Nickel(0)-Catalyzed Efficient 2:2 Double-Cycloaddition of Monoynes with N-Substituted Maleimides To Form Bicyclo[2.2.2]oct-7-enes and Its Development into Nickel(0)-Catalyzed Double-Cycloaddition Copolymerization of Diynes with N-Substituted Maleimides to Poly(bicyclo[2.2.2]oct-7-ene)s[†]

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Nickel(0)-catalyzed 2:2 double-cycloaddition reactions of phenylacetylene (**1a**), 1-pentyne (**1b**), and 3-hexyne (**12a**) with *N*-phenylmaleimide (**2a**), *N*-octylmaleimide (**2b**), and *N*-ethylmaleimide (**2c**) to form bicyclo[2.2.2]oct-7-enes were investigated in THF. The maleimide/monoyne molar ratio was important for an efficient formation of the bicyclo[2.2.2]oct-7-ene: the $Ni(CO)_2(PPh_3)_2$-catalyzed **2b**/**1a** = 2 reaction at 90 °C for 3 h afforded bicyclo[2.2.2]oct-7-ene **9ab** (hexahydro-2,6-octyl-4,9-diphenyl-4,8-ethenobenzo-[1,2-*c*:4,5-*c*′]dipyrrole-1,3,5,7(2*H*,6*H*)-tetrone) chemo- and regioselectively in excellent yield, while the **2b**/**1a** = 1 reaction gave **9ab** only in ca. 50% yield. The **1a**/**2c** reaction proceeded heterogeneously due to the poor solubility of the cycloadduct to give the corresponding bicyclo-[2.2.2]oct-7-ene in low yield. The **1b**/**2b** = 2 reaction gave two regioisomeric bicyclo[2.2.2]-oct-7-enes in high yield. Internal monoyne **12a** also underwent the 2:2 cycloaddition with **2a** or **2c**. X-ray structural analysis of the 2:2 **12a**/**2c** cycloadduct demonstrated an *endo*,*endo*-stereochemistry of its bicyclo[2.2.2]oct-7-ene ring. On the basis of these results, a nickel-(0)-catalyzed diyne/maleimide double-cycloaddition copolymerization was examined. 1,4-Diethynylbenzene (**16**) copolymerized with **2b** in the presence of the $Ni(CO)_2(PPh_3)_2$ catalyst to produce poly(bicyclo[2.2.2]oct-7-ene) **17b**, with a molecular weight up to 35 000, while the **16**/**2a** and **16**/**2c** copolymerizations produced insoluble copolymers. The copolymer **17b** is a new diyne cycloaddition copolymer having a wholly carbon backbone and has a unique rigid fence-like structure. 1,11-Dodecadiyne/**2a**−**c** and 3,11-tetradecadiyne/**2a** copolymerizations afforded soluble poly(bicyclo[2.2.2]oct-7-ene)s.

Introduction

Development of a new method of polymer synthesis and preparation of novel polymers utilizing the characteristic organic reactions of a transition metal catalyst are interesting and important.[1] We developed recently a transition-metal-catalyzed diyne cycloaddition copolymerization (Scheme 1),[2,3] which is a new method of the transition-metal-catalyzed polymer synthesis. In the presence of a transition metal catalyst, one molecule of the cycloaddition component (*Z*) connects two diyne molecules intermolecularly to afford a cycloaddition copolymer containing a carbo- or heterocycle in its repeat unit.

A variety of cycloaddition components, such as a heterocumulene and an unsaturated compound, could be used for the copolymerization. We already reported the syntheses of poly(2-pyrone)s[4] and poly(2-pyridone)s[5] by the nickel(0)-catalyzed cycloaddition copolymerization of diynes with carbon dioxide and isocyanates, respectively. Poly(pyridine)s were also obtained by a cobaltocene-catalyzed diyne/nitrile cycloaddition copolymerization.[2a,6] Carbene-type compounds, such as carbon monoxide, elemental sulfur, and low valent transition metals, which can donate an electron pair for the cycloaddition, are also interesting cycloaddition components. We recently found a palladium-catalyzed diyne/sulfur cycloaddition copolymerization to form poly-

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[†] For preliminary report of the synthesis of poly(bicyclo[2.2.2]oct-7-ene)s, see: Tsuda, T.; Tobisawa, A.; Mizuno, H.; Takeda, A. *J. Chem. Soc., Chem. Commun.* **1997**, 201.

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[§] Department of Synthetic Chemistry.

[⊗] Abstract published in *Advance ACS Abstracts*, February 1, 1997.

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(3) The expression of a repeat unit of the cycloaddition copolymer in Scheme 1 is based on the nonregiospecific formation of carbo- and heterocycles.

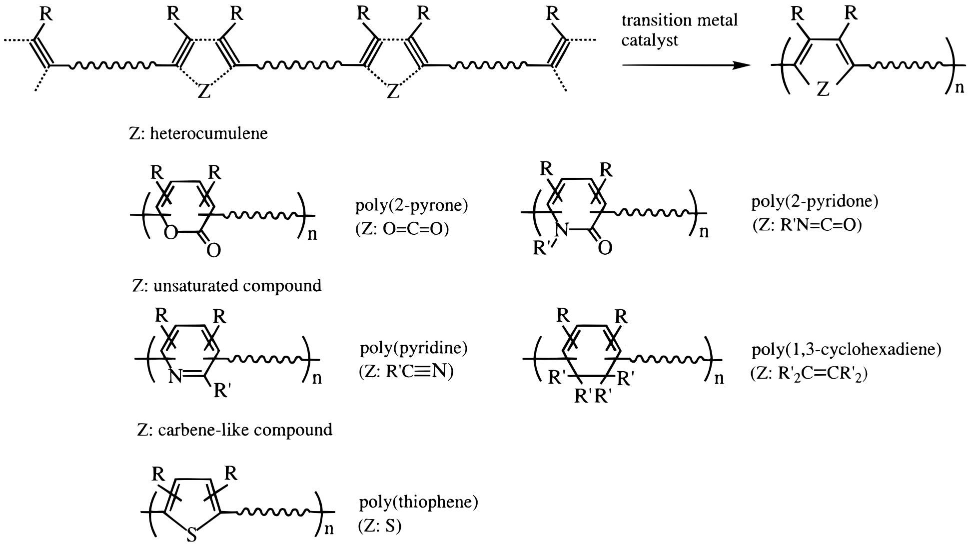
(4) (a) Tsuda, T.; Maruta, K.; Kitaike, Y. *J. Am. Chem. Soc.* **1992**, *114*, 1498. (b) Tsuda, T.; Maruta, K. *Macromolecules* **1992**, *25*, 6102. (c) Tsuda, T.; Ooi, O.; Maruta, K. *Macromolecules* **1993**, *26*, 4840. (d) Tsuda, T.; Kitaike, Y.; Ooi, O. *Macromolecules* **1993**, *26*, 4956. (e) Tsuda, T.; Hokazono, H. *Macromolecules* **1994**, *27*, 1289. (f) Tsuda, T.; Yasukawa, H.; Hokazono, H.; Kitaike, Y. *Macromolecules* **1995**, *28*, 1312. (g) Tsuda, T.; Yasukawa, H.; Komori, K. *Macromolecules* **1995**, *28*, 1356. For the spontaneous bis(ynamine)/CO_2 copolymerization to a poly(4-pyrone), see: (h) Tsuda, T.; Hokazono, H.; Toyota, K. *J. Chem. Soc., Chem. Commun.* **1995**, 2417.

(5) (a) Tsuda, T.; Hokazono, H. *Macromolecules* **1993**, *26*, 1796. (b) Tsuda, T.; Hokazono, H. *Macromolecules* **1993**, *26*, 5528. (c) Tsuda, T.; Tobisawa, A. *Macromolecules* **1994**, *27*, 5943. (d) Tsuda, T.; Tobisawa, A. *Macromolecules* **1995**, *28*, 1360.

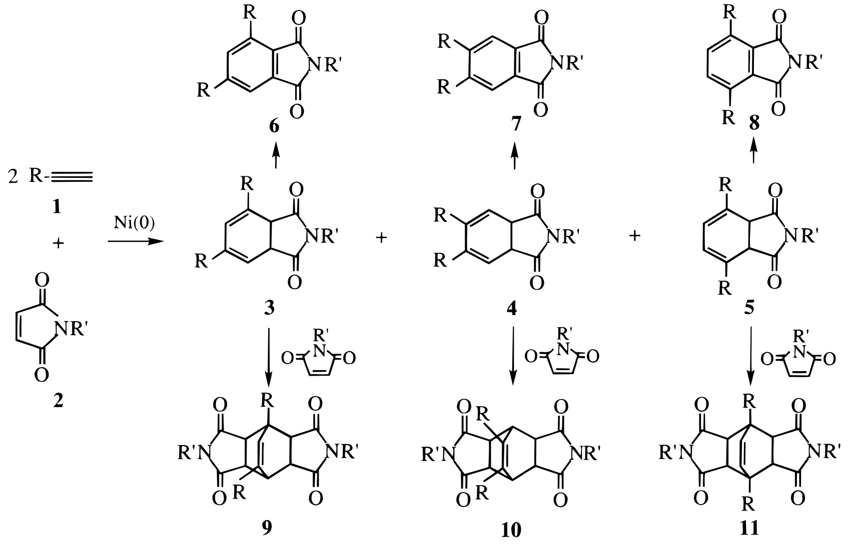
(6) Tsuda, T.; Maehara, H. *Macromolecules* **1996**, *29*, 4544.

