Investigation on Radical Polymerization Behavior of 4-Substituted Aromatic Enynes. Experimental, ESR, and Computational Studies[1]

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ABSTRACT: The radical polymerization of 4-substituted aromatic enynes was carried out to obtain polymers containing acetylene moieties in the side chain. The polymers prepared at 60 °C consisted of 1,2-polymerized units (i.e., units having pendent acetylene moieties) regardless of the character of the substituents. The Q and e values of enyne monomers were estimated from copolymerization with methyl methacrylate. The large Q values ($Q = 4.1-5.5$) indicate that the propagating radicals are highly stabilized by the arylethynyl groups which is supported by both the ESR experiments and molecular orbital calculations. The e values ($e = -0.1$ to -0.6) were in good agreement with the Hammett σ_p values of the substituents on the benzene rings.

Introduction

Polymers with unsaturated functional groups are applicable as reactive polymers which can be functionalized by polymer reactions. Polymerization of monomers with higher degrees of unsaturation is an attractive method to produce polymers bearing unsaturated moieties. These polymerizations, however, often include problems such as instability of monomers and side reactions giving unregulated polymer structures. To construct well-defined polymers bearing unsaturated moieties, many efforts have been made in the polymerizations of dienes,[2,3] acetylenes,[4] cyclic olefins,[5] heterocumulenes,[6] and so on. In this aspect, we have developed the selective polymerization of monomers with higher degrees of unsaturation to give polymers containing unsaturated bonds. For example, allenes bearing various functional groups were subjected to coordination polymerization by π-allylnickel catalysts to give polymers containing either one part of the double bonds quantitatively. Because the polymerization proceeds in a living fashion, the resulting polymers with narrowly dispersed molecular weight distributions are applicable as novel reactive polymers.[2]

Conjugated enynes, consisting of higher unsaturated systems, are also attractive candidates to provide polymers containing unsaturated bonds. Although several attempts to polymerize enyne derivatives have been reported, they are generally not informative enough in terms of the polymerization behavior and the polymer structure.[7] Recently, several controlled polymerizations of enyne derivatives have been gradually developed, including the anionic polymerization of lithium acetylides of 1-buten-3-yne[8] and 2-methyl-1-buten-3-yne,[9] which gives polymers having terminal acetylene moieties in the side chain. The resulting polymers are potentially applicable as precursors for carbon fiber[8] and reactive polymers yielding polymers bearing α,β-unsaturated carboxylic acid, ester, and ketone moieties.[9] Despite these remarkable aspects of the polymers, the reported polymerization system requires an excess (i.e., more than the stoichiometric amount) of butyllithium to generate lithium acetylides as a monomer. Recently, we communicated the living anionic polymerization of 4-phenyl-1-buten-3-yne (**1**) providing a polymer with well-defined structure.[10] Alternatively, the radical polymerization of monomer **1** at 60 °C using 2,2′-azobis(isobutyronitrile) (AIBN) as initiator provides a polymer having acetylene moieties in the side chain by means of selective 1,2-polymerization.[1] On the basis of the reactivity of the acetylene moieties, the resulting polymer is potentially applicable as a reactive polymer (e.g., thermally cross-linkable resin).[11]

To understand the scope of this polymerization system and to explore the details of the polymerization behavior, we wish to describe, in detail, the radical polymerization of 4-aromatic substituted enynes. High resonance stabilization of arylethynyl groups (i.e., the resonance-stabilized character of the arylpropargyl radicals) was evaluated by both electron spin resonance (ESR) experiments and molecular orbital (MO) calculations.

Experimental Section

Measurements. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were measured on a JEOL EX-400 instrument using tetramethylsilane as internal standard. Fourier transform infrared (FT-IR) spectra (thin films cast from chloroform solution for polymers and neat for monomers) were measured on a JASCO FT/IR-5300 instrument. ESR spectra were measured on a JEOL JES-RE3X instrument. The equipment parameters applied in the measurements were field modulation of 100 kHz, microwave frequency of 9.20 GHz, and microwave power of 0.4 mW. The concentrations of radicals were obtained by double integration of real spectra and calibrated using a standard solution of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) in **1**. The polymerization for the ESR study was carried out at 60 °C using a 0.25 M solution of AIBN in **1** under N_2, and the conversion of **1** was determined by gas chromatographic (GC) analyses on a Shimadzu GC-14B in-

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strument equipped with a FID detector using *n*-tetradecane as internal standard. Gel permeation chromatography (GPC) measurements were performed on a Tosoh HLC-8020 (TSK-gel G2500HXL and G3000HXL tandem columns) with a UV−visible detector (254 nm; Tosoh UV-8011) using tetrahydrofuran (THF) as an eluent at 30 °C at a flow rate of 1.0 mL/min. Polystyrene standards were used for calibration.

Materials. 4-Methoxyphenylacetylene,[13] 4-chlorophenylacetylene,[13] 4-trifluoromethylphenylacetylene,[13] and **1**[14] were prepared as reported. Benzene was distilled under N_2 from sodium benzophenone ketyl. Methyl methacrylate (MMA), *p*-trifluoromethylstyrene, and **1** was dried over CaH_2 and distilled under vacuum. TEMPO was sublimed under reduced pressure. Other solvents and materials were used as received, unless otherwise noted.

