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The Living Polymerization of Conjugated Enyne Derivative: Anionic Polymerization of 4-Phenyl-1-buten-3-yne

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Selective polymerization of highly unsaturated monomers is of importance to construct polymers having unsaturated bonds which are potentially applicable to reactive or functional polymers. In this point of view, we have reported the living polymerization of allene derivatives using π-allylnickel catalysts, giving polymers containing double bonds quantitatively.[1] Conjugated 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 the radical,[2] cationic,[3] and anionic[4] polymerizations of some 4-substituted or 2,4-disubstituted enynes have been reported to proceed through 1,2-polymerization, most of which gave an insufficient information on the polymer structure and the polymerization behavior. Namely, polymers having well-defined structures and molecular weights have not been obtained yet from any conjugated enynes.[5] From our recent study on the radical polymerization of 4-phenyl-1-buten-3-yne (**1**),[6] **1** was found to undertake the specific 1,2-polymerization.[7] Owing to a highly resonance-stabilizing phenylethynyl group, **1** reveals a high *Q* value ($Q = 4.13$), and its *e* value ($e = -0.52$) indicates that the vinyl moiety is slightly electron-deficient in comparison with those of styrene and butadiene. Accordingly, it might be of interest to examine the anionic polymerizability of **1**. We herein describe the first well-characterized example of the living anionic polymerization of **1** by using a *n*-butyllithium/(−)-spartein (*n*-BuLi/Sp) initiating system.

The anionic polymerization of **1** (20 equiv relative to *n*-BuLi) was carried out by using *n*-BuLi to give a polymer consisting mainly of the 1,2-polymerized unit in 98% yield. The molecular weight distribution (M_w/M_n) of the polymer was not narrow enough ($M_w/M_n = 1.91$) and the number average molecular weight (M_n) was not in accordance with the feed ratio of [**1**]/[*n*-BuLi] ($M_n = 10\,600$). In sharp contrast, we could obtain a remarkable improvement by using Sp as an additive (Scheme 1).[8] For instance, the anionic polymerization of **1** (20 equiv relative to *n*-BuLi) using *n*-BuLi/Sp catalyst system ([Sp]/[*n*-BuLi] = 2) gave a polymer in 98% yield,[9] whose M_w/M_n was narrow enough (1.07) and M_n (2700) was in quite good agreement with the feed ratio of [**1**]/[*n*-BuLi]. The polymer is soluble in common organic solvents such as THF, chloroform, ethyl acetate, and benzene but insoluble in hexane and alcohols.

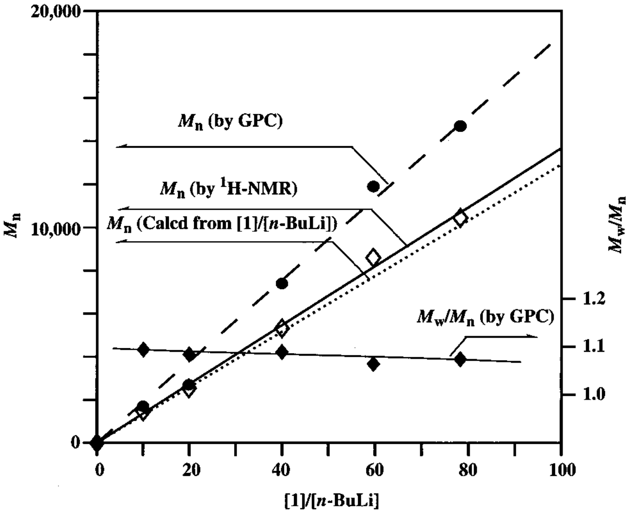
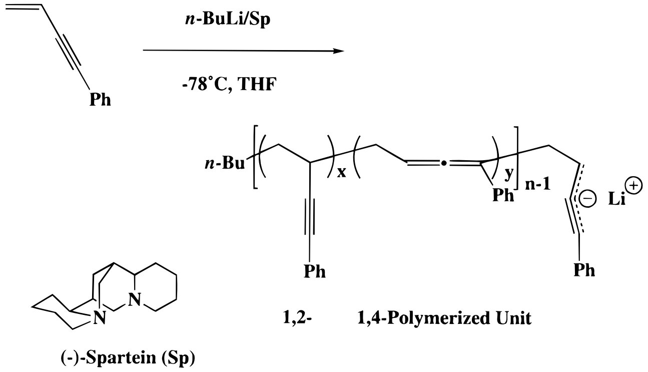