S0276-7333(96)00987-9 CCC: $14.00

Scheme 1



Scheme 2



R = Ph (**a**), Pr (**b**) R' = Ph (**a**), C_8H_{17} (**b**), Et (**c**), Me (**d**)

(thiophene)s[7] and a cobalt-catalyzed cycloaddition terpolymerization of diynes, carbon monoxide, and a diene to form poly(enone)s,[8] which is a modification of the diyne cycloaddition copolymerization. Other researchers have prepared transition-metal-containing polymers from diynes and low valent transition metal complexes by utilizing the technique of diyne cycloaddition copolymerization.[9]

The above-mentioned poly(2-pyrone)s, poly(2-pyridone)s, poly(pyridine)s, and poly(thiophene)s contain heterocycles in their repeat units. It is interesting, therefore, to prepare a new cycloaddition copolymer having a wholly carbon backbone, such as a poly(1,3-cyclohexadiene) by the diyne cycloaddition copolymerization with an alkene (Scheme 1). This copolymerization necessitates an efficient transition-metal-catalyzed cycloaddition of two monoyne molecules with one alkene molecule to form a 1,3-cyclohexadiene as an elementary reaction.

Extensive studies have been done on the transition-metal-catalyzed cycloaddition of alkynes.[10] However, examples of an efficient transition-metal-catalyzed intermolecular 2:1 monoyne/alkene cycloaddition to form the 1,3-cyclohexadiene are very limited,[10b,c] while some examples of the corresponding intramolecular cycloaddition involving enynes and diynes are known.[10d] To the best of our knowledge, the palladium-catalyzed cocyclotrimerization of dimethyl acetylenedicarboxylate with norbornene to form 1,2,3,4-tetrakis(methoxycarbonyl)benzene[11] is the only example of an efficient intermolecular 2:1 monoyne/alkene cycloaddition reaction. This reaction, however, cannot be used for the

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[7] Tsuda, T.; Takeda, A. *J. Chem. Soc., Chem. Commun.* **1996**, 1317.

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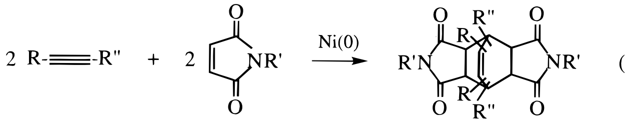
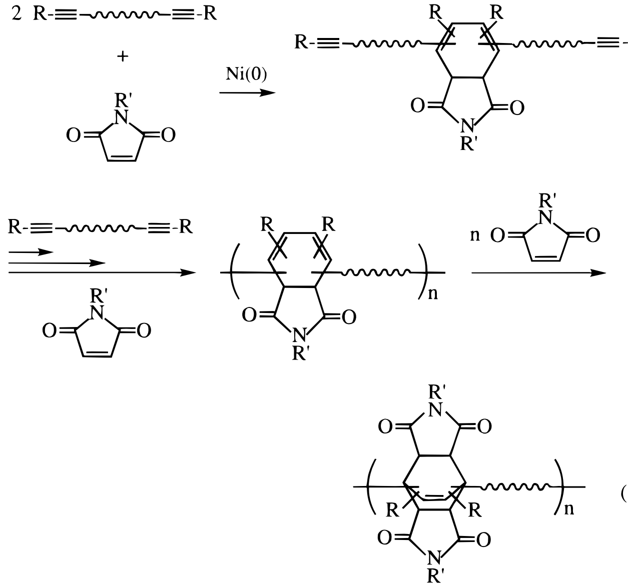
synthesis of a diyne cycloaddition copolymer having a wholly carbon backbone.

The interesting $Ni(CO)_2(PPh_3)_2$-catalyzed cycloaddition of phenylacetylene (**1a**) with *N*-methylmaleimide (**2d**) (**1a**/**2d** = 2) in refluxing benzene was reported by Chalk 24 years ago (Scheme 2).[12] The 1,3-cyclohexadiene derivative **3ad**, i.e., a 2:1 monoyne/maleimide adduct, was obtained as a major product in 50% yield, along with a minor product of a bicyclo[2.2.2]oct-7-ene derivative **9ad**, i.e., a 2:2 monoyne/maleimide adduct, in 27% yield. The cycloadduct **9ad** may be reasonably assumed to be formed by a noncatalyzed Diels–Alder cycloaddition of **3ad** with **2d**. Thus, the chemoselectivity and efficiency of this **1a**/**2d** cycloaddition reaction are not satisfactory for its utilization in a diyne/maleimide cycloaddition copolymerization to form a poly(1,3-cyclohexadiene) or a poly(bicyclo[2.2.2]oct-7-ene) (eq 2).

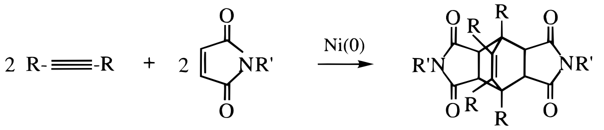


(1)



(2)

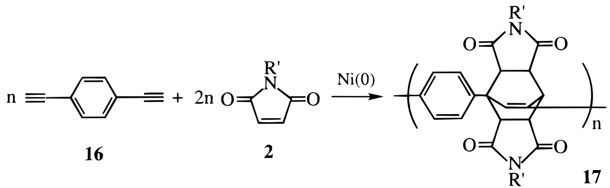
In this study, we have explored the efficient and chemoselective synthesis of bicyclo[2.2.2]oct-7-enes by the nickel(0)-catalyzed 2:2 double-cycloaddition of terminal and internal monoynes with N-substituted maleimides (eqs 1 and 3) and its development into the nickel(0)-catalyzed double-cycloaddition copolymerization of diynes with N-substituted maleimides to form poly(bicyclo[2.2.2]oct-7-ene)s having wholly carbon backbones (eqs 2 and 4–6).



(3)

12 **2** **13**

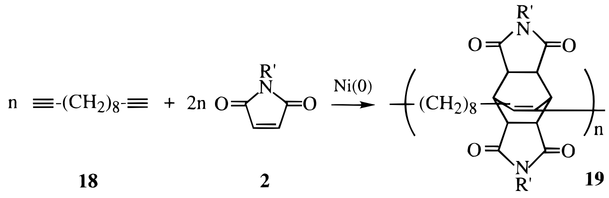
R = Et (**a**) R' = Ph (**a**), Et (**c**)



(4)

16 **2** **17**

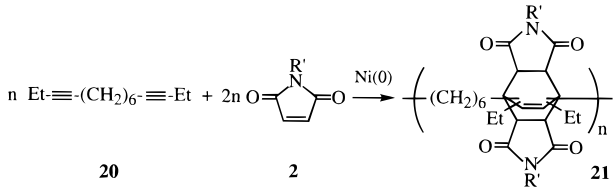
R' = Ph (**a**), C_8H_{17} (**b**), Et (**c**)



(5)

18 **2** **19**

R' = Ph (**a**), C_8H_{17} (**b**), Et (**c**)



(6)

20 **2** **21**

R' = Ph (**a**)

Experimental Section

General Procedures. ^{1}H NMR (270 MHz) and ^{13}C NMR (67.5 MHz) spectra were taken in $CDCl_3$ unless otherwise stated. Their chemical shifts are reported in ppm on the δ scale relative to $CHCl_3$ (7.26 ppm) and $CDCl_3$ (77.0 ppm), respectively, and coupling constants are reported in hertz. Preparative layer chromatography (PLC) was carried out by using 20/20/0.2 cm plates prepared with Merck silica gel 60 PF-254. Gel permeation chromatography (GPC) was performed in $CHCl_3$ using a SHODEX AC-804 gel column with polystyrene standards. Melting points were uncorrected. The thermogravimetric analysis (TGA) was performed on a Shimadzu DT-30 instrument. THF was distilled over $LiAlH_4$ under nitrogen. Phenylacetylene (**1a**), 1-pentyne (**1b**), 3-hexyne (**12a**), 1,11-dodecadiyne (**18**), and 3,11-tetradecadiyne (**20**) were commercial reagents and were distilled under nitrogen. 1,4-Diethynylbenzene (**16**) was a commercial reagent and was purified by sublimation. *N*-Phenylmaleimide (**2a**) and *N*-ethylmaleimide (**2c**) were commercial reagents and were purified by recrystallization. *N*-Octylmaleimide (**2b**) was prepared according to the literature procedure.[13] $Ni(CO)_2(PPh_3)_2$ was prepared according to the literature.[14] Bis(1,5-cyclooctadiene)nickel ($Ni(COD)_2$) was a commercial reagent. Triphenylphosphine, tri-*o*-tolylphosphine, tris(2,4,6-trimethylphenyl)phosphine, 1,2-bis(diphenylphosphino)ethane (dppe), 1,4-bis(diphenylphosphino)butane (dppb), and tricyclohexylphosphine were commercial reagents and were used as purchased. Triphenyl phosphite was a commercial reagent and was distilled under nitrogen.

Cycloaddition of Phenylacetylene (1a) with *N*-Octylmaleimide (2b) and Other Monoyne/Maleimide Cycloaddition Reactions. The reaction was carried out under nitrogen. In a 50 mL stainless steel autoclave were placed $Ni(CO)_2(PPh_3)_2$ (0.032 g, 0.050 mmol), **2b** (0.21 g, 1.0 mmol), THF (3.0 mL), and **1a** (0.055 mL, 0.50 mmol) in this order with magnetic stirring at ambient temperature. The reaction mixture was heated at 90 °C for 3 h with magnetic stirring. After the mixture was cooled by ice water, the reaction mixture was concentrated under vacuum to give a residue, which was purified by PLC (AcOEt/hexane = 2/1 (v/v)) to afford hexahydro-2,6-octyl-4,9-diphenyl-4,8-ethenobenzo[1,2-*c*:4,5-*c*′]dipyrrole-1,3,5,7(2*H*,6*H*)-tetrone, **9ab**, as a white powder (0.15 g, 97%), which was recrystallized from THF/diethyl ether. **9ab**: mp 192 °C; IR (KBr, cm^{-1}) 1768, 1702, 1402, 1345, 1145, 756; ^{1}H NMR (400 MHz, CD_2Cl_2) 0.86 (t, $J = 7.2$, 6 H), 0.91–1.30 (m, 24 H), 3.21 (t, $J = 6.6$, 4 H), 3.29 (dd, $J = 8.2, 3.1$, 2 H),