Synthesis of Monomers (2−5). The monomers were prepared by the palladium-catalyzed coupling reaction of corresponding acetylenes and vinyl bromide as reported for the synthesis of **1**.[14] All the monomers were dried over CaH_2 and purified by distillation under vacuum.

4-(4-Methoxyphenyl)-1-buten-3-yne (2). Yield: 98% (bp$_{0.4}$ = 60 °C). ^{1}H NMR ($CDCl_3$): δ 3.80 (s, 3H, CH_3O-), 5.50 (dd, 1H, J = 2.0, 11.3 Hz, Z-$CH_2=$), 5.69 (dd, 1H, J = 2.1, 17.6 Hz, E-$CH_2=$), 6.03 (dd, 1H, J = 11.3, 17.6 Hz, $=CH-C\equiv$), 6.84 (d, 2H, J = 8.5 Hz, $-C_6H_4-$), 7.38 (d, 2H, J = 8.5 Hz, $-C_6H_4-$) ppm. ^{13}C NMR ($CDCl_3$): δ 55.2 ($-OCH_3$), 86.8 ($=CH-C\equiv$), 90.0 ($=CH-C\equiv C-$), 117.3 ($H_2C=$), 113.9, 115.2, 133.0, 160.0 ($-C_6H_4-$), 126.0 ($H_2C=CH-$) ppm. IR (neat): 3100, 3044, 3007, 2959, 2936, 2837, 2542, 2214 ($C\equiv C$), 2184, 2045, 1844, 1750, 1717, 1699, 1684, 1647, 1601, 1562, 1541, 1510, 1464, 1443, 1416, 1292, 1173, 1107, 1080, 1032, 972, 918, 841, 785 cm^{-1}.

4-(4-Methylphenyl)-1-buten-3-yne (3). Yield: 73% (bp$_{0.5}$ = 82 °C). ^{1}H NMR ($CDCl_3$): δ 2.34 (s, 3H, CH_3-), 5.51 (dd, 1H, J = 2.4, 11.2 Hz, Z-$CH_2=$), 5.70 (dd, 1H, J = 2.0, 17.6 Hz, E-$CH_2=$), 6.02 (dd, 1H, J = 10.8, 17.6 Hz, $=CH-C\equiv$), 7.11 (d, 2H, J = 7.6 Hz, $-C_6H_4-$), 7.33 (d, 2H, J = 8.0 Hz, $-C_6H_4-$) ppm. ^{13}C NMR ($CDCl_3$): δ 21.5 (-CH_3), 87.5 ($=CH-C\equiv$), 90.2 ($=CH-C\equiv C-$), 117.3 ($H_2C=$), 120.1, 129.1, 131.5, 138.4 ($-C_6H_4-$), 126.4 ($H_2C=CH-$) ppm. IR (neat): 3100, 3077, 3030, 3009, 2922, 2866, 2733, 2585, 2299, 2218 ($C\equiv C$), 2186, 1906, 1840, 1796, 1649, 1603, 1508, 1449, 1412, 1379, 1290, 1265, 1211, 1181, 1117, 1105, 1078, 1040, 1020, 970, 916, 835, 701, 667 cm^{-1}.

4-(4-Chlorophenyl)-1-buten-3-yne (4). Yield: 99% (bp$_{0.5}$ = 50 °C). ^{1}H NMR ($CDCl_3$): δ 5.54 (dd, 1H, J = 2.0, 11.0 Hz, Z-$CH_2=$), 5.73 (dd, 1H, J = 1.9, 17.3 Hz, E-$CH_2=$), 6.03 (dd, 1H, J = 11.1, 17.4 Hz, $=CH-C\equiv$), 7.28 (d, 2H, J = 8.2 Hz, $-C_6H_4-$), 7.36 (d, 2H, J = 8.5 Hz, $-C_6H_4-$) ppm. ^{13}C NMR ($CDCl_3$): δ 88.7 ($=CH$-$C\equiv$), 98.9 ($=CH-C\equiv C-$), 116.9 ($H_2C=$), 121.6, 128.6, 132.7, 134.3 ($-C_6H_4-$), 127.2 ($H_2C=CH-$) ppm. IR (neat): 3100, 3050, 3011, 2222 ($C\equiv C$), 1900, 1846, 1647, 1609, 1588, 1397, 1290, 1267, 1094, 1015, 968, 922, 829, 743 cm^{-1}.

