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Articles

Radical Copolymerization of 2,4-Disubstituted Enynes with Electron-Accepting Comonomers

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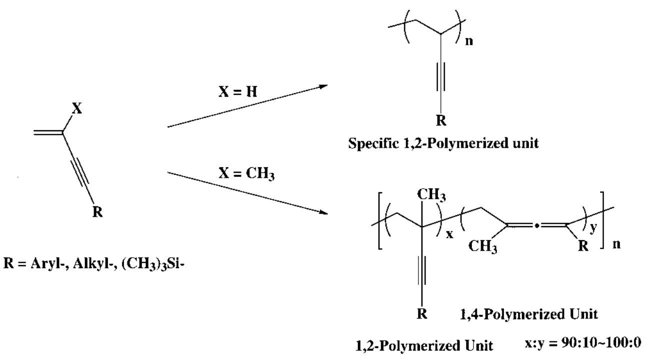
ABSTRACT: The radical copolymerization of 2,4-disubstituted enynes ($CH_2{=}C(CH_3){-}C{\equiv}C{-}R$: R = Ph (**1a**), *n*-Bu (**1b**), *t*-Bu (**1c**), and $(CH_3)_3Si$ (**1d**)) with various electron-accepting comonomers is described. The copolymerization gave corresponding copolymers whose yields were dependent upon the electronic character of the comonomers. The enyne components in the copolymers from **1a** and **1d** consisted of the specific 1,2-polymerized units, while those from **1b** and **1c** consisted of both the 1,2- and the 1,4-polymerized units. The copolymerization of **1b** (R = *n*-Bu) showed a significant change in the ratio of the 1,2- and the 1,4-polymerized units by the electronic character of the comonomers. Namely, the copolymers with a higher content of the 1,4-polymerized units were obtained by the copolymerization with comonomers having higher electron-accepting ability.

Introduction

Polymers having unsaturated systems are applicable as reactive and functional polymers. Many efforts have been made to develop and explore the polymerization systems that provide the polymers with unsaturated structures. In this point of view, we have reported the controlled polymerizations of highly unsaturated monomers. For example, the living coordination polymerization of a variety of allenes was achieved by π-allylnickel catalysts.[1−5] The resulting polymers contained either one part of double-bond moieties quantitatively.

Conjugated enynes are also attractive candidates to give polymers with unsaturated structure.[4−11] Recently, we reported the radical polymerization of 4-monosubstituted 1-buten-3-ynes ($CH_2{=}CH{-}C{\equiv}C{-}R$: R = aryl, *n*-Bu, *t*-Bu, and $(CH_3)_3Si$) to give polymers consisting of the specific 1,2-polymerized units (i.e., the units containing acetylene moieties in the side chain).[4−6] In contrast, the radical polymerization of 2,4-disubstituted 1-buten-3-ynes ($CH_2{=}C(CH_3){-}C{\equiv}C{-}R$: R = *n*-Bu and *t*-Bu) yielded polymers possessing both the 1,2- and the 1,4-polymerized units (i.e., the units containing allene moieties in the main chain) where the unit ratios are 90:10 and 95:5, respectively (Scheme 1).[6]

Scheme 1



The control of microstructure (i.e., the selectivity in the 1,2- and 1,4-polymerizations) is an important subject to construct the well-defined polymerization system for enynes. So far, the 1,2-specific polymerization[4,5,8−11] and that accompanied by a slight amount of the 1,4-polymerization[6,7] have been reported, while few successful examples have been reported to obtain polymers having higher content of the 1,4-polymerized units.

In the radical polymerization of 1,3-butadiene, a typical electron-donating monomer, the microstructure (i.e., the content of the 1,2- and 1,4-polymerized units) changes in the copolymerization with electron-accepting comonomers.[12] Since enynes can be regarded as electron-donating monomers judging from their *e* values,[4−6] the microstructure of the enyne unit in the polymer would also be controlled by the radical copolymerization with electron-accepting comonomers. Introduction of the methyl substituent at the 2-position to enynes might also facilitate the 1,4-polymerization. Accordingly, 2,4-disubstituted enynes were employed, and their radical copolymerization behavior with electron-accepting comonomers was studied in detail to explore the possibility to obtain polymers having a higher content of the 1,4-polymerized units.

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Experimental Section

Materials. 2-Methyl-4-phenyl-1-buten-3-yne (**1a**)[13] and 2-methyl-4-trimethylsilyl-1-buten-3-yne (**1d**)[14] were prepared according to the literature methods and distilled under vacuum after drying over $\mathrm{CaH_2}$. 2-Methyl-1-octen-3-yne (**1b**) and 2,5,5-trimethyl-1-hexen-3-yne (**1c**) were prepared as reported.[6] Benzene was dried over sodium benzophenone ketyl and distilled under $\mathrm{N_2}$. Methyl methacrylate (MMA), methyl acrylate (MA), and acrylonitrile (AN) were dried over $\mathrm{CaH_2}$ and distilled under vacuum. Maleic anhydride (Manh), *N*-phenylmaleimide (PM), and *N*-ethylmaleimide (EM) were recrystallized from benzene. Other reagents were used as received.