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3.45 (d, $J = 8.1$, 2 H), 4.33 (td, $J = 3.1, 1.6$, 1 H), 6.86 (br s, 1 H), 7.28−7.76 (m, 10 H); ^{13}C NMR (100 MHz, CD$_2$Cl$_2$) 14.2 (q), 23.0 (t), 27.0 (t), 28.0 (t), 29.34 (t), 29.36 (t), 32.1 (t), 37.6 (d), 39.0 (t), 44.9 (d), 47.9 (s), 49.3 (d), 123.9 (d), 125.9 (d), 127.4 (d), 127.6 (d), 128.1 (d), 128.2 (d), 128.8 (d), 129.0 (d), 129.1 (d), 137.0 (s), 138.7 (s), 142.7 (s), 174.6 (s), 176.3 (s); FAB MS *m/z* 623 (MH$^+$). Anal. Calcd for C$_{40}$H$_{50}$N$_2$O$_4$: C, 77.14; H, 8.09; N, 4.50. Found: C, 77.10; H, 8.10; N, 4.40. The **2b**/**1a** = 1 reaction, under conditions similar to the **2b**/**1a** = 2 reaction, gave the dehydrogenated 2:1 adduct **6ab** in 8% yield along with **9ab** (53% yield). **6ab**: IR (KBr, cm^{-1}) 1767, 1709, 1619, 748, 696; ^{1}H NMR 0.87 (t, $J = 6.9$, 3 H), 1.26−1.67 (m, 12 H), 3.67 (t, $J = 7.3$, 2 H), 7.26−8.07 (m, 12 H); ^{13}C NMR 14.5, 23.1, 27.4, 29.0, 29.6, 30.1, 32.2, 38.6, 121.0, 126.5, 127.7, 128.6, 129.2, 129.3, 129.6, 129.9, 134.7, 134.8, 136.8, 139.4, 141.7, 147.4, 168.3, 168.5; FAB MS *m/z* 412 (MH$^+$). Anal. Calcd for C$_{28}$H$_{29}$NO$_2$: C, 81.72; H, 7.10; N, 3.40. Found: C, 81.42; H, 7.40; N, 3.04. Other monoyne/maleimide cycloaddition reactions were carried out similarly to the **1a**/**2b** reaction to afford 2:2 adducts **9aa**, **9ac**, **9bb**, **10bb**, **9ba**, **10ba**, **13aa**, and **13ac**. **9aa**: IR (film, cm^{-1}) 1772, 1716, 1597, 1498, 1377, 1189, 745; ^{1}H NMR 3.53 (dd, $J = 8.3, 2.5$, 2 H), 3.74 (d, $J = 8.3$, 2 H), 4.63 (d, $J = 1.3$, 1 H), 7.12 (s, 1 H), 7.20−7.80 (m, 20 H); ^{13}C NMR 37.6, 44.1, 47.3, 48.6, 123.3, 125.2, 125.6, 126.0, 127.2, 127.9, 128.2, 128.3, 128.5, 128.6, 130.7, 135.9, 136.9, 142.3, 173.0, 174.4; FAB MS *m/z* 551 (MH$^+$). The compound **9ac** was obtained as a white powder, and the analytical sample was recrystallized from dioxane/hexane as fine needles. **9ac**: IR (KBr, cm^{-1}) 1768, 1700, 1401, 1350, 1231, 755; ^{1}H NMR 0.87 (t, $J = 6.9$, 6 H), 3.23−3.38 (m, 6 H), 3.47 (d, $J = 7.9$, 2 H), 4.40 (br s, 1 H), 6.89 (br s, 1 H), 7.28−7.75 (m, 10 H); ^{13}C NMR 12.8, 33.7, 37.3, 44.5, 47.4, 48.9, 123.3, 125.5, 126.5, 127.5, 127.6, 128.2, 128.7, 128.8, 136.3, 137.6, 142.3, 174.2, 175.6; FAB MS *m/z* 455 (MH$^+$). Anal. Calcd for C$_{28}$H$_{26}$N$_2$O$_4$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.74; H, 5.84; N, 6.11. The compound **9bb** was obtained as a colorless oil. **9bb**: IR (film, cm^{-1}) 1765, 1703, 1400, 1368, 1170; ^{1}H NMR 0.81 (t, $J = 7.3$, 3 H), 0.87 (t, $J = 6.3$, 6 H), 1.10 (t, $J = 7.1$, 3 H), 1.15−1.35 (m, 22 H), 1.42 (quint, $J = 6.6$, 4 H), 1.70 (sext, $J = 4.6$, 2 H), 1.90 (diffuse t, 2 H), 2.20−2.30 (m, 2 H), 2.80−3.00 (m, 4 H), 3.36 (t, $J = 7.3$, 4 H), 3.53 (br s, 1 H), 5.27 (br s, 1 H); ^{13}C NMR 13.7, 14.0, 14.4, 16.8, 19.3, 22.6, 26.7, 27.7, 29.1, 31.7, 33.6, 37.2, 37.9, 38.8, 43.6, 44.1, 44.3, 126.4, 143.4, 175.6, 176.6; FAB MS *m/z* 555 (MH$^+$). Anal. Calcd for C$_{34}$H$_{54}$N$_2$O$_4$: C, 73.61; H, 9.81; N, 5.05. Found: C, 73.22; H, 9.92; N, 4.99. The compound **10bb** was obtained as a colorless oil. **10bb**: IR (film, cm^{-1}) 1770, 1705, 1399, 1369, 1173; ^{1}H NMR 0.74−0.92 (m, 12 H), 1.09−1.33 (m, 24 H), 1.33−1.50 (m, 4 H), 1.77−1.91 (m, 4 H), 2.89 (s, 4 H), 3.34 (t, $J = 7.4$, 4 H), 3.58 (s, 2 H); ^{13}C NMR 14.5, 14.8, 21.4, 23.0, 27.2, 28.2, 29.6, 32.2, 33.9, 38.6, 39.4, 44.3, 135.2, 177.3; FAB MS *m/z* 555 (MH$^+$). Anal. Calcd for C$_{34}$H$_{54}$N$_2$O$_4$: C, 73.61; H, 9.81; N, 5.05. Found: C, 73.21; H, 9.92; N, 4.94. **9ba**: IR (film, cm^{-1}) 1772, 1712, 1597, 1499, 1381, 1194, 746; ^{1}H NMR 0.87 (t, $J = 7.3$, 3 H), 1.08 (t, $J = 7.1$, 3 H), 1.31−1.45 (m, 2 H), 1.69−1.83 (m, 2 H), 2.01−2.14 (m, 2 H), 2.25−2.39 (m, 2 H), 3.12−3.26 (m, 4 H), 3.75−3.80 (m, 1 H), 5.54−5.60 (m, 1 H), 7.12−7.53 (m, 10 H); ^{13}C NMR 13.9, 14.3, 16.8, 19.8, 33.5, 37.3, 38.3, 44.2, 44.4, 126.2, 126.8, 128.8, 129.1, 131.5, 144.1, 174.5, 175.6; FAB MS *m/z* 483 (MH$^+$). **10ba**: IR (film, cm^{-1}) 1773, 1715, 1596, 1498, 1376, 1190, 747; ^{1}H NMR 0.85 (t, $J = 7.3$, 6 H), 1.20−1.37 (m, 4 H), 1.97−2.10 (m, 4 H), 3.17 (t, $J = 1.5$, 4 H), 3.82 (s, 2 H), 7.10−7.52 (m, 10 H); ^{13}C NMR 14.5, 21.4, 33.6, 38.6, 43.8, 126.1, 128.8, 129.2, 131.5, 135.4, 175.8; FAB MS *m/z* 483 (MH$^+$). The compound **13aa** was obtained as a white powder, and the analytical sample was recrystallized from AcOEt/hexane as small prisms. **13aa**: IR (KBr, cm^{-1}) 1768, 1712, 1597, 1498, 1379, 1201, 741; ^{1}H NMR 0.90 (t, $J = 7.6$, 6 H), 1.31 (t, $J = 7.1$, 6 H), 2.17 (q, $J = 7.6$, 4 H), 2.64 (q, $J = 7.3$, 4 H), 3.18 (s, 4 H), 7.10−7.48 (m, 10 H); ^{13}C NMR 8.27, 14.7, 20.2, 20.5, 43.9, 45.2, 126.2, 128.6, 129.0, 131.6, 139.9, 174.7; FAB MS *m/z* 511 (MH$^+$). Anal. Calcd for C$_{32}$H$_{34}$N$_2$O$_4$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.06; H, 6.65; N, 5.41. **13ac**: mp 167.0−167.5 °C; IR (film, cm^{-1}) 1762, 1699, 1405, 1350, 1231, 1108, 811; ^{1}H NMR 0.78 (t, $J = 7.6$, 6 H), 1.05 (t, $J = 7.1$, 6 H), 1.25 (t, $J = 7.3$, 6 H), 1.99 (q, $J = 7.6$, 4 H), 2.55 (q, $J = 7.3$, 4 H), 2.90 (s, 4 H), 3.39 (q, $J = 7.3$, 4 H); ^{13}C NMR 8.25, 12.9, 14.3, 19.9, 20.5, 33.4, 43.6, 44.7, 139.3, 175.7; FAB MS *m/z* 415 (MH$^+$). The structure of **13ac** was confirmed by X-ray crystallography.

X-ray Analysis of 13ac. The colorless prismatic crystals of **13ac** were obtained from a diethyl ether/hexane solution at 0 °C. The compound **13ac** crystallized in the monoclinic space group $P2_1/c$ ($Z = 4$). The unit cell dimensions were $a = 9.72(2)$ Å, $b = 13.715(10)$ Å, $c = 17.03(1)$ Å, $\beta = 97.6(1)°$, $V = 2249$ (4) Å^3. A total of 7189 reflections were measured by graphite-monochromated Mo Kα radiation up to $\theta = 30.0°$ on a Rigaku AFC7R diffractometer at the temperature of 20 ± 1 °C. The data were corrected for Lorentz and polarization factors. The structure was solved by direct methods and refined to $R = 0.064$. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included, but their positions were not refined; isotropic B values were refined.