4-(4-Trifluoromethylphenyl)-1-buten-3-yne (5). Yield: 67% (bp$_{0.7}$ = 35 °C). ^{1}H NMR ($CDCl_3$): δ 5.61 (dd, 1H, J = 2.4, 11.0 Hz, Z-$CH_2=$), 5.79 (dd, 1H, J = 2.0, 17.6 Hz, E-$CH_2=$), 6.02 (dd, 1H, J = 11.2, 17.6 Hz, $=CH-C\equiv$), 7.46−7.65 (4H, $-C_6H_4-$) ppm. ^{13}C NMR ($CDCl_3$): δ 88.5 ($=CH$-$C\equiv$), 90.3 ($=CH-C\equiv C-$), 116.7 ($H_2C=$), 125.3, 128.6, 128.1, 131.8 ($-C_6H_4-$), 126.9 ($H_2C=CH-$) 125.2 (CF_3-) ppm. IR (neat): 3106, 3056, 3017, 2934, 2641, 2224 ($C\equiv C$), 2103, 1921, 1854, 1794, 1750, 1676, 1616, 1514, 1486, 1406, 1325, 1267, 1231, 1169, 1130, 1107, 1067, 1017, 970, 926, 841, 775, 737, 704, 673 cm^{-1}.

Radical Polymerization of Enyne Monomers. A typical procedure was 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 (10 mL) and the solution was poured into hexane (300 mL) to precipitate the polymer (poly(**1**)). The hexane-insoluble product was collected by filtration and dried under vacuum (yield 1.76 g, 71%). ^{1}H NMR ($CDCl_3$): δ 0.7−4.6 (3H, $-CH_2-CH-$), 6.0−8.0 (5H, C_6H_5-) ppm. ^{13}C NMR ($CDCl_3$): δ 26−32 ($-CH_2-$), 35−45 ($-CH-C\equiv$), 80−81, 81−83 ($-C\equiv C-Ph$), 90−95 ($-C\equiv C-Ph$), 122−124, 125−130, 130−132 (C_6H_5-) ppm. IR (thin film): 3079, 3054, 3023, 2922, 2855, 2226 ($C\equiv C$), 1948, 1879, 1804, 1752, 1665, 1597, 1572, 1489, 1443, 1329, 1177, 1157, 1100, 1071, 1028, 1001, 984, 966, 912, 843, 754, 693 cm^{-1}.

Poly(2). Yield: 80%. ^{1}H NMR ($CDCl_3$): δ 1.0−4.3 (6H, $-CH_2-CH-$, CH_3O-), 6.0−8.0 (4H, $-C_6H_4-$) ppm. ^{13}C NMR ($CDCl_3$): δ 23−35 ($-CH_2-$), 35−45 ($-CH-C\equiv$), 55−56 (CH_3O-), 80−82, 82−83 ($-C\equiv C-Ar$), 87−95 ($-C\equiv C-Ar$), 113−114, 115−116, 127−129, 130−131, 157−159 ($-C_6H_4-$) ppm. IR (thin film): 3034, 2926, 2857, 2569, 2228 ($C\equiv C$), 1900, 1777, 1649, 1591, 1489, 1451, 1397, 1348, 1308, 1262, 1175, 1092, 1015, 943, 909, 828, 733, 650 cm^{-1}.

Poly(3). Yield: 62%. ^{1}H NMR ($CDCl_3$): δ 1.0−3.6 (6H, $-CH_2-CH-$, CH_3-), 6.0−7.8 (4H, $-C_6H_4-$) ppm. ^{13}C NMR ($CDCl_3$): δ 21−22 (CH_3-), 25−35 ($-CH_2-$), 39−42 ($-CH-C\equiv$), 79−82, 82−83 ($-C\equiv C-Ar$), 90−94 ($-C\equiv C-Ar$), 120−121, 125−130, 130−132, 133−136, 136−138 ($-C_6H_4-$) ppm. IR (thin film): 3081, 3027, 2920, 2865, 2731, 2226 ($C\equiv C$), 1904, 1705, 1651, 1609, 1562, 1510, 1449, 1362, 1217, 1181, 1107, 1038, 1020, 945, 816, 758, 710, 667 cm^{-1}.

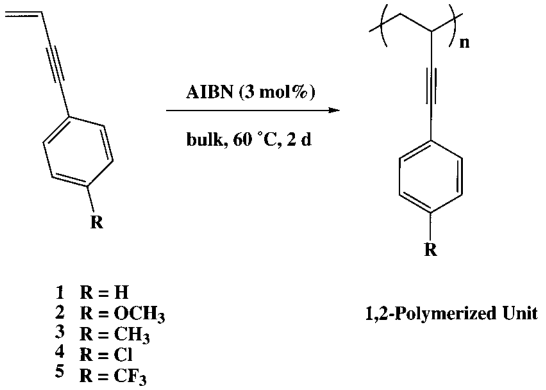
Poly(4). Yield: 71%. ^{1}H NMR ($CDCl_3$): δ 0.7−4.6 (3H, $-CH_2-CH-$), 6.0−8.0 (4H, $-C_6H_4-$) ppm. ^{13}C NMR ($CDCl_3$): δ 25−35 ($-CH_2-$), 35−45 ($-CH-C\equiv$), 79−81, 81−84 ($-C\equiv C-Ar$), 90−95 ($-C\equiv C-Ar$), 120−122, 126−129, 129−130, 131−133, 133−134 ($-C_6H_4-$) ppm. IR (thin film): 3034, 2926, 2857, 2569, 2228 ($C\equiv C$), 1900, 1777, 1649, 1591, 1489, 1451, 1397, 1348, 1308, 1262, 1175, 1092, 1015, 943, 909, 828, 733, 650 cm^{-1}.

