Nickel(0)-catalyzed monoyne-maleimide double-cycloaddition and its application to nickel(0)-catalyzed diyne-maleimide, monoyne-dimaleimide, and diyne-dimaleimide double-cycloaddition copolymerizations

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Abstract

Nickel(0)-catalyzed double-cycloaddition reactions of phenylacetylene (**1a**), 1-pentyne (**1b**), and 3-hexyne (**8a**) with *N*-phenyl- (**2a**), *N*-octyl- (**2b**), and *N*-ethylmaleimide (**2c**) to afford bicyclo[2.2.2]oct-7-enes were investigated in THF. The $Ni(CO)_2(PPh_3)_2$-catalyzed **2b**/**1a** = 2 reaction produced bicyclo[2.2.2]oct-7-ene **6ab** chemo- and regioselectively in excellent yield. The **2b**/**1b** = 2 reaction gave two regioisomeric bicyclo[2.2.2]oct-7-enes in high yield. Internal monoyne **8a** also underwent the double-cycloaddition with **2a** or **2c**. X-ray structural analysis of the **8a**–**2c** cycloadduct demonstrated an *exo*, *exo*-stereochemistry of its bicyclo[2.2.2]oct-7-ene ring. On the basis of these results, nickel(0)-catalyzed diyne-maleimide double-cycloaddition copolymerization was examined. 1,4-Diethynylbenzene (**10a**) copolymerized with **2b** to produce a poly(bicyclo[2.2.2]oct-7-ene) with the molecular weight up to 35,000 while **10a**–**2a**,**c** copolymerizations produced insoluble copolymers. 1,11-Dodecadiyne-**2a**–**c** and 3,11-tetradecadiyne-**2a** copolymerizations yielded soluble poly(bicyclo[2.2.2]oct-7-ene)s. A variety of poly(imide)s with complex structures were prepared by nickel(0)-catalyzed monoyne-dimaleimide and diyne-dimaleimide double-cycloaddition copolymerizations. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Nickel; Alkyne cycloaddition; Cycloaddition copolymerization; Poly(bicyclooctene); Poly(imide)

1. Introduction

The development of a new method of polymer synthesis utilizing a transition metal catalyst's characteristic organic reaction has attracted recent attention [1,2]. The transition metal-catalyzed alkyne cycloaddition reaction has widely been studied as a tool for organic synthesis [3–6] and, in particular, the transition metal-catalyzed intramolecular diyne cycloaddition reaction provides a useful synthetic method of a cyclic compound [6].

On the basis of a new concept, i.e., transition metal-catalyzed intermolecular diyne cycloaddition in the presence of a cycloaddition component, we have recently developed a transition metal-catalyzed diyne cycloaddition copolymerization as a new method of polymer synthesis (Scheme 1) [7–10]. A C≡C bond of the diyne, which undergoes intramolecular cycloaddition with difficulty, is intermolecu-
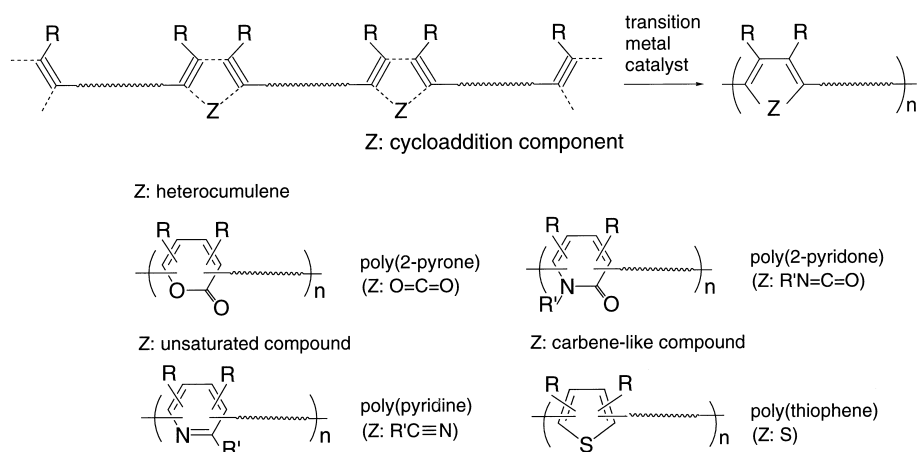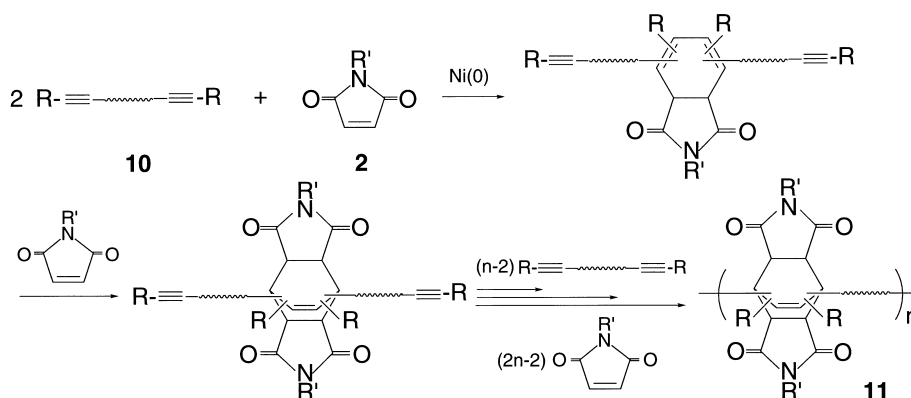
Scheme 1.