Copolymerization of 1,4-Diethynylbenzene (16) with *N*-Octylmaleimide (2b) and Other Diyne/Maleimide Copolymerizations. The reaction was carried out under nitrogen. In a 50 mL stainless steel autoclave were placed Ni(CO)$_2$(PPh$_3$)$_2$ (0.016 g, 0.025 mmol), **16** (0.032 g, 0.25 mmol), **2b** (0.105 g, 0.500 mmol), and THF (5.0 mL) in this order with magnetic stirring at ambient temperature. The reaction mixture was heated at 90 °C for 20 h with magnetic stirring. After the mixture was cooled by ice water, the reaction mixture was evaporated under vacuum. Addition of ether (20 mL) to a resulting residue precipitated copolymer **17b**, which was further purified by dissolution in CH$_2$Cl$_2$ (2 mL) and addition of ethyl acetate (20 mL). This residue was dried in vacuo at room temperature and gave **17b** as a pale yellow powder (0.067 g, 51% based on 100% conversion of **16** to **17b**). **17b**: IR (film, cm^{-1}) 1771, 1703, 1398, 1348, 1170, 822; ^{1}H NMR 0.85 (br s, 6 H), 0.94−1.60 (m, 24 H), 3.31 (br s, 4 H), 3.44 (br s, 2 H), 3.60 (br s, 2 H), 4.28−4.53 (m, 1 H), 6.71−7.12 (m, 1 H), 7.22−8.10 (m, 4 H); ^{13}C NMR 14.1, 22.6, 26.7, 27.6, 29.1, 31.7, 37.5 (m), 38.9 (m), 44.6 (m), 47.8 (m), 49.1 (m), 123.2−129.4 (m), 135.0−138.7 (m), 141.5−142.6 (m), 173.7−175.1 (m), 175.1−176.8 (m). The copolymer sample for elemental analysis was obtained by treating its CHCl$_3$ solution with a disodium ethylenediaminetetraacetate dihydrate aqueous solution, which was adjusted to ca. pH = 8 by ammonia and ammonium chloride, by washing the resulting CHCl$_3$ solution, evaporating the solvent, and drying under vacuum at ambient temperature. Anal. Calcd for (C$_{34}$H$_{44}$N$_2$O$_4$)$_n$: C, 74.97; H, 8.14; N, 5.14. Found: C, 74.07; H, 8.01; N, 4.84. Other diyne/maleimide copolymerizations were carried out similarly to the **16**/**2b** copolymerization. Copolymers **19a**, **19b**, **19c**, and **21a** were isolated by CH$_2$Cl$_2$/diethyl ether, CH$_2$Cl$_2$/hexane, CH$_2$Cl$_2$/diethyl ether, and CH$_2$Cl$_2$/hexane solvent systems, respectively. **19a**: IR (film, cm^{-1}) 3066, 1772, 1711, 1597, 1376, 1190, 744, 690; ^{1}H NMR 0.90−1.55 (m), 1.55−1.85 (m), 1.85−2.17 (m), 2.17−2.44 (m), 2.93−3.24 (m), 3.58−3.81 (m), 5.49 (br s), 7.03−7.53 (m); ^{13}C NMR 23.5−44.3 (m), 126.1, 126.3, 126.8, 128.8, 129.1, 131.5, 135.3, 144.1, 174.6, 175.6, 175.8. **19b**: IR (film, cm^{-1}) 1767, 1698, 1399, 1171, 775; ^{1}H NMR 0.84 (t, $J = 6.6$), 0.97−1.75 (m), 1.75−1.97 (m), 2.15−2.36 (m), 2.80−3.00 (m), 3.22−3.49 (m), 3.52 (br s), 3.58 (br s), 5.28 (br s); ^{13}C NMR 14.0−31.7 (m), 35.1, 38.0, 38.7, 38.8, 43.6, 43.7, 44.1, 126.3, 134.6, 143.5, 175.5, 176.5, 176.7. Anal. Calcd for (C$_{36}$H$_{56}$N$_2$O$_4$)$_n$: C, 74.44; H, 9.27; N, 4.82. Found: C, 73.12; H, 9.55; N, 4.64. **19c**: IR (film, cm^{-1}) 1767, 1699, 1405, 1349, 1226, 1127, 754; ^{1}H NMR 0.96−1.13 (m), 1.13−1.76 (m), 1.76−2.00 (m), 2.18−2.36 (m), 2.84−3.00 (m), 3.31−3.68 (m), 5.24−5.32 (m); ^{13}C NMR 12.6−44.1 (m), 126.2, 134.6, 143.3, 175.4, 176.4, 176.6. **21a**: IR (film, cm^{-1}) 3066, 1768, 1712, 1597, 1498, 1379, 1199, 742, 690; ^{1}H NMR 0.69−0.93 (m, 6 H), 0.93−1.86 (m, 8 H), 1.86−2.20 (m, 4 H), 2.34−2.66 (m, 4 H), 2.84−3.27 (m, 4 H), 7.00−7.60 (m, 10 H); ^{13}C NMR 8.2−45.0 (m), 126.2, 128.5, 129.0, 131.6, 138.58, 138.90, 139.83, 140.01, 140.16, 174.8.

Table 1. Nickel(0)-Catalyzed Cycloaddition of Phenylacetylene (1a) with N-Substituted Maleimides (2) To Form Bicyclo[2.2.2]oct-7-enes (9) (Eq 1)[a]

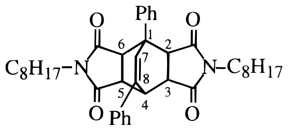
					9	
2	**2**/**1a**[b]	catalyst	temp, °C	time, h		yield, %[c]
a	2	Ni(COD)$_2$/2 PPh$_3$	90	3	**aa**	68
b	1	Ni(CO)$_2$(PPh$_3$)$_2$	90	3	**ab**	53
	1		90	20		54
	2		90	3		97
	2		60	3		39
	2		40	3		11
	1	Ni(COD)$_2$/2 PPh$_3$	90	3		30
	1		90	20		31
	2		90	3		99
	2		90	3		88[d]
	2	Ni(COD)$_2$	90	3		40
c	2	Ni(COD)$_2$/2 PPh$_3$	90	3	**ac**	20[e]

[a] **1a**, 0.5 mmol; Ni/**1a** = 0.10; solvent, THF, 3 mL. [b] A molar ratio. [c] Isolated yield by PLC, based on 100% conversion of **1a** to **9**. [d] Ni/**1a** = 0.02. [e] Heterogeneous reaction.

Results and Discussion

Synthesis of Bicyclo[2.2.2]oct-7-enes. The Ni(CO)$_2$(PPh$_3$)$_2$-catalyzed cycloaddition of phenylacetylene (**1a**) with *N*-methylmaleimide (**2d**) reported by Chalk proceeded heterogeneously on account of the poor solubility of the 2:1 adduct **3ad** in the benzene reaction solvent (precipitation of **3ad** occurred during the reaction (Scheme 2)).[12] The low solubility of the cycloadduct may complicate the reaction and may be inconvenient for its application to the synthesis of a soluble diyne/maleimide cycloaddition copolymer (eq 2). It is expected that the introduction of a long *N*-alkyl substituent into the maleimide will generate a soluble cycloadduct. Therefore, the nickel(0)-catalyzed 2:2 double-cycloaddition reaction of **1a** with *N*-octylmaleimide (**2b**) was studied first. In addition, THF, which is more polar than benzene, was used as the reaction solvent.

The results of the Ni(CO)$_2$(PPh$_3$)$_2$-catalyzed cycloaddition of **1a** with **2b** in THF are summarized in Table 1. The reaction proceeded homogeneously. An equimolar **1a**/**2b** reaction (**2b**/**1a** = 1) at 90 °C for 3 h gave bicyclo[2.2.2]oct-7-ene **9ab** (hexahydro-2,6-octyl-4,9-diphenyl-4,8-ethenobenzo[1,2-*c*:4,5-*c*′]dipyrrole-1,3,5,7-(2*H*,6*H*)-tetrone), which is a 2:2 monoyne/maleimide cycloadduct, only in ca. 50% yield. The molar ratio of **2b** to **1a** was found to be important for the efficient formation of **9ab**. Use of a 2-fold excess of **2b** to **1a** (**2b**/**1a** = 2) afforded **9ab** chemo- and regioselectively in excellent yield (Scheme 2).



9ab

Aromatization of the 1,3-cyclohexadiene cycloadduct by dehydrogenation is known to be a secondary reaction in the transition-metal-catalyzed 2:1 monoyne/alkene cycloaddition.[10a,b] The aromatized product **6ab** of the 2:1 adduct **3ab** was obtained as a side product in 8% yield, along with the decreased formation of **9ab** (53% yield) in the equimolar **1a**/**2b** reaction.[15] This result suggests that the use of a 2-fold excess of **2b** to **1a** promoted the noncatalyzed Diels–Alder cycloaddition reaction of **3ab** with **2b** to form **9ab**, suppressing the formation of **6ab** (Scheme 2). 1,3,5-Triphenylbenzene was not detected by GC to be a side product in the equimolar **1a**/**2b** reaction.

Table 2. Ligand Effect upon the Nickel(0)-Catalyzed Cycloaddition of Phenylacetylene (1a) with *N*-Octylmaleimide (2b) To Form Bicyclo[2.2.2]oct-7-ene (9ab) (Eq 1)[a]

catalyst	**2b**/**1a**[b]	**9ab** yield, %[c]
Ni(COD)$_2$/2 PPh$_3$	1	30
	2	99
Ni(COD)$_2$/2 P(2-MeC$_6$H$_4$)$_3$	2	62
Ni(COD)$_2$/2 P(2,4,6-Me$_3$C$_6$H$_2$)$_3$	2	38
Ni(COD)$_2$/dppe	1	23
	2	72
Ni(COD)$_2$/dppb	2	61
Ni(COD)$_2$/2 P(*c*-C$_6$H$_{11}$)$_3$	2	74
Ni(COD)$_2$	2	40

[a] **1a**, 0.5 mmol; Ni/**1a** = 0.10; solvent, THF, 3 mL; temperature, 90 °C; time, 3 h. [b] A molar ratio. [c] Isolated yield by PLC, based on 100% conversion of **1a** to **9ab**.