Poly(5). Yield: 20%. ^{1}H NMR ($CDCl_3$): δ 0.4−4.6 (3H, $-CH_2-CH-$), 5.5−8.2 (4H, $-C_6H_4-$) ppm. ^{13}C NMR ($CDCl_3$): δ 23−35 ($-CH_2-$), 35−45 ($-CH-C\equiv$), 80−82, 82−84 ($-C\equiv C-Ar$), 90−95 ($-C\equiv C-Ar$), 117−119, 120−122, 122−126, 126−130, 130−133 ($-C_6H_4-$, CF_3-) ppm. IR (thin film): 3052, 2932, 2861, 2641, 2230 ($C\equiv C$), 2095, 1921, 1798, 1730, 1676, 1616, 1572, 1516, 1451, 1406, 1325, 1167, 1126, 1069, 1019, 955, 843, 760 cm^{-1}.

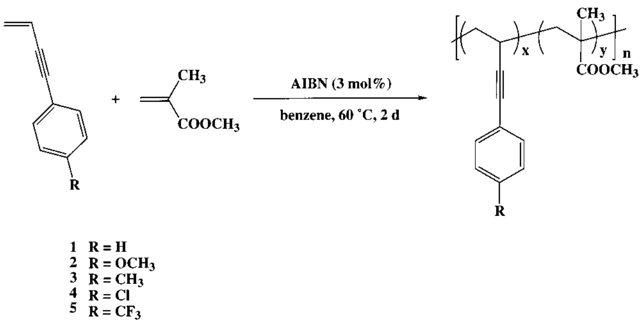
Radical Copolymerization of Enyne Monomers with MMA. A typical procedure was as follows: a benzene solution (1 mL) of **1** (0.19 g, 1.5 mmol), MMA (0.14 g, 1.4 mmol), and AIBN (0.015 g, 0.09 mmol) was heated at 60 °C for 2 days in a degassed sealed tube. After the reaction, the solution was poured into methanol−water (v/v = 5/1) to precipitate the polymer. After filtration and drying under vacuum, the copolymer was obtained in 28% yield (0.091 g, $M_n = 1000$, $M_w/M_n = 1.30$). The molar ratio of each monomer in the copolymer was determined from its ^{1}H NMR spectrum (**1**:MMA = 74:26, error < 2%). ^{1}H NMR ($CDCl_3$): δ 0.2−4.6 ($3 \times 0.74 + 8 \times 0.26$H, $-CH_2-CH-$, $-CH_2-C(CH_3)-$, $-COOCH_3$), 6.0−8.4 (5×0.74H, C_6H_5-) ppm. ^{13}C NMR ($CDCl_3$): δ 22−50 ($-CH_2-CH-C\equiv$, $-CH_2-C(CH_3)-$), 30−31 ($-CH_2-C(CH_3)-$), 51−52 ($-COOCH_3$), 80−86 ($-C\equiv C-Ph$), 91−95($-C\equiv C-Ph$), 123−125, 125−130, 130−132 ($-C_6H_5$), 175−180 ($-COOCH_3$) ppm. IR (thin film): 3056, 3023, 2926, 2855, 2232 ($C\equiv C$), 1946, 1890, 1802, 1730, 1638, 1599, 1572, 1543, 1491, 1443, 1375, 1200, 1121, 1071, 1028, 914, 845, 756, 693, 613 cm^{-1}.

Copolymer of 2 with MMA (from 2 (1.5 mmol) and MMA (1.5 mmol)). Yield: 24% (**2**:MMA = 73:27, error < 3%). ^{1}H NMR ($CDCl_3$): δ 0.4−4.0 ($6 \times 0.73+8 \times 0.27$H, $-CH_2-CH-$, $-CH_2-C(CH_3)-$, CH_3O-, $-COOCH_3$), 5.7−7.8 (4×0.73H, $-C_6H_4-$) ppm. ^{13}C NMR ($CDCl_3$): δ 21−50 ($-CH_2-CH-C\equiv$, $-CH_2-C(CH_3)-$), 30−31 ($-CH_2-C(CH_3)-$), 51−52 ($-COOCH_3$), 54−55 (CH_3O-), 79−84 ($-C\equiv C-Ar$), 87−93 ($-C\equiv C-Ar$), 112−115, 115−118, 123−131, 131−136, 156−159 ($-C_6H_4-$), 175−177 ($-COOCH_3$) ppm. IR (thin film): 2951, 2838, 2539, 2232 ($C\equiv C$), 1728, 1607, 1572, 1510, 1464, 1443, 1289, 1248, 1175, 1107, 1034, 831, 758 cm^{-1}.