Measurements. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were measured on a JEOL EX-400 instrument using tetramethylsilane as an internal standard (400 and 100 MHz for ^{1}H and ^{13}C NMR, respectively). The copolymer composition was determined within ±3% errors by the ^{13}C NMR spectra measured under conditions without the nuclear Overhauser effect (NOE). Fourier transform infrared (FT-IR) spectra were measured on a JASCO FT/IR-5300 instrument. UV−vis spectra were measured by a Shimadzu UV-3100PC instrument. Gel permeation chromatography (GPC) measurements were performed on a Tosoh TSK-gel G2500HXL and G3000HXL or G4000HXL and G5000HXL tandem columns using tetrahydrofuran (THF) as an eluent at 30 °C. Polystyrene standards were used for calibration.

Radical Copolymerization of Enynes 1a−1d with Electron-Accepting Comonomers. A typical copolymerization procedure is shown as follows: a benzene solution (1 mL) of **1a** (286 mg, 2.0 mmol), Manh (195 mg, 2.0 mmol), and 2,2′-azobis(isobutyronitrile) (AIBN, 20 mg, 0.12 mmol) was heated at 60 °C for 2 days in a degassed sealed tube. After the reaction, the solution was poured into hexane to precipitate the polymer. The precipitated product was collected by filtration and dried under vacuum (yield 162 mg, 32%). The molar ratio of each monomer in the copolymer was determined by its ^{1}H NMR spectrum (**1a**:Manh = 50:50). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.5−4.3 $\mathrm{(C\mathit{H}_3-, -C\mathit{H}_2-, -C\mathit{H}-)}$, 6.8−8.3 ppm $\mathrm{(-C_6\mathit{H}_5)}$. ^{13}C NMR ($\mathrm{CDCl_3}$): δ 17.3−61.2 $\mathrm{(-\mathit{C}H_2-\mathit{C}(\mathit{C}H_3)-, -\mathit{C}H-)}$, 86.0−91.5 $\mathrm{(-\mathit{C}\equiv\mathit{C}-)}$, 119.3−123.9, 123.9−130.0, 130.0−132.8, 132.8−140.6 $\mathrm{(-\mathit{C}_6H_5)}$, 167.6−170.5 ppm $\mathrm{(-\mathit{C}=O)}$. IR (thin film): 3059, 2978, 2930, 2600, 2234, 1858, 1780, 1713, 1634, 1599, 1491, 1445, 1383, 1265, 1217, 1073, 1024, 932, 860, 758, 737, 694 $\mathrm{cm^{-1}}$.

Copolymer of 1b and Manh. Yield 86% (copolymer composition **1b**:Manh = 50:50). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.7−1.0 $\mathrm{(C\mathit{H}_3-CH_2-)}$, 1.1−1.6 $\mathrm{(CH_3-(C\mathit{H}_2)_2-, -C\mathit{H}_2-C(CH_3)-)}$, 1.6−1.9 $\mathrm{(-CH_2-C(C\mathit{H}_3)-)}$, 2.0−2.3 $\mathrm{(CH_3-(CH_2)_2-C\mathit{H}_2-)}$, 2.3−4.0 ppm $\mathrm{(-C\mathit{H}-)}$. ^{13}C NMR ($\mathrm{CDCl_3}$): δ 13.4−14.0 $\mathrm{(\mathit{C}H_3-)}$, 17.9−18.2 $\mathrm{(CH_3-\mathit{C}H_2-)}$, 21.8−22.2 $\mathrm{(CH_3CH_2-\mathit{C}H_2-)}$, 22.2−45.2 $\mathrm{(\mathit{C}H_2-(\mathit{C}H_3)C=C=C, -\mathit{C}H_2-C(\mathit{C}H_3)-)}$, 29.8−31.5 $\mathrm{(-\mathit{C}H_2-C\equiv C-)}$, 37.8−45.2 $\mathrm{(-\mathit{C}H-)}$, 45.2−58.5 $\mathrm{(-CH_2-\mathit{C}(CH_3)-)}$, 79.0−79.9 $\mathrm{(-\mathit{C}\equiv C-Bu^{\mathit{n}})}$, 73.8−80.0 $\mathrm{(-C\equiv\mathit{C}-Bu^{\mathit{n}})}$, 97.6−103.9 $\mathrm{(\mathit{C}=C=\mathit{C})}$, 169.3−173.3 $\mathrm{(-\mathit{C}=O)}$, 196.2−202.0 ppm $\mathrm{(C=\mathit{C}=C)}$. IR (thin film): 2971, 2934, 2870, 2241, 1861, 1784, 1478, 1458, 1364, 1263, 1225, 1090, 990, 943, 806, 735 $\mathrm{cm^{-1}}$.