A reaction temperature around 90 °C was necessary for the efficient formation of **9ab**. A nickel(0) catalyst generated from bis(1,5-cyclooctadiene)nickel (Ni(COD)$_2$) and 2 equiv of PPh$_3$ was also effective. This finding suggests that a CO ligand of the Ni(CO)$_2$(PPh$_3$)$_2$ catalyst did not participate in the nickel-catalyzed **1a**/**2b** cycloaddition reaction. Ni(COD)$_2$ itself also induced the formation of **9ab**, although its efficiency was not high. The effect of the ligand upon **9ab** formation was examined using the nickel(0) catalyst generated from Ni(COD)$_2$ and ligand (Table 2). Introduction of a methyl group to an *ortho*-position of the phenyl group of PPh$_3$ decreased the ligand efficiency. Introduction of three methyl groups to the 2,4,6-positions of the phenyl group of PPh$_3$ completely suppressed the reaction. 1,2-Bis(diphenylphosphino)ethane, 1,4-bis(diphenylphosphino)butane, and tricyclohexylphosphine were less effective than PPh$_3$. Triphenyl phosphite also gave **9ab**, but its yield was not determined due to unsuccessful purification. Thus, PPh$_3$ was the most effective among the various ligands examined. Detection of other two regioisomers, **10ab** and **11ab**, was not carried out because regioisomer **9ab** was obtained in excellent yield, provided a 2-fold excess of **2b** to **1a** was used.

The compound **9ab** was identified by IR, ^{1}H NMR, and ^{13}C NMR spectroscopies, and FAB mass spectroscopy together with elemental analysis. The IR spectrum showed ν(C=O) absorptions that are indicative of a five-membered cyclic imide at 1768 and 1702 cm^{-1}. Its ^{1}H NMR spectrum exhibited three kinds of methine proton signals typical of a cyclohexane skeleton at δ 4.33 (td, J = 3.1, 1.6, 1 H, H-4), 3.45 (d, J = 8.1, 2 H, H-2, 6), and 3.29 (dd, J = 8.2, 3.1, 2 H, H-3, 5), along with an olefinic proton signal at δ 6.86 (br s, 1 H, H-7). The ^{13}C NMR spectrum of **9ab** (Figure 1) showed 2 C=O signals at δ 174.6 and 176.3, 3 signals for the C=C carbon atoms without protons at δ 137.0, 138.7, and 142.7, 9 signals for the C=C carbon atoms with protons at δ 123.9–129.1, and 12 saturated carbon signals at δ 14.2–49.3. The compound **9ab** should exhibit 7 signals for the C=C carbon atoms with protons. The 9 signals observed suggest restricted rotation of the phenyl group.

The stereochemistry of the nickel(0)-catalyzed monoyne/maleimide cycloaddition reaction was not investi-

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[15] The aromatization of the 2:1 alkyne/alkene cycloadduct was described in the nickel(0)-catalyzed cycloaddition of hexa-2,4-diyne, i.e., a conjugated diyne with **1a**.[12]

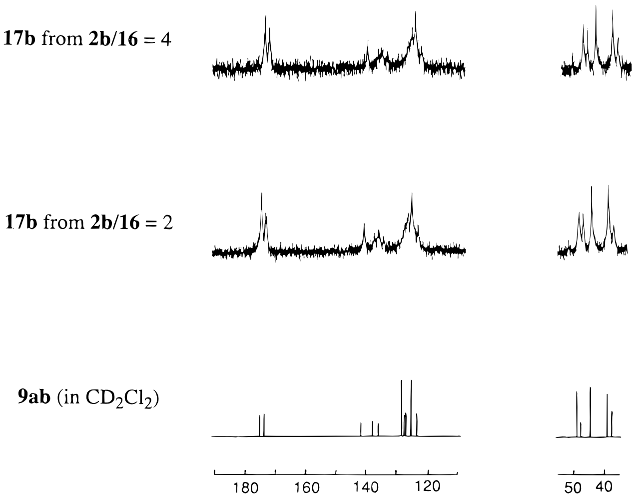

Figure 1. ^{13}C NMR spectra of the C=C, C=O, cyclohexane ring consisting of C-1–C-6, and NCH$_2$ signals of the bicyclo[2.2.2]oct-7-ene derivative **9ab** and the poly(bicyclo[2.2.2]oct-7-ene) **17b** (CDCl$_3$, δ-ppm).

gated in the previous study.[12] As for the stereochemistry of the bicyclo[2.2.2]oct-7-ene ring of **9ab**, there are three possibilities, i.e., *exo,exo*-, *exo,endo*-, and *endo,endo*-stereochemistries. The three kinds of ^{1}H NMR methine signals and two kinds of ^{13}C NMR C=O signals indicate that **9ab** exists as an *exo,exo*- or *endo,endo*-stereoisomer. It is known that racemic (1*S*,2*R*,3*R*)-3-methyl-4-cyclohexene-1,2-dicarboxylic anhydride isomerizes to the more stable racemic (1*R*,2*S*,3*R*)-isomer at 190 °C in the presence of *N*,*N*-dibutylaniline.[16] No change was observed when **9ab** was heated with *N*,*N*-dibutylaniline at 220 °C. This finding suggests that **9ab** is the more stable stereoisomer, namely, the *exo,exo*-isomer (*vide post*).

Phenylacetylene (**1a**) also reacted with *N*-phenylmaleimide (**2a**) homogeneously in THF to afford bicyclo[2.2.2]oct-7-ene **9aa** in 68% yield (Table 1). In contrast, the reaction of **1a** with *N*-ethylmaleimide (**2c**) was heterogeneous in THF: a precipitate was formed during the reaction, and bicyclo[2.2.2]oct-7-ene **9ac** was obtained only in 20% yield (Table 1). Thus, the homogeneity or the heterogeneity of the nickel(0)-catalyzed monoyne/maleimide cycloaddition reaction in THF depended upon the monoyne/maleimide combination, and the use of *N*-octylmaleimide was significant to the efficient 2:2 monoyne/maleimide cycloaddition. These results were related to the synthesis of a soluble poly(bicyclo[2.2.2]oct-7-ene) by the nickel(0)-catalyzed diyne/maleimide cycloaddition copolymerization (eq 2, *vide post*).

As for the nickel(0)-catalyzed cycloaddition of an aliphatic terminal monoyne with the N-substituted maleimide, Chalk reported only the formation of one regioisomer **10** (R = Bu, R′ = Me) in 32% yield in the Ni(CO)$_2$(PPh$_3$)$_2$-catalyzed reaction of 1-hexyne with **2d**.[12] We have now found that another new regioisomeric bicyclo[2.2.2]oct-7-ene **9bb** is formed along with **10bb** in the Ni(CO)$_2$(PPh$_3$)$_2$-catalyzed reaction of 1-pentyne (**1b**) with **2b** (Table 3). An excess of **2b** relative to **1b** was also necessary for the efficient formation of **9bb** and **10bb**. The effect of two of the ligands, i.e., tri-*o*-tolylphosphine and dppe, upon the regiochemistry of the reaction was not remarkable, although **10bb** was produced in higher yield than **9bb** in the reaction using the former ligand. It is noteworthy that Ni(COD)$_2$ itself produced **9bb** without **10bb**, although its yield was not high. Detection of the third regioisomer **11bb** was not carried out because the combined yield of **9bb** and **10bb** was excellent, provided a 2-fold excess of **2b** to **1b** was used. The monoyne **1b** also underwent a nonregioselective cycloaddition with **2a** to give two regioisomers, **9ba** and **10ba**, efficiently (Table 3).

Table 3. Nickel(0)-Catalyzed Cycloaddition of 1-Pentyne (1b) with N-Substituted Maleimides (2) To Form Bicyclo[2.2.2]oct-7-enes (9 and 10) (Eq 1)[a]

			9		10	
2	catalyst	2/1[b]		yield, %[c]		yield, %[c]
a	Ni(COD)$_2$/2 PPh$_3$	2	**ba**	55	**ba**	44
b	Ni(CO)$_2$(PPh$_3$)$_2$	1	**bb**	36	**bb**	26
		2		52		35
	Ni(COD)$_2$/2 PPh$_3$	2		51		45
	Ni(COD)$_2$/2 P(2-MeC$_6$H$_4$)$_3$	2		42		58
	Ni(COD)$_2$/dppe	2		46		*d*
	Ni(COD)$_2$	2		54		0

[a] **1b**, 0.5 mmol; Ni/**1b** = 0.10; solvent, THF, 3 mL; temperature, 90 °C; time, 3 h. [b] A molar ratio. [c] Isolated yield by PLC, based on 100% conversion of **1b** to **9** or **10**. [d] Isolation of pure **10bb** by PLC was unsuccessful.

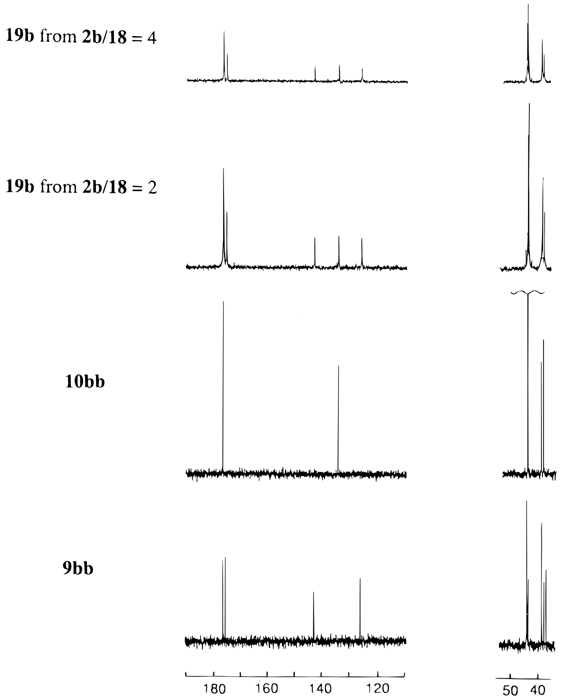

Figure 2. ^{13}C NMR spectra of the C=C, C=O, cyclohexane ring consisting of C-1–C-6, and NCH$_2$ signals of the bicyclo[2.2.2]oct-7-ene derivatives **9bb** and **10bb** along with those of the poly(bicylo[2.2.2]oct-7-ene)s **19a** and **19b** (CDCl$_3$, δ-ppm).