Copolymer of 3 with MMA (from 3 (1.6 mmol) and MMA (1.6 mmol)). Yield: 31% (**3**:MMA = 76:24, error < 3%). ^{1}H NMR ($CDCl_3$): δ 0.4−3.8 ($6 \times 0.76+8 \times 0.24$H, $CH_3-C_6H_4-$, $-CH_2-CH-$, $-CH_2-C(CH_3)-$, $-COOCH_3$), 6.0−8.0 (4×0.76H, $-C_6H_4-$) ppm. ^{13}C NMR ($CDCl_3$): δ 21−22 ($CH_3-C_6H_4-$), 24−49 ($-CH_2-CH-C\equiv$, $-CH_2-C(CH_3)-$), 30−31 ($-CH_2-C(CH_3)-$), 52−53 ($-COOCH_3$), 82−84 ($-C\equiv C-Ar$), 87−93 ($-C\equiv C-Ar$), 119−122, 125−130, 130−133, 134−140 ($-C_6H_4-$), 175−178 ($-COOCH_3$) ppm. IR (thin film): 2922, 2853, 2232 ($C\equiv C$), 1904, Scheme 1



Scheme 2



Scheme 3

$$R{-}CH_3 + CH_3\bullet \longrightarrow R{-}CH_2\bullet + CH_4$$

1730, 1607, 1510, 1454, 1379, 1262, 1196, 1150, 1107, 1022, 816, 758 cm^{-1}.

Copolymer of 4 with MMA (from 4 (1.6 mmol) and MMA (1.6 mmol)). Yield: 18% (**4**:MMA = 80:20, error < 2%). ^{1}H NMR (CDCl$_3$): δ 0.4−4.0 (3 × 0.8+8 × 0.2H, $-CH_2-CH-$, $-CH_2-C(CH_3)-$, $-COOCH_3$), 6.0−8.0 (4 × 0.8H, $-C_6H_4-$) ppm. ^{13}C NMR (CDCl$_3$): δ 21−49 ($-CH_2-CH-C\equiv$, $-CH_2-C(CH_3)-$), 30−31 ($-CH_2-C(CH_3)-$), 52−53 ($-COOCH_3$), 79−84 ($-C\equiv C-Ar$), 87−95 ($-C\equiv C-Ar$), 121−122, 126−129, 129−131, 132−134, 134−135 ($-C_6H_4-$), 176−179 ($-COOCH_3$) ppm. IR (thin film): 2951, 2232 ($C\equiv C$), 1900, 1728, 1645, 1591, 1489, 1453, 1397, 1262, 1215, 1092, 1015, 828, 758, 667 cm^{-1}.

Copolymer of 5 with MMA (from 5 (1.5 mmol) and MMA (1.5 mmol)). Yield: 28% (**5**:MMA = 90:10, error < 2%). ^{1}H NMR (CDCl$_3$): δ 0.6−4.0 (3 × 0.9 + 8 × 0.1H, $-CH_2-CH-$, $-CH_2-C(CH_3)-$, $-COOCH_3$), 6.2−8.0 (4 × 0.9H, $-C_6H_4-$) ppm. ^{13}C NMR (CDCl$_3$): δ 21−50 ($-CH_2-CH-C\equiv$, $-CH_2-C(CH_3)-$), 30−31 ($-CH_2-C(CH_3)-$), 52−53 ($-COOCH_3$), 79−84 ($-C\equiv C-Ar$), 90−96 ($-C\equiv C-Ar$), 119−121, 123−126, 126−127, 127−132, 132−134 ($-C_6H_4-$, $-CF_3$), 175−179 ($-COOCH_3$) ppm. IR (thin film): 2928, 2855, 2232 ($C\equiv C$), 1923, 1800, 1730, 1684, 1616, 1572, 1514, 1458, 1406, 1325, 1167, 1127, 1069, 1019, 843, 760 cm^{-1}.

Estimation of Monomer Reactivity Ratios. The monomer reactivity ratios in the copolymerization of enynes with MMA were estimated from the compositions of the copolymers obtained by the copolymerization of **2**−**5** with MMA under varied feed ratios. The reaction was terminated before the conversions of monomers reached 5%.

Molecular Orbital Calculation. Reaction energies represented by Scheme 3 were calculated from the total energies of the model compounds whose geometry was optimized by MacSpartan *Plus* using the 3-21G basis set on the restricted (for closed-shell system) or unrestricted (for open-shell system) Hartree−Fock level.

Results and Discussion

Radical Polymerization of Aromatic Enyne Monomers. The radical polymerization of enyne monomers (**1**−**5**) was carried out in bulk at 60 °C using 3 mol % of AIBN as an initiator to give glassy polymers in good yields (Scheme 1, Table 1). The polymers thus obtained consist of the specific 1,2-polymerized unit (i.e., the unit having acetylene moieties in the side chain) regardless of the substituents on the benzene ring.[15,16]

Table 1. Radical Polymerization of 4-Substituted Aromatic Enynes[a]

run	monomer	yield (%)[b]	M_n[c]	M_w/M_n[c]
1	**1**	71	3400	1.49
2	**2**	80	5400	1.61
3	**3**	62	5100	1.28
4	**4**	41	5900	1.26
5	**5**	20	4900	1.22

[a] The polymerization was carried out in bulk at 60 °C for 2 days using 3 mol % of AIBN. [b] Isolated yield after precipitation with hexane. [c] Estimated by GPC (THF, polystyrene standard).