Copolymer of 1c and Manh. Yield 91% (copolymer composition **1c**:Manh = 55:45). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.0−1.3 $\mathrm{((C\mathit{H}_3)_3C-)}$, 1.3−2.8 $\mathrm{(-C\mathit{H}_2-C(C\mathit{H}_3)-)}$, 3.0−4.0 ppm $\mathrm{(-C\mathit{H}-)}$. ^{13}C NMR ($\mathrm{CDCl_3}$): δ 20.9−43.5 $\mathrm{(\mathit{C}H_2-(\mathit{C}H_3)C=C=C, -\mathit{C}H_2-C(\mathit{C}H_3)-)}$, 27.3−27.6 $\mathrm{((CH_3)_3\mathit{C}-)}$, 29.4−30.6 $\mathrm{((\mathit{C}H_3)_3C-)}$, 36.5−42.9 $\mathrm{(-\mathit{C}H-)}$, 43.5−60.1 $\mathrm{(-CH_2-\mathit{C}(CH_3)-)}$, 94.0−97.4 $\mathrm{(-\mathit{C}\equiv\mathit{C}-)}$, 103.4−104.9 $\mathrm{(\mathit{C}=C=\mathit{C})}$, 170.0−173.5 $\mathrm{(-\mathit{C}=O)}$, 198.3−201.0 ppm $\mathrm{(C=\mathit{C}=C)}$. IR (thin film): 2971, 2870, 2228, 1860, 1782, 1476, 1458, 1391, 1366, 1341, 1260, 1221, 1074, 932, 799, 758, 669 $\mathrm{cm^{-1}}$.

Copolymer of 1d and Manh. Yield 81% (copolymer composition **1d**:Manh = 65:35). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.0−0.4 $\mathrm{((C\mathit{H}_3)_3Si-)}$, 1.3−2.8 $\mathrm{(-C\mathit{H}_2-C(C\mathit{H}_3)-)}$, 3.0−3.8 ppm $\mathrm{(-C\mathit{H}-)}$. ^{13}C NMR ($\mathrm{CDCl_3}$): δ −0.5−0.9 $\mathrm{((\mathit{C}H_3)_3Si-)}$, 21.9−43.2 $\mathrm{(-\mathit{C}H_2-C(\mathit{C}H_3)-)}$, 36.9−43.2 $\mathrm{(-\mathit{C}H-)}$, 43.2−59.8 $\mathrm{(-CH_2-\mathit{C}(CH_3)-)}$, 88.5−99.7 $\mathrm{(-\mathit{C}\equiv C-Si)}$, 104.0−113.5 $\mathrm{(-C\equiv\mathit{C}-Si)}$, 169.5−173.8 ppm $\mathrm{(-\mathit{C}=O)}$. IR (thin film): 2961, 2907, 2164, 1941, 1860, 1782, 1508, 1447, 1375, 1252, 1074, 1011, 934, 843, 712, 700, 667, 629 $\mathrm{cm^{-1}}$.

Copolymer of 1b and MMA. Yield 26% (copolymer composition **1b**:MMA = 60:40). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.7−1.0 $\mathrm{(C\mathit{H}_3-CH_2-)}$, 1.0−2.3 $\mathrm{(CH_3-(C\mathit{H}_2)_2-, -C\mathit{H}_2-C(C\mathit{H}_3)-, -C\mathit{H}_2-CH-)}$, 2.0−2.3 $\mathrm{(CH_3-(CH_2)_2-C\mathit{H}_2-)}$, 3.5−3.7 ppm $\mathrm{(-OC\mathit{H}_3)}$. ^{13}C NMR ($\mathrm{CDCl_3}$): δ 13.4−14.1 $\mathrm{(\mathit{C}H_3-)}$, 18.5−18.7 $\mathrm{(CH_3-\mathit{C}H_3-)}$, 22.0−22.5 $\mathrm{(CH_3CH_2-\mathit{C}H_2-)}$, 25.4−37.1 $\mathrm{(\mathit{C}H_2-(\mathit{C}H_3)C=C=C, -\mathit{C}H_2-C(\mathit{C}H_3)-)}$, 29.8−30.6 $\mathrm{(-\mathit{C}H_2-C\equiv C-)}$, 37.0−53.7 $\mathrm{(-CH_2-\mathit{C}(CH_3)-)}$, 51.1−51.5 $\mathrm{(-O\mathit{C}H_3)}$, 82.0−86.2 $\mathrm{(-\mathit{C}\equiv\mathit{C}-Bu^{\mathit{n}})}$, 174.0−178.9 $\mathrm{(-\mathit{C}=O)}$, 200.1−202.0 ppm $\mathrm{(C=\mathit{C}=C)}$. IR (thin film): 2957, 2872, 2735, 2255, 1962, 1738, 1435, 1377, 1329, 1262, 1194, 1161, 1036, 982, 914, 860, 827, 735, 648 $\mathrm{cm^{-1}}$.