Figure 1. M_n and M_w/M_n vs [**1**]/[*n*-BuLi].

Scheme 1



The anionic polymerization of **1** by the *n*-BuLi/Sp catalyst system was carried out in various [**1**]/[*n*-BuLi] ratios. Regardless of [**1**]/[*n*-BuLi] ratio, we could obtain the polymers in quantitative yields with narrow molecular weight distributions revealing single modal elution peaks in GPC. It is of notice that the molecular weight of the polymers had a linear relationship with [**1**]/[*n*-BuLi] (Figure 1). Although the number average molecular weights of these polymers estimated by GPC (THF as an eluent, calibrated against the standard polystyrene samples) were a little higher than those expected from the feed ratio (i.e., (formula weight (FW) of **1**) × [**1**]/[*n*-BuLi] + (FW of end groups (*n*-Bu and H)) by ca. 1.3 times, those determined by ^{1}H NMR (based on the integral ratio of the phenyl protons in the repeating unit to the methyl protons of the initiating end) were in good agreement with the expected ones. Accordingly, it was supported that the present system proceeds in a living mechanism and that the initiation efficiency is quantitative.

The structural elucidation of the polymer by ^{1}H and ^{13}C NMR spectra confirms that the polymer obtained by the living anionic polymerization consists of both 1,2- and 1,4-polymerization units (Figure 2). Although major peaks in both ^{1}H and ^{13}C NMR spectra are attributable to the 1,2-polymerized unit by comparing with those of the 1,2-specific polymer obtained by the radical polymerization, the peaks at 5.8 and 6.1 ppm in ^{1}H NMR

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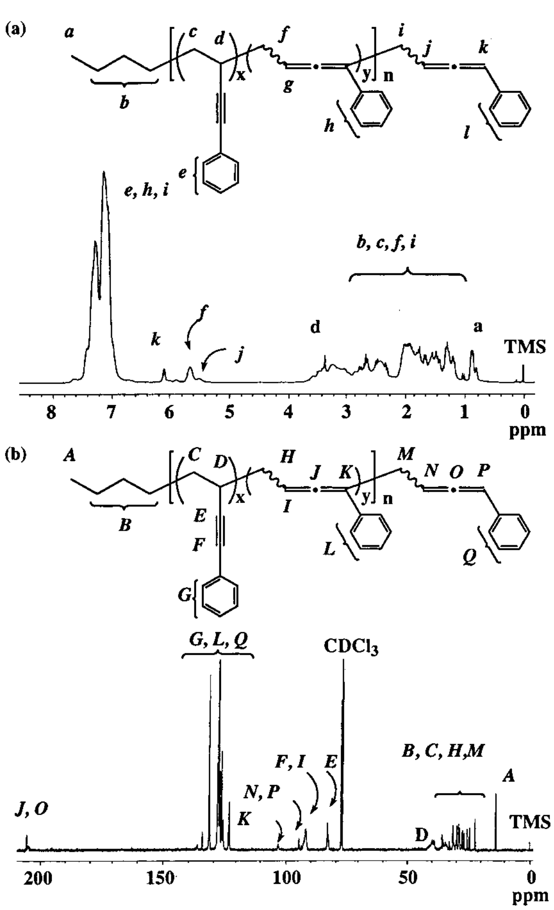
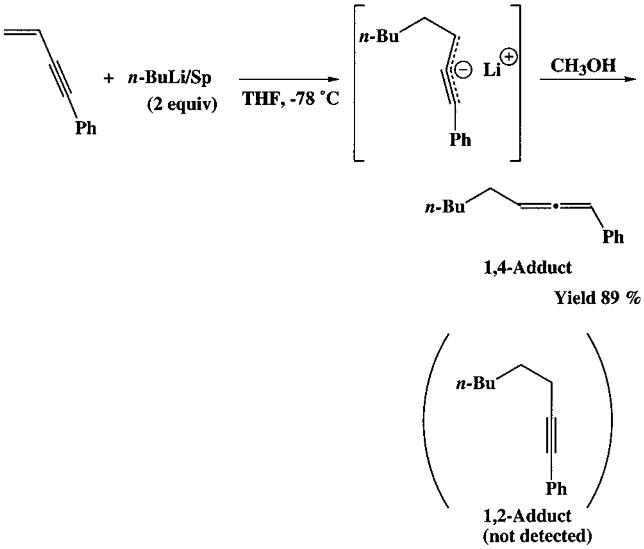