Table 2. Radical Copolymerization of Aromatic Enynes with MMA[a]

run	monomer	yield (%)[b]	M_n[c]	M_w/M_n[c]	x:y[d]
1	**1**	28	1000	1.30	76:24
2	**2**	24	1500	1.23	73:27
3	**3**	31	1000	1.33	76:24
4	**4**	18	1400	1.25	80:20
5	**5**	28	1800	1.22	90:10

[a] The polymerization was carried out in benzene at 60 °C for 2 days (feed ratio 1:1). [b] Isolated yield after precipitation with methanol−water (v/v = 5/1). [c] Estimated by GPC (THF, polystyrene standard). [d] Determined by ^{1}H NMR.

Although there is no significant difference in the molecular weight of the polymers, their yield seems to be correlated with the electronic character of the substituents on the benzene ring. That is, the polymerization of monomers carrying electron-withdrawing groups (**4** and **5**) gave lower yields of polymers, while that of a monomer carrying an electron-donating group (**2**) provided a polymer in higher yield. The reason for the decrease of the polymer yields by the introduction of the electron-withdrawing groups might be due to the "too stable" character of the propagating radicals that cannot attack the monomers smoothly.

The radical copolymerization of the aromatic enyne monomers (**2**−**5**) with MMA was carried out in benzene at 60 °C for 2 days using AIBN as an initiator to give the corresponding copolymers in moderate yields (Table 2, Scheme 2). The enyne components in the copolymers also consisted of specific 1,2-polymerized units. Both the yields and the molecular weights of the resulting copolymers are lower than those of the corresponding homopolymers. The content of the enyne component in the copolymers (>70%) was higher than the feed ratio (50:50) which becomes more pronounced upon introduction of substituents with stronger electron-withdrawing ability in the enynes. The results indicate that the enynes have higher polymerizability than MMA in this copolymerization system.

Monomer Reactivity Ratio of Aromatic Enyne Monomers. As communicated previously,[1] the monomer reactivity ratio of **1** (M_1) with MMA (M_2) was estimated to be r_1 = 3.46 and r_2 = 0.12 from their copolymerization system, indicating a higher reactivity of **1** toward both of their propagating radicals. The Q and e values of **1** were estimated from the monomer reactivity ratio to be 4.13 and −0.52, respectively. The large Q value indicates that the radical polymerization of **1** proceeds through more highly resonance-stabilized

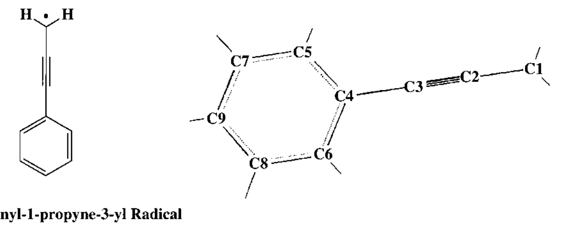
Table 3. Monomer Reactivity Ratios and *Q* and *e* Values of Aromatic Enynes

monomer	R	r_1	r_2	$r_1 \times r_2$	Q	e	σ_p
1	H	3.46	0.12	0.43	4.13	−0.52	0
2	OCH_3	4.04	0.09	0.37	5.45	−0.60	−0.27
3	CH	4.23	0.10	0.42	5.15	−0.53	−0.17
4	Cl	4.63	0.11	0.51	4.84	−0.42	+0.23
5	CF_3	6.19	0.12	0.75	4.93	−0.14	+0.54

propagating radical than other conjugated monomers such as styrene ($Q = 1.00$) and butadiene ($Q = 1.70$[17]).[18] The *e* value indicates that the vinyl moiety in **1** is more electron deficient than styrene ($e = -0.80$) and butadiene ($e = -1.05$[17]).

Because the copolymerization of the other aromatic enynes (**2**−**5**) with MMA took place to give copolymers (vide supra), the monomer reactivity ratios were estimated from the copolymerization system at the initial stage (i.e., conversion < 5%) (Table 3). In all cases, r_1 is much larger than r_2, supporting the point that the reactivity of the aromatic enynes (**2**−**5**) toward the propagating radicals is higher than that of MMA. Especially, the monomers with electron accepting groups (**4** and **5**) have larger r_1, indicating that their polymerization proceeds more predominantly over that of MMA, probably because the electron-withdrawing substituents on the enynes reduce the possibility of the interaction with MMA.

The *Q* and *e* values were estimated from the monomer reactivity ratios. The large *Q* values determined from the monomer reactivity ratios might indicate that the radical polymerization of **2**−**5** also proceeds through highly resonance-stabilized propagating radicals as is the case of **1**. The monomers bearing substituents on the benzene rings (**2**−**5**) revealed higher *Q* values than **1**, which is in good accordance with the case of styrene derivatives.[17,19] That is, the propagating radicals from **2**−**5** most probably conjugate not only through the triple bond moieties but also through the benzene rings. The *e* values of **1**−**5** were estimated to be from −0.14 to −0.60, which indicated that their double bond moieties are slightly more electron deficient than those of styrene derivatives.[17,19] This result is in good accordance with the chemical shifts of olefinic protons at 1-position ($-CH{=}CH_2$) in the ^1H NMR spectra, as indices for electron density of the double bond moieties. Especially, the less magnetically shielded trans protons revealed significant difference: those of aromatic enyne monomers (**1-5**) are observed at 5.50−5.61, being in the order of the estimated *e* value, while those of the corresponding styrenes are observed at 5.13−5.36.[20] The *e* values are correlated well with the Hammet σ_p value of the substituents, which also supports the supposition that the propagating radicals are conjugated through the benzene rings.