Copolymer of 1b and MA. Yield 21% (copolymer composition **1b**:MA = 60:40). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.7−1.0 $\mathrm{(C\mathit{H}_3-CH_2-)}$, 1.0−2.3 $\mathrm{(CH_3-(C\mathit{H}_2)_2-, -C\mathit{H}_2-C(C\mathit{H}_3)-, -C\mathit{H}_2-CH-)}$, 2.0−2.3 $\mathrm{(CH_3-(CH_2)_2-C\mathit{H}_2-)}$, 3.5−3.7 ppm $\mathrm{(-OC\mathit{H}_3)}$. ^{13}C NMR ($\mathrm{CDCl_3}$): δ 13.4−14.1 $\mathrm{(\mathit{C}H_3-)}$, 18.5−18.7 $\mathrm{(CH_3-\mathit{C}H_3-)}$, 22.0−22.5 $\mathrm{(CH_3CH_2-\mathit{C}H_2-)}$, 25.4−42.1 $\mathrm{(-\mathit{C}H_2-(\mathit{C}H_3)C=C=C, -\mathit{C}H_2-C(\mathit{C}H_3)-, -\mathit{C}H_2-\mathit{C}H-)}$, 29.8−30.7 $\mathrm{(-\mathit{C}H_2-C\equiv C-)}$, 42.1−57.6 $\mathrm{(-CH_2-\mathit{C}(CH_3)-)}$, 51.1−51.5 $\mathrm{(-O\mathit{C}H_3)}$, 82.0−86.2 $\mathrm{(-\mathit{C}\equiv\mathit{C}-Bu^{\mathit{n}})}$, 175.0−177.7 $\mathrm{(-\mathit{C}=O)}$, 196.0−202.0 ppm $\mathrm{(C=\mathit{C}=C)}$. IR (thin film): 2957, 2872, 2735, 2255, 1962, 1738, 1435, 1377, 1329, 1262, 1194, 1161, 1036, 982, 914, 860, 827, 735, 648 $\mathrm{cm^{-1}}$.

Copolymer of 1b and AN. Yield 18% (copolymer composition **1b**:AN = 70:30). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.7−1.0 $\mathrm{(C\mathit{H}_3-CH_2-CH_2-)}$, 1.0−2.3 $\mathrm{(CH_3-(C\mathit{H}_2)_3-, -C\mathit{H}_2-C(C\mathit{H}_3)-)}$, 2.3−3.5 ppm $\mathrm{(-C\mathit{H}_2-C\mathit{H}-)}$. ^{13}C NMR ($\mathrm{CDCl_3}$): δ 12.5−12.7 $\mathrm{(\mathit{C}H_3-(CH_2)_2-)}$, 17.7−19.6 $\mathrm{(CH_3-\mathit{C}H_2-)}$, 20.5−25.0 $\mathrm{(CH_3-CH_2-\mathit{C}H_2-)}$, 25.0−30.5 $\mathrm{(-\mathit{C}H_2-C=C=C, -\mathit{C}H_2-C(\mathit{C}H_3)-, -\mathit{C}H_2-CH-)}$, 32.0−34.9 $\mathrm{(-\mathit{C}H_2-C\equiv C-)}$, 44.1−47.9 $\mathrm{(-\mathit{C}H-)}$, 40.8−52.5 $\mathrm{(-CH_2-\mathit{C}(CH_3)-)}$, 80.1−81.9 $\mathrm{(-\mathit{C}\equiv C-Bu^{\mathit{n}})}$, 82.0−85.9 $\mathrm{(-C\equiv\mathit{C}-Bu^{\mathit{n}})}$, 97.1−100.3 $\mathrm{(\mathit{C}=C=\mathit{C})}$, 120.0−126.7 $\mathrm{(-\mathit{C}N)}$, 197.5−201.4 ppm $\mathrm{(C=\mathit{C}=C)}$. IR (thin film): 2959, 2932, 2872, 2238, 2018, 1958, 1730, 1624, 1462, 1379, 1329, 1262, 1233, 1159, 1101, 1028, 862, 804, 754 $\mathrm{cm^{-1}}$.