Figure 2. ^{1}H (a) and ^{13}C NMR (b) spectra of poly(**1**) (prepared under the condition of [**1**]/[*n*-BuLi] = 10).

Scheme 2



spectrum and 94, 103, and 205 ppm in the ^{13}C NMR spectrum are unattributable to the 1,2-unit. These peaks are characteristic to the allenic structures (i.e., Ph-C=C=C and PhCH=C=C) originated from 1,4-polymerization.

The ratio of 1,2- and 1,4-units was estimated to be 9:1 on the basis of the integral ratio of the phenyl protons to the allenic protons (5.3−6.0 ppm) in the ^{1}H NMR spectrum. The peak at 6.1 ppm in the ^{1}H NMR spectrum is attributable to the terminal Ph-CH=C=C moieties produced by quenching with methanol, whose intensity decreased as the increase of the molecular weight (i.e., the [**1**]/[*n*-BuLi] ratio). The specific 1,4-termination could be confirmed by the model experiment. That is, an excess *n*-BuLi/Sp was reacted with **1** to generate an anion of a 1:1 adduct which was quenched by the addition of methanol.[10] As a result, we could isolate the 1,4-adduct, 1-phenyl-1,2-octadiene, as a single product in 89% yield, while the 1,2-adduct, 1-phenyl-1-octyne, could not be detected (Scheme 2).

In summary, the first well-characterized example of the living polymerization of an enyne derivative was attained by the anionic polymerization using *n*-BuLi/Sp catalyst system. Further studies on the polymerization and the application of the resulting polymers are in progress.

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(5) In ref 4b, the polymer obtained by the anionic polymerization of trimethylsilylvinylacetylene is reported to be “living”, capable of initiating the recharged monomer to give a polymer with higher viscosity. However, the direct observation for the living character of the polymerization process has not been supported sufficiently.

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

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(9) A typical example of the anionic polymerization is shown as follows: A THF solution of Sp (1.0 M, 0.20 mL, 0.20 mmol) was placed in a flask containing a magnetic stirrer bar under N_2. After the evaporation of THF under vacuum, a hexane solution of *n*-BuLi (1.6 M, 0.63 mL, 0.10 mmol) was added at room temperature and stirred for 30 min. THF (1.0 mL) was introduced after the flask was cooled to −78 °C. After 30 min, **1** (0.25 g, 2.0 mmol) was added slowly and stirred for 30 min at that temperature. The reaction was terminated by the addition of a small portion of methanol. A pale yellow colored polymer was isolated by filtration following by precipitation with methanol (yield 98%, M_n = 2700, M_w/M_n = 1.07). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.8−1.0 (CH_3−), 1.9−2.9 (−CH_2−), 2.9−3.7 (−CH−), 5.3−6.0 (Ph-C=C=CH−), 6.0−6.1 (Ph−CH=C=C), 6.8−7.8 (C_6H_5−). ^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 14.1 (CH_3−), 22.4−39.2 (−CH_2−), 40.0−42.5 (−CH−), 82.3−82.9 (Ph-C≡*C*−), 91.9−92.8 (Ph−*C*≡C−, Ph−C=C=*C*H− (repeating unit)) 94.5−94.8 (Ph−*C*H=C=C−, Ph−CH=C=*C*− (termi-