Spin Density

C1	C2	C3	C4	C5	C6	C7	C8	C9
1.17	-1.35	1.44	-0.96	0.88	0.88	-0.82	-0.82	0.85

Figure 1. Spin density isosurface map of SOMO of **1a**.

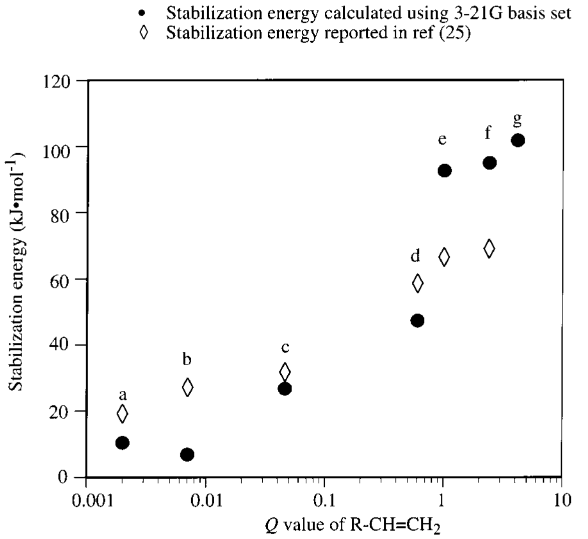


Figure 2. *Q* values of $RCH{=}CH_2$ vs stabilization energies of $RCH_2^{\bullet}$ toward $CH_3^{\bullet}$ (or of $RC(CH_3)_2^{\bullet}$ toward $HC(CH_3)_2^{\bullet}$ calculated in ref 25): (a) R = $-CH_3$ (propene); (b) R = $-{}^tBu$ (3,3-dimethyl-1-butene); (c) R = −OPh (phenyl vinyl ether); (d) R = −CN (acrylonitrile); (e) R = −Ph (styrene); (f) R = $CH_2{=}CH-$ (butadiene); (g) R = $-C{\equiv}C-Ph$ (**1**).

Molecular Orbital Calculation. As mentioned above, the large *Q* values of the aromatic enynes are supposed to originate from highly resonance-stabilized growing radicals. Although the *Q* value is convenient to estimate the resonance effect of the substituent, it is often influenced by steric and polar factors. Thus, alternative methods such as kinetic studies of radical reactions,[21,22] electron affinity measurement of bond dissociation,[23] and MO calculations[24] have been employed to estimate the real resonance effect. Among them, MO calculations are the most convenient method to get information on active short-lived molecules. Thus, the MO calculation was performed to estimate the resonance-stabilizing ability of the propagating radicals in the polymerization of aromatic enynes.

To estimate the delocalization of the propagating radical in the polymerization of **1**, the distribution of spin (i.e., the spin density at each atom) on the model system, 1-phenyl-1-propyne-3-yl radical (**1a**), was calculated using the 3-21G basis set. The spin density isosurface map of the singly occupied molecular orbital (SOMO) of **1a** revealed that the spin is not localized at C1 but delocalized through C3, C5, C7, and C9, which supports that the radicals delocalize through the propargyl and the allenyl positions but also the benzene ring (Figure 1).

The stabilization ability of the phenylethynyl moieties was compared with that of the substituents of conventional vinyl monomers from the change in the total energy via the hydrogen abstraction process in Scheme 3. When the stabilization energies of the substituents (R) were estimated from MO calculations by using the 3-21G basis set, the relative stabilization energy of the phenylethynyl group, the substituent of the propagating radical of **1**, was found to be highest among those of the substituents examined (Figure 2).[25] Namely, the origin of the high *Q* value of **1** is ascribable to the large stabilization energy of the phenylethynyl substituent. As is clear from Figure 2, the calculated energies are correlated with the *Q* values reported for each vinyl

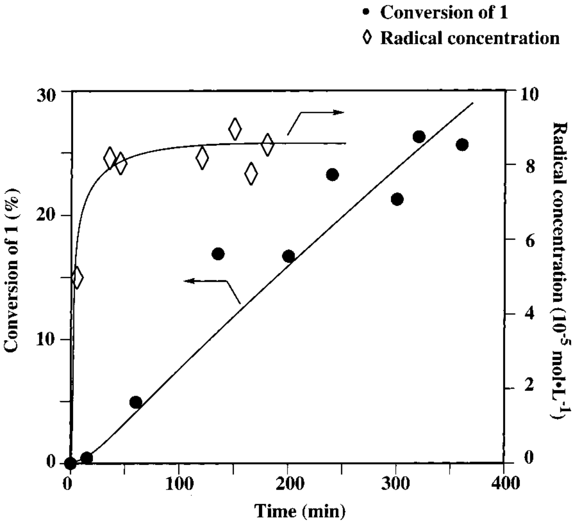


Figure 3. Time vs conversion of **1** and the radical concentration.

monomer.[26] This correlation is also in good accord with that obtained from kinetic study of the thermolysis of substituted azopropanes.[21]

ESR Study. The electron spin resonance (ESR) technique has been reported to be a useful method to determine the structure of propagating radicals, to quantify radical concentrations, and to estimate rate constants for the propagation and termination processes.[27] Therefore, the ESR spectra of the polymerization of **1** were evaluated in bulk at 60 °C using AIBN (0.25 M solution of **1**) as a radical initiator under N_2 to reveal the nature of the present polymerization system.