Copolymer of 1b and PM. Yield 95% (copolymer composition **1b**:PM = 50:50). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.7−1.0 $\mathrm{(C\mathit{H}_3-CH_2-CH_2-)}$, 1.0−3.5 $\mathrm{(CH_3-(C\mathit{H}_2)_2-, -C\mathit{H}_2-C(CH_3)-, -CH_2-C(C\mathit{H}_3)-, CH_3-(CH_2)_2-C\mathit{H}_2-)}$, 3.5−4.0 $\mathrm{(-C\mathit{H}-)}$, 6.8−7.6 ppm $\mathrm{(C_6\mathit{H}_5-)}$. ^{13}C NMR ($\mathrm{CDCl_3}$): δ 13.0−13.9 $\mathrm{(\mathit{C}H_3-(CH_2)_2-)}$, 17.9−20.0 $\mathrm{(CH_3-\mathit{C}H_2-)}$, 21.5−22.4 $\mathrm{(CH_3-CH_2-\mathit{C}H_2-)}$, 22.6−35.9 $\mathrm{(-\mathit{C}H_2-(\mathit{C}H_3)C=C=C, -\mathit{C}H_2-C(\mathit{C}H_3)-}$, 30.3−30.6 $\mathrm{(-\mathit{C}H_2-C\equiv C-)}$, 35.9−44.8 $\mathrm{(-\mathit{C}H-)}$, 45.2−58.9 $\mathrm{(-CH_2-\mathit{C}(CH_3)-)}$, 80.0−82.9 $\mathrm{(-\mathit{C}\equiv C-Bu^{\mathit{n}})}$, 85.3−86.9 $\mathrm{(-C\equiv\mathit{C}-Bu^{\mathit{n}})}$, 99.2−104.1 $\mathrm{(\mathit{C}=C=\mathit{C})}$, 126.0−132.1 $\mathrm{(\mathit{C}_6H_5-)}$, 174.0−179.3 $\mathrm{(-\mathit{C}=O)}$, 196.6−203.4 ppm $\mathrm{(C=\mathit{C}=C)}$. IR (thin film): 2957, 2930, 2872, 2340, 1777, 1713, 1599, 1501, 1458, 1318, 1188, 910, 754, 691, 667 $\mathrm{cm^{-1}}$.

Copolymer of 1b and EM. Yield 98% (copolymer composition **1b**:EM = 50:50). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.7−1.0 $\mathrm{(C\mathit{H}_3-CH_2-CH_2-)}$, 1.0−1.9 $\mathrm{(C\mathit{H}_3-CH_2-N, CH_3-(C\mathit{H}_2)_2-, -C\mathit{H}_2-C(CH_3)-, -CH_2-C(C\mathit{H}_3)-)}$, 1.9−2.2 $\mathrm{(CH_3-(CH_2)_2-C\mathit{H}_2-)}$, 2.2−3.5 $\mathrm{(-C\mathit{H}-)}$, 3.5−3.8 ppm $\mathrm{(CH_3-C\mathit{H}_2-N)}$. ^{13}C NMR ($\mathrm{CDCl_3}$): δ 12.5−12.7 $\mathrm{(\mathit{C}H_3-(CH_2)_2-)}$, 13.3−13.6 $\mathrm{(\mathit{C}H_3-CH_2-N)}$, 17.9−20.0 $\mathrm{(CH_3-\mathit{C}H_2-)}$, 20.5−25.0 $\mathrm{(CH_3-CH_2-\mathit{C}H_2-)}$, 25.0−35.0 $\mathrm{(-\mathit{C}H_2-(\mathit{C}H_3)C=C=C, -\mathit{C}H_2-C(\mathit{C}H_3)-)}$, 30.0−31.5 $\mathrm{(-\mathit{C}H_2-C\equiv C-)}$, 31.6−34.8 $\mathrm{(CH_3-\mathit{C}H_2-N)}$, 35.0−45.4 $\mathrm{(-\mathit{C}H-)}$, 45.4−58.9 $\mathrm{(-CH_2-\mathit{C}(CH_3)-)}$, 77.4−82.5 $\mathrm{(-\mathit{C}\equiv C-Bu^{\mathit{n}})}$, 83.3−86.6 $\mathrm{(-C\equiv\mathit{C}-Bu^{\mathit{n}})}$, 96.7−106.0 $\mathrm{(\mathit{C}=C=\mathit{C})}$, 173.0−180.1 $\mathrm{(-\mathit{C}=O)}$, 194.6−203.4 ppm $\mathrm{(C=\mathit{C}=C)}$. IR (thin film): 2959, 2936, 2874, 2236, 1771, 1699, 1443, 1404, 1377, 1350, 1229, 1134, 1032, 941, 862, 801, 737, 704 $\mathrm{cm^{-1}}$.

Results and Discussion

Radical Copolymerization of 2,4-Disubstituted Enynes with Maleic Anhydride. The radical copolymerization of 2,4-disubstituted enynes (**1a−1d**) with Manh was carried out to elucidate the effect of the substituent at the 4-position on the copolymerization behavior (Scheme 2, Table 1). Under the conditions of

Scheme 2

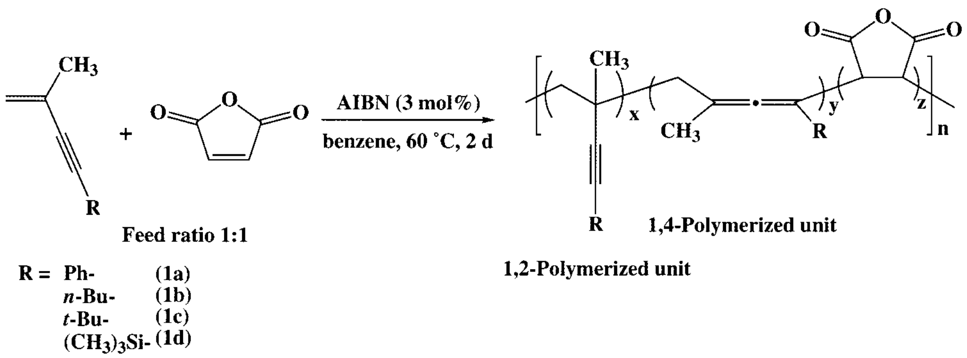


Table 1. Radical Copolymerization of 2,4-Disubstituted Enynes with Maleic Anhydride[a]