nating end)), 103.3 ($\mathrm{Ph}-C=\mathrm{C}=\mathrm{C}$ (repeating unit)), 123.5−136.4 ($C_6\mathrm{H}_5-$), 204.9−207.2 ($=C=$). IR (neat) 3081, 3057, 3032, 2922, 2855, 2361, 2336, 2228, 1950, 1881, 1806, 1723, 1672, 1597, 1572, 1491, 1443, 1348, 1314, 1277, 1217, 1177, 1157, 1101, 1071, 1026, 1001, 912, 876, 842, 756, 691 cm^{-1}.

(10) The experimental procedure is shown as follows: A THF solution of Sp (1.0 M, 4.0 mL, 4.0 mmol) was placed in a flask containing a magnetic stirrer bar under N_2. After the evaporation of THF under vacuum, a hexane solution of *n*-BuLi (1.6 M, 1.3 mL, 2.0 mmol) was added at room temperature and stirred for 30 min. THF (5.0 mL) was introduced after the flask was cooled to −78 °C. After 30 min, **1** (0.13 g, 1.0 mmol) was added slowly. Immediately after the complete addition, methanol was added slowly until the yellow color of the solution became colorless. After the evaporation of the solvents, the product was isolated by aluminum oxide column chromatography (hexane as an eluent) giving pure 1-phenyl-1,2-octadiene (yield 89%, 0.17 g, 0.89 mmol). ^{1}H NMR (400 MHz, CDCl_3, δ, ppm): 0.88 (t, $J = 6.8$ Hz, 3H, $\mathrm{C}H_3$-), 1.2−1.4 (m, 4H, $\mathrm{CH_3}$-$(\mathrm{C}H_2)_2$-), 2.11 (m, 2H, $-\mathrm{C}H_2-\mathrm{C}=\mathrm{C}$), 5.55 (dd, $J = 6.8$, 13 Hz, 1H, $\mathrm{Ph}-\mathrm{C}=\mathrm{C}=\mathrm{C}H$), 6.11 (dd, $J = 6.8$, 13 Hz, 1H, $\mathrm{Ph}-\mathrm{C}H=\mathrm{C}=\mathrm{C}$), 7.1−7.3 (m, 5H, C_6H_5-). ^{13}C NMR (400 MHz, CDCl_3, δ, ppm): 14.1 ($C\mathrm{H}_3-$), 22.4 ($\mathrm{CH}_3-C\mathrm{H}_2-$), 28.7, 28.8 ($\mathrm{CH}_3-\mathrm{CH}_2-C\mathrm{H}_2-C\mathrm{H}_2-$), 31.4 ($-C\mathrm{H}_2-\mathrm{C}=\mathrm{C}=\mathrm{C}$), 94.5 ($\mathrm{Ph}-\mathrm{C}=\mathrm{C}=C-$), 95.1 ($\mathrm{Ph}-C=\mathrm{C}=\mathrm{C}$), 126.5, 128.5, 135.2 ($C_6\mathrm{H}_5-$), 205.1 ($\mathrm{C}=C=\mathrm{C}$). IR (neat) 3063, 3032, 2957, 2928, 2857, 1948, 1599, 1495, 1460, 1379, 1262, 1196, 1103, 1071, 1028, 910, 876, 775, 691, 627 cm^{-1}.

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