Bicyclo[2.2.2]oct-7-enes **9bb** and **10bb** were identified by IR, ^{1}H NMR, and ^{13}C NMR spectroscopies. The ^{1}H NMR spectrum of **9bb** exhibited an olefinic proton signal at δ 5.27 (br s, 1 H, H-7) and three kinds of methine proton signals at δ 3.53 (br s, 1 H, H-4) and 2.80–3.00 (m, 4 H, H-2, 3, 5, 6), while the ^{1}H NMR spectrum of **10bb** showed two kinds of methine proton signals at δ 3.58 (s, 2 H, H-1,4) and 2.89 (s, 4 H, H-2, 3, 5, 6) without an olefinic proton signal. The partial and characteristic ^{13}C NMR signals are shown in Figure 2: **9bb** exhibited two C=O, two C=C, and four cyclohexane ring carbon atom signals along with one NCH$_2$ signal,

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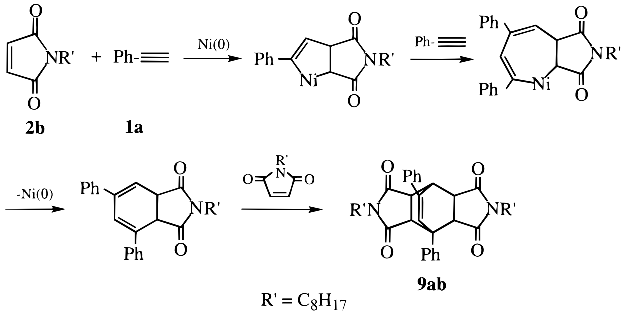
(16) Itamura, S.; Yamada, M.; Tamura, S.; Matsumoto, T.; Kurosaki, T. *Macromolecules* **1993**, *26*, 3490.

Table 4. Nickel(0)-Catalyzed Cycloaddition of 3-Hexyne (12a) with *N*-Substituted Maleimides (2) To Form Bicyclo[2.2.2]oct-7-enes (13) (Eq 3)[a]

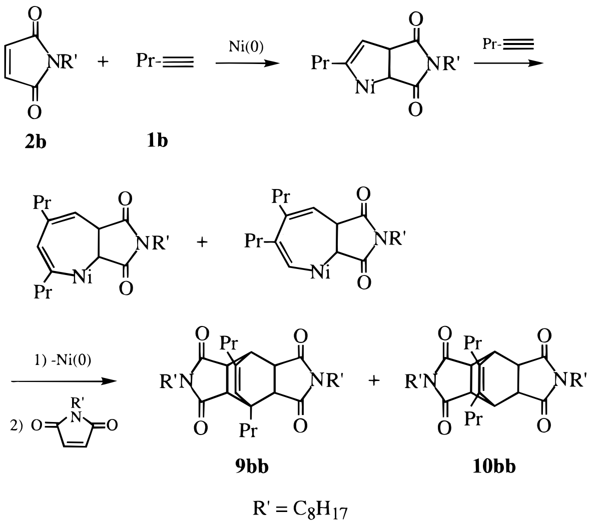
			13	
2	**2**/**12a**[b]	temp, °C		yield, %[c]
a	2	90	**aa**	51
	2	90		80[d]
	2	90		91[e]
	2	110		100
c	2	110	**ac**	88

[a] **12a**, 0.5 mmol; Ni(COD)$_2$/**12a** = 0.10; PPh$_3$/Ni = 2; solvent, THF, 3 mL; time, 3 h. [b] A molar ratio. [c] Isolated yield by PLC, based on 100% conversion of **12a** to **13**. [d] **12a**, 1 mmol; solvent, 4 mL. [e] **12a**, 1.5 mmol.

Scheme 3



Scheme 4



while **10bb** showed those of one C=O, one C=C, and two cyclohexane ring carbon atoms. The cycloadducts **9ba** and **10ba** were similarly identified.

There was previously no report of the cycloaddition of an ordinary internal monoyne with the N-substituted maleimide. 3-Hexyne (**12a**) was found to react with **2a** to afford bicyclo[2.2.2]oct-7-ene **13aa** in excellent yield at the elevated reaction temperature of 110 °C, while the reaction at 90 °C gave **13aa** only in 51% yield (eq 3, Table 4). This result suggests that the internal monoyne was less reactive than the terminal monoyne in the nickel(0)-catalyzed 2:2 monoyne/maleimide cycloaddition reaction. An increase of the substrate concentration raised the yield of **13aa** up to 91% at 90 °C. The **12a**/**2c** reaction in THF was homogeneous and afforded **13ac** in high yield, but the corresponding reaction in benzene was heterogeneous. Thus, the use of the THF solvent was also important.

The nickel(0)-catalyzed **1a**/**2b** double-cycloaddition reaction afforded the 1,8-diphenyl-substituted bicyclo[2.2.2]oct-7-ene **9ab** regioselectively. This regiochemistry is unusual[10b,c] and suggests that the reaction does not proceed predominantly via the usual 2,5-diphenylnickelacyclopentadiene intermediate, which produces the 1,4-diphenyl-substituted bicyclo[2.2.2]oct-7-ene **11ab** (Scheme 2) after the reaction with **2b**. Therefore, it is reasonable to assume that an initial monoyne/alkene coupling to generate a metallacyclopentene intermediate occurs (Scheme 3):[10c] **1a**, **2b**, and the nickel(0) catalyst first form a nickelacyclopentene intermediate in which a phenyl group takes the position adjacent to the nickel atom to avoid a steric interaction with an imide carbonyl group. Subsequent **1a** insertion into the nickelacyclopentene proceeds, so as to diminish a steric interaction between two phenyl groups, to produce a seven-membered nickelacycle intermediate having a second phenyl group at the position distant from the first phenyl group. Reductive elimination of the nickel(0) catalyst from the seven-membered nickelacycle intermediate generates **9ab** regioselectively. On the contrary, in the nickel(0)-catalyzed **1b**/**2b** reaction (Scheme 4), the formation of the nickelacyclopentene intermediate occurs similarly to the **1a**/**2b** reaction, but the second **1b** insertion into the nickelacyclopentene occurs nonregioselectively to afford the two regioisomers **9bb** and **10bb** because the Pr group is less sterically demanding than the phenyl group.

The stereochemistry of the nickel(0)-catalyzed bicyclo[2.2.2]oct-7-ene formation was not investigated previously.[12] In the present study, we determined decisively the stereochemistry of the bicyclo[2.2.2]oct-7-ene. There are three possibilities, i.e., *exo*,*exo*-, *exo*,*endo*-, and *endo*,*endo*-stereochemistries. The ^{1}H and ^{13}C NMR spectral data indicate that the bicyclo[2.2.2]oct-7-ene has an *exo*,*exo*- or *endo*,*endo*-stereochemistry. Thus, in its ^{1}H NMR spectrum, no difference was observed between H-2 and H-6 and also between H-3 and H-5. Similarly, in the ^{13}C NMR spectrum of the bicyclo[2.2.2]oct-7-ene, the C-2 and C-6 and also the C-3 and C-5 showed the same signals, respectively. Moreover **10ba**, **10bb**, **13aa**, and **13ac** showed one ^{13}C NMR C=O signal while **9aa**, **9ab**, **9ac**, and **9bb** exhibited two ^{13}C NMR C=O signals. These findings indicate that all of the bicyclo[2.2.2]oct-7-enes were formed stereoselectively and have an *exo*,*exo*- or *endo*,*endo*-stereochemistry. No isomerization of **9ab** by the base suggests the *exo*,*exo*-stereoisomer formation (vide ante). Crystallization of **9ab** was unsuccessful, but a colorless prismatic crystal of **13ac** was obtained from diethyl ether/hexane at 0 °C. X-ray structural analysis confirmed the *exo*,*exo*-stereochemistry of **13ac**. The stereoview of **13ac** is given in Figure 3. It is reasonable to assume that other bicyclo[2.2.2]oct-7-enes, other than **13ac**, have the same *exo*,*exo*-stereochemistry based on the two findings, i.e., the determined *exo*,*exo*-stereochemistry of **13ac** and their ^{1}H and ^{13}C NMR spectral data. A reasonable explanation for the *exo*,*exo*-stereochemistry is given in Scheme 5, in which the cycloaddition of acetylene with N-substituted maleimide is represented as the simplest example: the addition of the second maleimide molecule to the 1,3-cyclohexadiene intermediate proceeds from the opposite side of the imide group, according to the *endo*-selectivity of the Diels–Alder reaction, to produce the *exo*,*exo*-fused bicyclo[2.2.2]oct-7-ene ring.