run	R	yield (%)	M_n[b]	M_w/M_n[b]	$(x + y):z$[c]	$x:y$[c]
1	Ph	32[d]	2100	1.72	50:50	100:0
2	*n*-Bu	86[e]	10500	1.43	50:50	55:45
3	*t*-Bu	91[e]	10700	1.39	55:45	90:10
4	$(CH_3)_3Si$	81[e]	8000	1.35	65:35	100:0

[a] Copolymerization was carried out in benzene at 60 °C for 2 days using 3 mol % of AIBN. [b] Estimated by GPC (THF, polystyrene standard). [c] Determined by ^{13}C NMR (measured under conditions without NOE). [d] Isolated yield after precipitation with hexane. [e] Isolated yield after precipitation with MeOH/water (v/v = 5/1).

1:Manh = 1:1 molar ratio, the corresponding copolymers were obtained in remarkably high yields compared to the cases of their homopolymerizations.[6,15] The better yields of the copolymers are supposed to originate from the interaction of the propagating radicals with the comonomers (vide infra). The copolymer composition ($(x + y):z$ in Scheme 2) is nearly 1:1, except for the cases of the enynes with bulkier substituents at the 4-position (**1c** and **1d**) which tend to give copolymers with enyne-rich compositions.

As we described previously,[6] the radical polymerization of some 2,4-disubstituted enynes proceeds mainly through the 1,2-polymerization accompanied by less than 10% of the 1,4-polymerization, while that of 4-monosubstituted enynes proceeds through the specific 1,2-polymerization. The difference in the selectivity seems to originate from the steric hindrance of the methyl substituent at the 2-position that restrains the 1,2-polymerization. In these cases, the substituents at the 4-position slightly affect the unit ratio. For example, the 1,4-unit contents in poly(**1b**) and poly(**1c**) are 10% and 5%, respectively, while poly(**1a**) and poly(**1d**) consist of the specific 1,2-polymerized units. In the present copolymerization, the microstructure of the enyne components in the copolymer of **1a** and that of **1d** consist of the specific 1,2-polymerized unit similar to the cases of the corresponding homopolymers (runs 1 and 4). In contrast, the copolymer of **1b** and that of **1c** have both the 1,2- and 1,4-polymerized enyne units which could be determined by their ^{1}H NMR, ^{13}C NMR, and IR spectra (runs 2 and 3). The ^{13}C NMR spectrum (measured under the conditions without NOE) of the copolymer from **1b** and Manh (Figure 1a) indicated that the content of the 1,4-polymerized unit in the copolymer is remarkably higher than that of the homopolymer (poly(**1b**)) (Figure 1b). That is, the peaks attributable to the allene moieties in the 1,4-polymerized unit were observed in both spectra at 95−105 ppm ($C{=}C{=}C$) and at 195−205 ppm ($C{=}C{=}C$) whose relative intensities with respect to the acetylenic peaks are obviously higher in the case of the copolymer than that of poly(**1b**). The unit ratio was estimated to be 55:45 and 90:10 for the copolymer and poly(**1b**), respectively, by comparing the integral ratio of the peaks attributable to the acetylene and the allene moieties. To the best of our knowledge, this copolymer has the highest content of the 1,4-polymerized unit obtained from enynes. In the case of **1c**, the 1,4-content also increased slightly by the copolymerization with Manh.

These results can taken to mean that the steric bulkiness of the substituent at the 4-position of enynes plays an important role in determining the 1,4-content in the copolymers. That is, the substituent at the 4-position may affect the interaction between enyne monomers and Manh or that between the propagating radicals and the comonomer, although the former interaction cannot be observed from the ^{1}H NMR, ^{13}C NMR, and UV−vis spectra of the mixture of the enynes and Manh.[16] On assuming the latter possibility, the higher 1,4-content in the copolymer of **1b** and Manh might be caused by the interaction of the electron-accepting Manh with the propagating radical of the enynes having electron-rich triple-bond moieties where **1b** having sterically less hindered *n*-butyl group can interact easily with Manh at the triple-bond moieties to give 1,4-polymerized unit ((a) in Scheme 3). However, **1c** has a sterically hindered *tert*-butyl group at the 4-position that prevents the corresponding interaction ((b) in Scheme 3).