Figure 3 shows the time−conversion curve of **1** determined by GC and the radical concentration by ESR after the designated reaction periods. The radical concentration ($[\mathrm{M}^\bullet]$) reached a nearly constant value (8.28×10^{-5} mol·L^{-1}) after reaction for 30 min. After the radical concentration became almost constant, a linear relationship between conversion and time was observed, from which the rate of the polymerization (R_p) was estimated to be 1.34×10^{-5} s^{-1}. On the basis of eq 1 where X is the conversion of the monomer,[27] the rate constant for the propagation (k_p) could be estimated as a function of the conversion of **1**. By extrapolating X to 0, $k_p{}^0$ was found to be 1.62×10^{-1} L·mol^{-1}·s^{-1} which indicates the polymerization of **1** proceeds much slower than styrene ($k_p{}^0 = 10^2$ L·mol^{-1}·s^{-1}) or MMA ($k_p{}^0 = 10^2$−10^3 L·mol^{-1}·s^{-1}).[28]

$$k_p = R_p/([\mathrm{M}^\bullet][1 - X]) \qquad (1)$$

In the radical polymerization of styrene, the radical concentration was estimated to be ca. 10^{-7} mol·L^{-1} at the initial stage.[29] In contrast, the radical concentration of the polymerization of **1** was estimated to be 10^2−10^3 times higher than that of styrene. The high radical concentration and the low $k_p{}^0$ most probably originate from the highly stable nature of the growing radical. That is, the propagating radical has lower reactivity for both the termination and the propagation. The results obtained here also support the resonance-stabilized character of the propagating radical from **1**.

Conclusions

The radical polymerization of 4-substituted aromatic enynes gave polymers consisting of the specific 1,2-polymerized unit (i.e., the unit having acetylene moieties) regardless of the polar and electronic character of the substituent on the benzene ring. The large Q values ($Q = 4.1$−5.5) of these monomers indicated that the propagating radicals are highly stabilized by the arylethynyl groups, which was also supported by the MO calculation of the model system of the propagating species and the ESR study. The MO calculations suggested that the high resonance-stabilized character of the propagating radicals originates from their delocalization through both the triple bond and the benzene rings. The ESR study revealed that the present polymerization system proceeds with a high radical concentration and slow propagation. The e values ($e = -0.1$ to -0.6) could be correlated with the Hammet σ_p values of the substituents on the benzene rings, supporting the supposition that the propagating radicals conjugate not only through the triple bond moieties but the benzene rings.

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(16) The polymers obtained by radical polymerization of the aromatic enynes consist of 1,2-polymerized units while those obtained by anionic polymerization consist of both 1,2- and 1,4-polymerized units. This difference in the 1,2- and the 1,4-selectivity can be also found in addition reactions. That is, the addition of the radicals to 4-monosubstituted 1,3-enynes gives acetylenic compounds (i.e., 1,2-adducts) as the main products regardless of the conditions, while allenic compounds (i.e., 1,4-adducts) are not produced or detected. See: (a) Poutsma, M. L.; Ibarbia, P. A. *J. Org. Chem.* **1970**, *35*, 4038. (b) Poutsma, M. L.; Ibarbia, P. A. *J. Am. Chem. Soc.* **1973**, *95*, 6000. (c) Sulimov, I. G.; Stadnichuk, M. D. *J. Gen. Chem. USSR* **1966**, *37*, 1814. (d) Sulimov, I. G.; Stadnichuk, M. D. *J. Gen. Chem. USSR* **1966**, *37*, 2215. In contrast, the nucleophilic additions of alkyllithiums to the enynes gives allenic in addition to acetylenic compounds in a ratio that was influenced by the character of electrophiles used for quenching. See: (e) Kormer, V. A.; Petrov, A. A. *J. Gen. Chem. USSR* **1960**, *30*, 231. (f) Kormer, V. A.; Petrov, A. A.; Savich, G.; Podporina, T. R. *J. Gen. Chem. USSR* **1962**, *32*, 313. (g) Wakefield, B. J. In *The Chemistry of Organolithium Compounds*; Pergamon: Oxford, Engand, 1974; p III-89. See also ref 10.

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(19) Because we could not find reported *Q* and *e* values of *p*-trifluoromethylstyrene, the copolymerization with MMA was performed by the same procedure as that of enyne monomers to estimate the copolymerization parameters and *Q* and *e* values ($r_1 = 1.16$, $r_2 = 0.42$, $Q = 1.25$, and $e = -0.44$).

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