Thus, we have developed in the present study the efficient and chemoselective nickel(0)-catalyzed 2:2 monoyne/maleimide double-cycloaddition to the bicyclo-

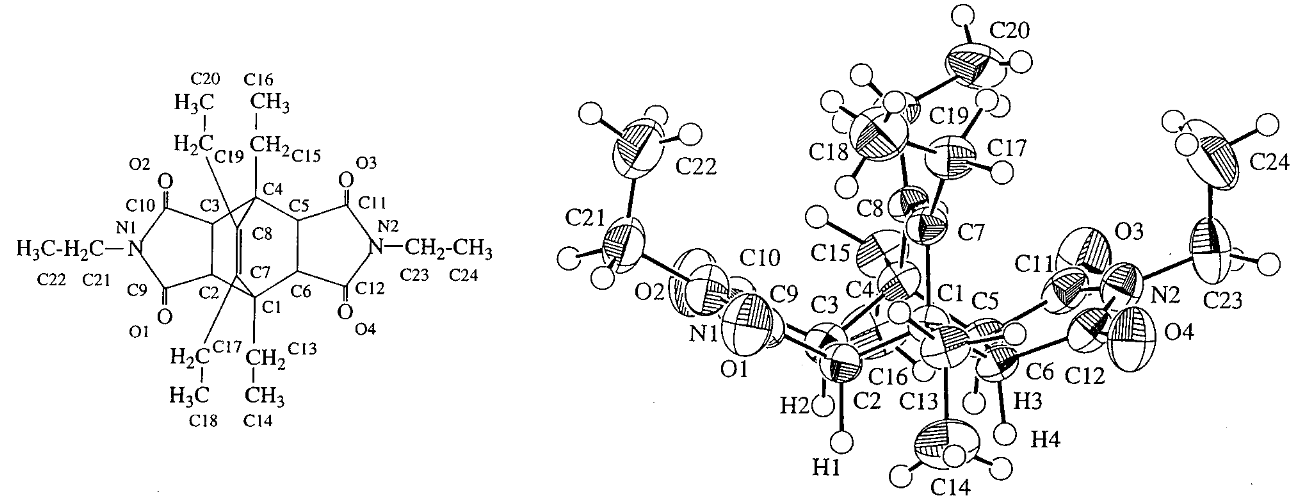
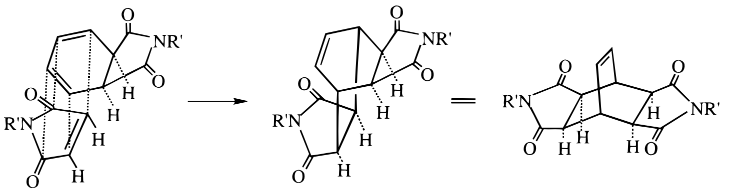


Figure 3. ORTEP view and numbering scheme of the bicyclo[2.2.2]oct-7-ene derivative **13ac**.

Scheme 5



[2.2.2]oct-7-ene (eq 1) by using a highly soluble N-substituted maleimide, such as *N*-octylmaleimide, an excess amount of maleimide relative to monoyne, and THF as the solvent. A variety of bicyclo[2.2.2]oct-7-enes were prepared in high to excellent yields from the aromatic and aliphatic terminal monoynes, along with the aliphatic internal monoyne, and N-alkyl- and N-aryl-substituted maleimides. This reaction is the first example of an efficient transition-metal-catalyzed intermolecular 2:2 monoyne/alkene double-cycloaddition reaction involving the 1,3-cyclohexadiene intermediate. Examples of an effective transition-metal-catalyzed intermolecular 2:1 monoyne/alkene cycloaddition to the 1,3-cyclohexadiene cycloadduct are few,[10a−c] while some efficient transition-metal-catalyzed partially intramolecular diyne/alkene and enyne/monoyne cycloadditions to form the 1,3-cyclohexadiene moieties are known.[10d] The palladium-catalyzed cycloaddition of dimethyl acetylenedicarboxylate with norbornene to form 1,2,3,4-tetrakis(methoxycarbonyl)benzene seems to be the only example of the former cycloaddition.[11] The generalization of this chemistry to more electron-rich alkynes, however, has not been reported.[10c] Formation of a mixture of isomeric 1,3-cyclohexadienes by the titanium-catalyzed 2:1 alkyne/alkene cycloaddition has recently been reported, but its synthetic aspect is not clear.[17] Therefore, the present bicyclo[2.2.2]oct-7-ene synthesis via the 1,3-cyclohexadiene intermediate generated by the nickel(0)-catalyzed intermolecular 2:1 monoyne/maleimide cycloaddition is noteworthy.

Synthesis of Poly(bicyclo[2.2.2]oct-7-ene)s. On the basis of the efficient nickel(0)-catalyzed 2:2 monoyne/maleimide double-cycloaddition reaction (eq 1) presently found, it would be interesting to develop a nickel(0)-catalyzed diyne/maleimide double-cycloaddition copolymerization to form a poly(bicyclo[2.2.2]oct-7-ene) (eq 2). This copolymerization is characterized by a unique process in which two maleimide molecules connect two diyne molecules by the double-cycloaddition to generate a copolymer repeat unit containing the bicyclo[2.2.2]oct-7-ene ring and provides a cycloaddition copolymer of poly(bicyclo[2.2.2]oct-7-ene) having a wholly carbon backbone with an imide functionality. This poly(bicyclo[2.2.2]oct-7-ene) synthesis is a new type of transition-metal-catalyzed diyne cycloaddition copolymerization.

The results of the copolymerization of 1,4-diethynylbenzene (**16**) with **2b** (eq 4) are summarized in Table 5. Both $Ni(CO)_2(PPh_3)_2$ and $Ni(COD)_2/2\ PPh_3$ catalysts were effective to afford poly(bicyclo[2.2.2]oct-7-ene) **17b** with a GPC molecular weight as high as 35 000, which corresponds to n (a calculated degree of polymerization, eq 4) = 64. The copolymer **17b** was obtained as a pale yellow powder, which is soluble in THF, CH_2Cl_2, and $CHCl_3$, but insoluble in AcOEt and diethyl ether. $Ni(COD)_2$ alone gave an insoluble copolymer, the formation of which may be ascribed to copolymer branching and/or cross-linking[5c,d] originating from the formation of diyne trimerization units in the copolymer.

The poly(bicyclo[2.2.2]oct-7-ene) **17b** was identified by IR, ^1H NMR, and ^{13}C NMR spectroscopies. It is noteworthy that copolymer **17b** obtained from monomer feed ratios of **2b**/**16** = 2 and 4 showed almost identical IR, ^1H NMR, and ^{13}C NMR spectra. The copolymer **17b** showed two IR ν(C=O) absorptions indicative of a five-membered cyclic imide at 1771 and 1703 cm^{-1}. Its ^1H NMR spectrum exhibited the signals of the bicyclo[2.2.2]oct-7-ene ring protons at δ 3.44 (br s), 3.60 (br s), 4.28−4.53 (m), and 6.71−7.12 (m). The ^{13}C NMR spectrum of **17b** showed the saturated carbon signals at δ 14.1, 22.6, 26.7, 27.6, 29.1, 31.7, 37.5 (m), 38.9 (m), 44.6 (m), 47.8 (m), and 49.1 (m) and the unsaturated carbon signals at δ 123.2−129.4 (m, CH=), 135.0−138.7 (m, C=C), 141.5−142.6 (m, C=C), 173.7−175.1 (m, C=O), and 175.1−176.8 (m, C=O). These signals were similar

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(17) Balaich, G. J.; Rothwell, I. P. *J. Am. Chem. Soc.* **1993**, *115*, 1581.

Table 5. Nickel(0)-Catalyzed Cycloaddition Copolymerization of 1,4-Diethylbenzene (16) with *N*-Octylmaleimide (2b) To Form Poly(bicyclo[2.2.2]oct-7-ene) (17b) (Eq 4)[a]

				17b		
catalyst	Ni/**16**[b]	**2b**/**16**[b]	temp, °C	yield, %[c]	M_n[d]	M_w/M_n[d]
$Ni(CO)_2(PPh_3)_2$	0.1	4	90	50	19 800	1.9
	0.1	2	90	51	27 200	2.1
	0.05	2	90	50	26 800	3.5
	0.1	2	110	60	34 600	1.9
	0.1	2	130	36	27 100	2.6
$Ni(COD)_2$/2 PPh_3	0.1	2	90	50	16 000	2.4
$Ni(COD)_2$	0.1	2	90	91[e]		

[a] **16**, 0.25 mmol; solvent, THF, 5 mL; time, 20 h. [b] A molar ratio. [c] Based on 100% conversion of **16** to **17b**. [d] Determined by GPC with polystyrene standards in $CHCl_3$. [e] A CH_2Cl_2-insoluble copolymer.

Table 6. Nickel(0)-Catalyzed Cycloaddition Copolymerization of 1,11-Dodecadiyne (18) and 3,11-Tetradecadiyne (20) with N-Substituted Maleimides (2) To Form Poly(bicyclo[2.2.2]oct-7-ene)s (19) and (21) (Eqs 5 and 6)[a]

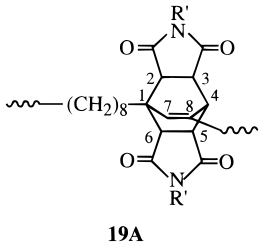
				19 and **21**			
diyne	**2**	**2**/diyne[b]	temp, °C		yield, %[c]	M_n[d]	M_w/M_n[d]
18	**a**	4	110	**19a**	70	15 900	1.3
		2	110		75	12 400	2.3
	b	4	90	**19b**	96	9 300	1.8
		2	90		70	12 400	2.4
	c	4	110	**19c**	78	5 000	1.6
20	**a**	4	110	**21a**	75	6 300	2.8

[a] Diyne, 0.25 mmol; $Ni(CO)_2(PPh_3)_2$/diyne = 0.1; solvent, THF, 2 mL; time, 20 h. [b] A molar ratio. [c] Based on 100% conversion of **18** and **20** to **19** and **21**, respectively. [d] Determined by GPC with polystyrene standards in $CHCl_3$.

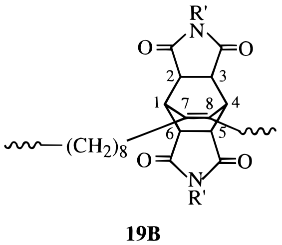
to those of **9ab**, which is a model compound of the repeat unit of **17b** (Figure 1). These spectral results indicate that the **16**/**2b** cycloaddition copolymerization occurred efficiently to produce **17b**, which has the *exo,exo*-fused 1,8-phenylene-substituted bicyclo[2.2.2]oct-7-ene ring in its repeat unit.