Radical Copolymerization of 2-Methyl-1-octen-3-yne (1b) with Various Electron-Accepting Comono-

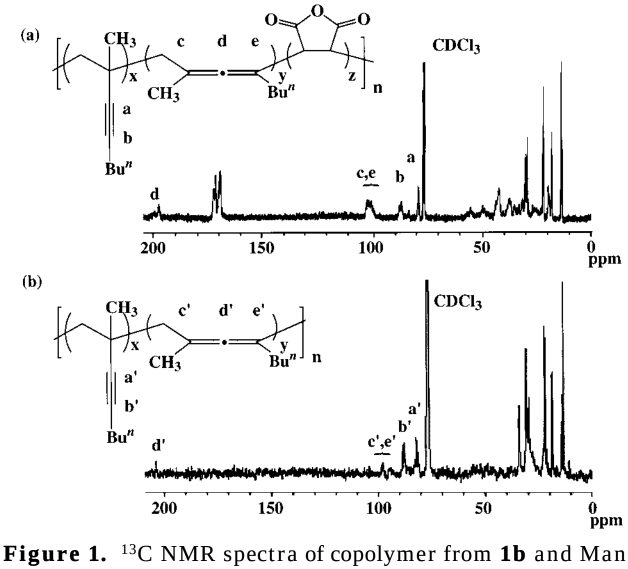
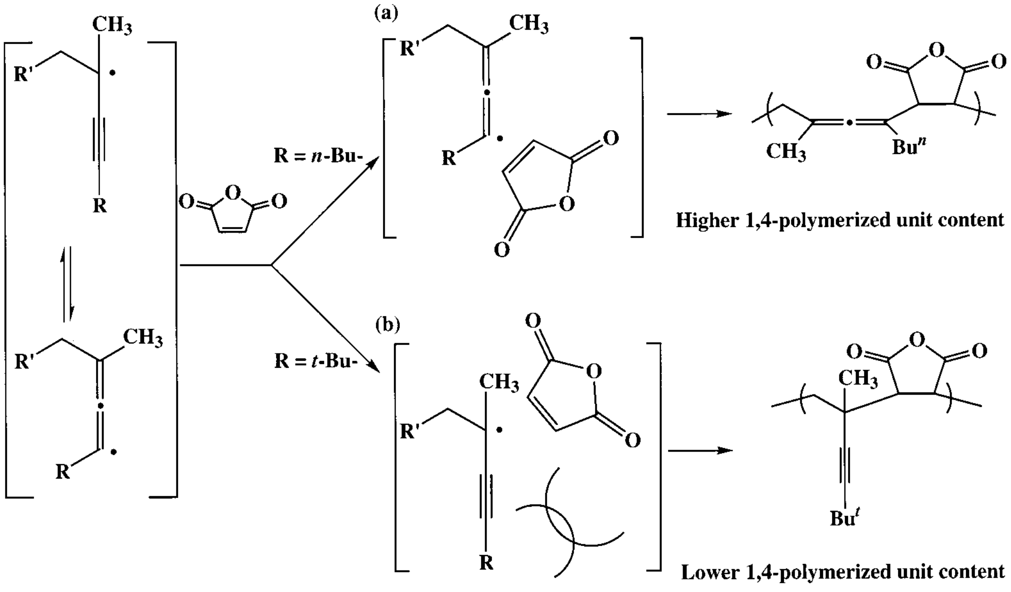


Figure 1. ^{13}C NMR spectra of copolymer from **1b** and Manh (a) and poly(**1b**) (b).

Scheme 3



Scheme 4

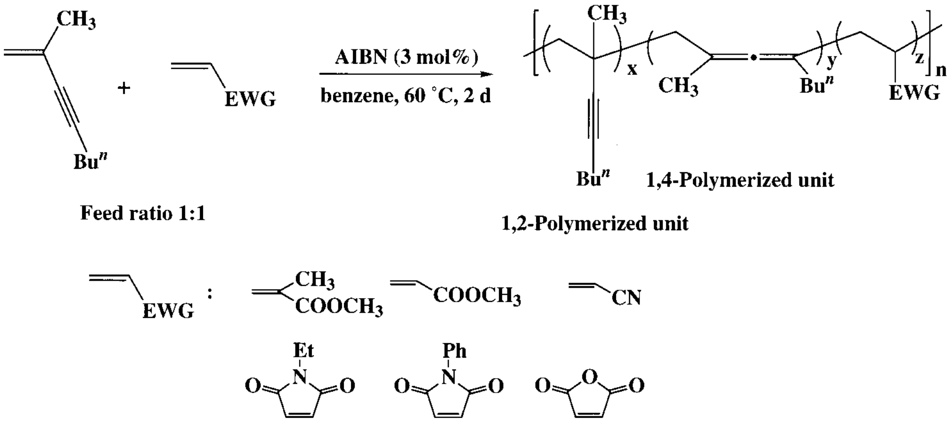


Table 2. Radical Copolymerization of 2-Methyl-1-octen-3-yne with Various Electron-Accepting Comonomers[a]

run	comonomer	e value	yield (%)[b]	M_n[c]	M_w/M_n[c]	$(x + y):z$[c]	$x:y$[c]
1	MMA	0.40	26	2200	1.46	60:40	70:30
2	MA	0.64	21	2700	1.36	60:40	70:30
3	AN	1.23	18	1900	1.71	70:30	80:20
4	EM	1.69[e]	98	9900	1.30	50:50	65:35
5	PM	3.24	95	13100	1.37	50:50	65:35
6	Manh	3.68	86	10500	1.43	50:50	55:45

