazhev, *Vysokomol. Soyed.*, **A15**, 1783 (1973). b) A. C. Davis and R. F. Hunter, *J. Appl. Chem.*, **9**, 137 (1959). c) A. Pineda, R. Salcedo, F. Rio, and T. Ogawa, *Eur. Polym. J.*, **29**, 497 (1993).

8 The monomer (**1**) was prepared by the reported procedure. See: K. Sonogashira, Y. Tohda, and N. Hagiwara, *Tetrahedron Lett.*, **50**, 4467 (1975).

9 The experimental procedure is shown as follows: a mixture of **1** (2.49 g, 19.5 mmol) and AIBN (0.098 g, 0.60 mmol) was heated at 60 °C for 2 days in a degassed sealed tube. After the reaction, the resulting glassy solid was dissolved in THF and the solution was poured into hexane to precipitate the polymer. The hexane-insoluble product was collected by filtration and dried under vacuum (Yield 1.76 g, 71%). ^{1}H-NMR (90 MHz, in $CDCl_3$, δ, ppm) 0.7-4.6 (-CH_2-CH-, 3H), 6.0-8.0 (C_6H_5-, 5H); ^{13}C-NMR (400 MHz, in $CDCl_3$, δ, ppm) 28.8, 39-41, 82.7, 82.9, 91.8, 123.3, 128.0, 131.6; IR (KBr disk) 3079, 3054, 3023, 2922, 2855, 2226, 1948, 1879, 1804, 1752, 1665, 1597, 1572, 1489, 1443, 1329, 1177, 1157, 1071, 1028, 912, 843, 754, 700 cm^{-1}

10 In the ^{13}C-NMR spectra of the polymers obtained at 120 °C and 80 °C, small peak at ca. 140 ppm attributed to tetra-substituted double bond moieties which was not present in that of the polymer prepared at 60 °C was observed. Since there was no signal attributed to allene moieties (i.e., 1,4-polymerized unit) at 200-210 ppm in the ^{13}C-NMR spectrum or at 1950 cm^{-1} in the IR spectrum, it may be taken to mean that the polymer produced at higher polymerization temperature was contaminated with other structural units not originated from 1,2-, 3,4-, or 1,4- polymerization. However, the contaminated structure could not be determined yet.

11 The thermal polymerization of aromatic acetylenes and the thermal curing of resins containing the phenylacetylene units have been reported to proceed with the formation of aromatic rings. Thus, the present crosslinking may also proceed by the aromatization of the acetylene moieties. For the thermal polymerization of aromatic acetylenes, see: S. Gandon, P. Mison, M. Bartholin, R. Mercier, B. Sillion, E. Geneve, E. Grenier, and M. -F. Grenier-Loustalot, *Polymer*, **38**, 1439 (1997), and S. Gandon, P. Mison, and B. Sillion, *Polymer*, **38**, 1449 (1997). For the thermal curing of resins containing the phenylacetylene units, see: F. L. Hedberg and F. E. Arnold, *J. Polym. Sci.: Polym. Chem. Ed.*, **14**, 2607 (1976).

12 The experimental procedure is shown as follows: a benzene solution (1 ml) of **1** (0.19 g, 1.5 mmol), MMA (0.14 g, 1.4 mmol) and AIBN (0.015 g, 0.09 mmol) was heated at 60 °C for 2 days in a degassed sealed tube. After the reaction, the solution was poured into methanol-water (2:1) to precipitate the polymer. The methanol-water-insoluble product was collected by filtration and dried under vacuum (Yield 0.091 g, 28%, M_n=1,000, M_w/M_n=1.30). The molar ratio of each monomer in the copolymer was determined by ^{1}H-NMR spectrum (**1**:MMA=74:26). ^{1}H-NMR (90 MHz, in $CDCl_3$, δ, ppm) 0.2~4.6 (-CH_2-CH-, -CH_2-C(CH_3)-, CH_3O-), 6.0~8.4 (C_6H_5-); ^{13}C-NMR (400 MHz, in $CDCl_3$, δ, ppm) 22~35, 27.8, 30.3, 35~50, 51.8, 80~86, 91~95, 123.7, 126.8, 128.1, 131.5, 175~180; IR (KBr disk) 3056, 3023, 2926, 2855, 2369, 2346, 2232, 1946, 1890, 1802, 1730, 1599, 1491, 1443, 1375, 1120, 1121, 1071, 1028, 914, 845, 756, 693, 529 cm^{-1}

13 L. J. Young, *J. Polym. Sci.*, **54**, 411 (1961).

14 D. H. Lewis, R. C. Kneisel, and B. W. Ponder, *Macromolecules*, **6**, 660 (1973).