The copolymerization of **16** with **2a** or **2c** gave copolymer **17a** or **17c** (eq 4), respectively, which are insoluble in common organic solvents. Thus, in the **16**/**2** copolymerization, the introduction of a long N-alkyl substituent, such as the octyl group, was necessary for preparing a soluble poly(bicyclo[2.2.2]oct-7-ene) **17**.[18]

Furthermore, 1,11-dodecadiyne (**18**) copolymerized with **2b** to give copolymer **19b** as a colorless resinous solid with a GPC molecular weight as high as 12 400 (n = 21, eq 5 and Table 6). On the basis of the model **1b**/**2b** cycloaddition reaction, **19b** is considered to have two regioisomeric repeat units **19A** and **19B**. Actually, the ^{13}C NMR C=O and C=C signals of **19b** were a superposition of those of **9bb** and **10bb**, which are model compounds of the repeat units of **19A** and **19B**, respectively (Figure 2). The cyclohexane ring C-1–C-6 and NCH_2 carbon signals of **19b** were also clear. There was no difference between the ^{13}C NMR spectra of **19b** prepared from monomer feed ratios of **2b**/**18** = 2 and 4 (Figure 2). In the ^1H NMR spectrum of **19b**, the signals due to H-7, H-4, and H-2,3,5,6 of the bicyclo[2.2.2]oct-7-ene ring of **19A** appeared at δ 5.28 (br s), 3.52 (br s), and 2.80–3.00 (m), respectively, and the signals assignable to H-1,4 and H-2,3,5,6 of **19B** were observed at δ 3.58 (br s) and 2.80–3.00 (m), respectively. These ^1H NMR signals corresponded to those of **9bb** and **10bb**. These spectral results indicate that the **18**/**2b** cycloaddition copolymerization took place efficiently to form **19b**, which has the *exo,exo*-bicyclo[2.2.2]oct-7-ene ring in its repeat unit. The relative content of the two repeat units **19A** and **19B** in **19b** was determined by using the ^1H NMR relative peak areas of the signals at δ 5.28 (H-7 of **19A**) and 2.80–3.00 (H-2,3,5,6 of **19A** and **19B**): **19A**/**19B** = 1.4 for **19b** prepared from **18**/**2b** = 2 and **19A**/**19B** = 1.3 for **19b** prepared from **18**/**2b** = 4. These values corresponded well to those of the model **1b**/**2b** cycloaddition reaction (Table 3), i.e., **9bb**/**10bb** = 1.4 in the **2b**/**1b** = 1 reaction and **9bb**/**10bb** = 1.5 in the **2b**/**1b** = 2 reaction.



19A



19B

The copolymerization of the aromatic diyne **16** with the maleimides **2a** and **2c** not having a long N-alkyl substituent produced insoluble copolymers **17a** and **17c** (vide ante). On the contrary, the aliphatic diyne **18** with an octamethylene chain tethering two C≡C bonds of the diyne afforded soluble copolymers **19a** and **19c** (Table 6). Their ^{13}C NMR C=O and C=C signals were a superposition of those of **9bb** and **10bb**, except for the phenyl signals of **19a**. 3,11-Tetradecadiyne (**20**) copolymerized with **2a** at 110 °C to afford **21a** (eq 6, Table 6).

In the nickel(0)-catalyzed **1a**/**2b** and **1b**/**2b** cycloaddition reactions, the maleimide/monoyne molar ratio was important for the efficient formation of the bicyclo[2.2.2]oct-7-ene: the equimolar reaction did not produce the bicyclo[2.2.2]oct-7-ene in high yield, and the use of a 2-fold excess of the maleimide to the monoyne was necessary for its effective formation (Tables 1 and 3). On the contrary, in the nickel(0)-catalyzed **16**/**2b**, **18**/**2a**, and **18**/**2b** cycloaddition copolymerizations, use of a 2-fold excess of the maleimide (maleimide/diyne =

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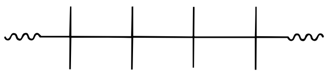
(18) The solubilizing effect of a long alkyl side chain upon a polymer solubility is known. See: (a) Majnusz, J.; Catala, J. M.; Lenz, R. W. *Eur. Polym. J.* **1983**, *19*, 1043. (b) Ballauff, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 253. (c) Rehahn, M.; Schlüter, A-D.; Wegner, G. *Makromol. Chem.* **1990**, *191*, 1991.

4) did not influence remarkably the yield and molecular weight of the poly(bicyclo[2.2.2]oct-7-ene) in comparison to the stoichiometric copolymerization (maleimide/diyne = 2, Tables 5 and 6). These contrasting results are understandable because a copolymer growth reaction of the nickel(0)-catalyzed diyne/maleimide cycloaddition copolymerization is the 1,3-cyclohexadiene ring formation by the cycloaddition involving each one of the terminal C≡C bonds of the two growing poly(bicyclo[2.2.2]oct-7-ene)s and the C═C bond of the maleimide (eq 2), in which the excess maleimide, i.e., maleimide/diyne = 4, may not be necessary.

In the equimolar **1a**/**2b** reaction, the aromatized 2:1 monoyne/maleimide cycloadduct **6ab** was formed as a side product. This type of aromatization reaction is one possible side reaction of the diyne/maleimide cycloaddition copolymerization, which produces the poly(bicyclo[2.2.2]oct-7-ene) contaminated with benzene rings. It is noteworthy, however, that the maleimide/diyne feed ratio did not affect the poly(bicyclo[2.2.2]oct-7-ene) structure: **17b**, **19a**, and **19b** prepared from the maleimide/diyne feed ratios of 2 and 4 showed almost identical IR, ^{1}H and ^{13}C NMR spectra (Figures 1 and 2) each other. This fact indicates that the aromatization of the intermediate 1,3-cyclohexadiene unit of the polymer is not significant in the stoichiometric **16**/**2b**, **18**/**2a**, and **18**/**2b** copolymerization to afford **17b**, **19a**, and **19b**. The difference in the aromatization reactivity between the 1,3-cyclohexadiene ring of the copolymer and that of the 2:1 monoyne/maleimide cycloadduct may partly be ascribed to a sterically suppressed dehydrogenation reaction of the intermediate 1,3-cyclohexadiene moieties of the poly(bicyclo[2.2.2]oct-7-ene).

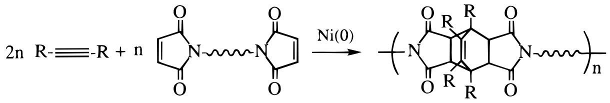
The poly(bicyclo[2.2.2]oct-7-ene)s **17b** and **19b** containing two octyl groups per repeat unit have a unique fence-like structure, **22**. Examples of such fence-like polymers are scarce, although flexible fence-like polymers were prepared by a radical polymerization of diesters of itaconic acid.[19] The poly(bicyclo[2.2.2]oct-7-ene) **17b** may be especially interesting because it has a rigid fence-like structure. The structurally related comb-like polymers have been well-known and have attracted much attention on account of their specific properties, such as side chain crystallization, peculiar mechanical properties, ability for liquid crystal formation, and formation of Langmuir−Blodgett film.[20] Therefore, examination of the physical properties of poly(bicyclo[2.2.2]oct-7-ene)s obtained is a further interesting research subject. The thermal stability of **17b** was examined by TGA under nitrogen: T_{10}, which is the temperature causing a 10% weight loss, was 322 °C.



22

Thus, on the basis of the nickel(0)-catalyzed efficient 2:2 monoyne/maleimide double-cycloaddition reaction, we have synthesized, in the present study, four poly(bicyclo[2.2.2]oct-7-ene)s by the nickel(0)-catalyzed diyne/maleimide double-cycloaddition copolymerization. Previously the poly(2-pyrone)s,[4] poly(2-pyridone)s,[5] poly(pyridine)s,[6] and poly(thiophene)s[7] were prepared by the transition-metal-catalyzed simple diyne cycloaddition copolymerizations with CO_2, isocyanates, nitriles, and elemental sulfur, respectively (Scheme 1). The poly(enone)s were obtained by the diyne terpolymerization with CO and a diene.[8] Except for the poly(pyridine)s[21] and poly(thiophene)s,[22] these cycloaddition copolymers are novel and cannot be easily prepared by other methods of polymer synthesis. These facts indicate that the transition-metal-catalyzed diyne cycloaddition copolymerization has a variety of modifications, i.e., the simple diyne cycloaddition copolymerization, the diyne cycloaddition terpolymerization, and diyne double-cycloaddition copolymerization, and is a useful method of polymer synthesis.

Synthesis of Poly(imide)s. Another interesting application of the nickel(0)-catalyzed efficient 2:2 monoyne/maleimide double-cycloaddition reaction to the synthesis of a novel polymer, besides the poly(bicyclo[2.2.2]oct-7-ene) synthesis, is the nickel(0)-catalyzed monoyne/dimaleimide double-cycloaddition copolymerization to a poly(imide) (eq 7); a preliminary report has recently been published.[23]



(7)

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Supporting Information Available: Text giving experimental details of X-ray data collection and reduction and structure solution and refinement, tables of experimental details, atomic coordinates, anisotropic displacement parameters, bond lengths, bond angles, and torsion angles, and ORTEP views of **13ac** (25 pages). Ordering information is given on any current masthead page.

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(20) For examples: (a) Plate, N. A.; Shibaev, V. P. *J. Polym. Sci., Part D: Macromol. Rev.* **1974**, *8*, 117. (b) Yuki, Y.; Kunisada, H.; Miyake, Y. *Polym. J.* **1991**, *23*, 939.

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(22) For example: Roncali, J. *Chem. Rev.* **1992**, *92*, 711.

(23) Tsuda, T.; Shimada, M.; Mizuno, H. *J. Chem. Soc., Chem. Commun.* **1996**, 2371.