[a] Copolymerization was carried out in benzene at 60 °C for 2 days using 3 mol % of AIBN. [b] Isolated yield after precipitation with MeOH/water (v/v = 5/1). [c] Estimated by GPC (THF, polystyrene standard). [d] Determined by ^{13}C NMR (measured under conditions without NOE). [e] Since we could not find the e value of EM, that of N-n-butylmaleimide is shown instead.

mers. The radical copolymerization of **1b** was carried out with various electron-accepting comonomers to evaluate the effect of the electronic character on the copolymerization (Scheme 4, Table 2). As a result, the yield, the composition, and the microstructure of the copolymer proved to be dependent upon the character of the comonomers. That is, the comonomers with higher electron-accepting ability (i.e., EM, PM, and Manh) gave the copolymers in higher yield. The lower yield of the copolymers from comonomers with lower electron-accepting ability (i.e., MMA, MA, and AN) might be due to the insufficient ability to make up for the low polymerizability of **1b**. Besides, the resulting copolymers possessed enyne-rich compositions in which the polymerization of **1b** occurred predominantly by decreasing the electron-accepting ability of the comonomers. In contrast, those from the comonomers with higher electron-accepting ability had almost 1:1 composition, suggesting the alternating character of the copolymerization. The alternating nature of the copolymerization of **1b** (M_1) with PM (M_2) was evaluated from the composition of the copolymers obtained at the initial stage (i.e., conversion < 10%) under the varied feed ratio. As is clear from Figure 2, the copolymer composition is constantly 1:1 regardless of the feed ratio. A very small r_1r_2 (3.4×10^{-4}) obtained from the monomer reactivity ratio ($r_1 = 0.032$ and $r_2 = 0.011$) further supports the alternating nature of the copolymerization.

The microstructure of the enyne components (i.e., the content of the 1,2- and 1,4-polymerized units) in the copolymers seemed to be correlated with the e value of comonomers. That is, the copolymers from the comonomers with higher electron-accepting ability have a higher content of the 1,4-polymerized unit indicating that the interaction of the radicals of the enynes with the comonomers induces the 1,4-polymerization, as we proposed in the copolymerization of **1b** and Manh (vide supra).

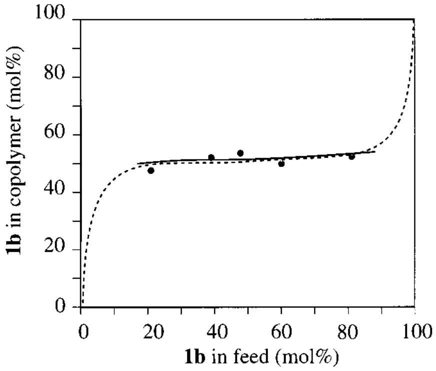


Figure 2. Relationship between feed ratio ([**1b**]:([**1b**] + [PM]) and copolymer composition at the initial stage (polymerization conditions; in benzene at 60 °C using 1 mol % of AIBN). Best-fitted curve is indicated with dotted line.

Conclusions

The radical copolymerization of 2,4-disubstituted enynes ($CH_2{=}C(CH_3){-}C{\equiv}C{-}R$. R = Ph, *n*-Bu, *t*-Bu, $(CH_3)_3Si$) with various electron-accepting comonomers gave corresponding copolymers where the yield, the composition, and the content of 1,4-polymerized unit in the enyne components are dependent upon the character of both the enynes and the comonomers. Especially, the comonomers having higher electron-accepting ability gave the copolymers in higher yield. The enyne contents in the copolymers ranged from 50% to 70%, which decreased by the increase of the electron-accepting character of the comonomers. The copolymerization of the enyne bearing sterically less hindered substituent (**1b**, R = *n*-Bu) showed a significant change in the ratio of the 1,2- to 1,4-polymerized unit by the character of the comonomers, where the content of the 1,4-polymerized unit increased as the electron-accepting ability of comonomers increased. The copolymer obtained from **1b** and maleic anhydride has the highest 1,4-polymerized unit content (45%) among the examined combination of the monomers.

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(15) The lower yield of the copolymer from **1a** might originate from the highly resonance stabilized character of the propagating radical from **1a** as was the case of the homopolymerization. See ref 6.
(16) The chemical shifts of the peaks observed for the mixture of **1b** and Manh in its ^1H and ^{13}C NMR spectra were almost identical to those of the individual solutions (the differences were within ±0.018 ppm). Likewise, the UV−vis spectra of the mixture of **1b** and Manh, **1b**, and Manh revealed no change in their λ_{max}.

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