larly connected in the presence of a cycloaddition component (Z) by a transition metal catalyst to produce a cycloaddition copolymer containing a heterocycle.

We reported already syntheses of a poly(2-pyrone) [11–17] and a poly(2-pyridone) [18–21] by the nickel(0)-catalyzed diyne cycloaddition copolymerizations with carbon dioxide and an isocyanate, respectively. A poly(pyridine) was obtained by the cobaltocene-catalyzed diyne-nitrile cycloaddition copolymerization [22]. Carbene-type compounds such as carbon monoxide, elemental sulfur, and a low valent transition metal, which can donate an electron pair for cycloaddition, are also interesting cycloaddition components. We recently found the palladium-catalyzed diyne-sulfur cycloaddition copolymerization to form a poly(thiophene) [23] and the cobalt-catalyzed diyne-diene-carbon monoxide cycloaddition terpolymerization to produce a poly(enone) [24]. Other researchers prepared transition metal-containing polymers from diynes and low valent transition metal complexes by utilizing the technique of diyne cycloaddition copolymerization [25–27]. These cycloaddition polymers are novel and cannot easily be prepared by other known methods of polymer synthesis except for the poly(pyridine) [28,29] and poly(thiophene) [30]. The poly(pyridine) and poly(thiophene)
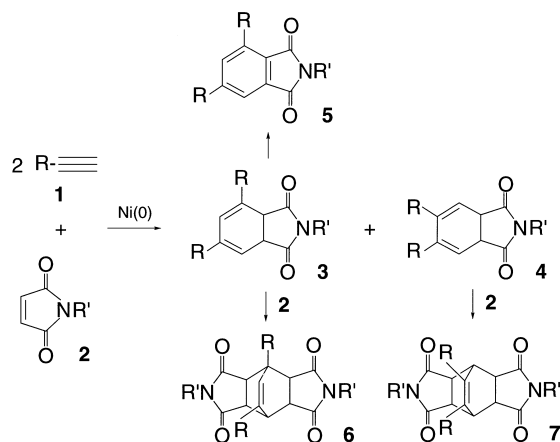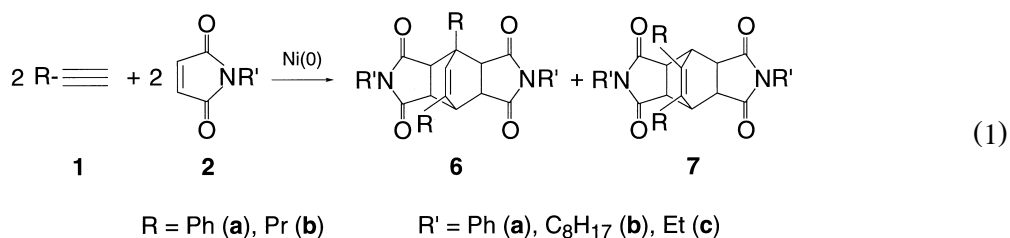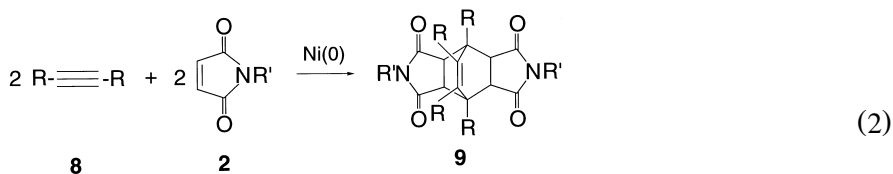

Scheme 2.

Scheme 3.

prepared in this study have new structures. These facts indicate that the transition metal-catalyzed diyne cycloaddition copolymerization and terpolymerization are a useful method of polymer synthesis.

The poly(2-pyrone), poly(2-pyridone), poly(pyridine), and poly(thiophene) contain heterocycles in their repeat units. It is interesting therefore to prepare a new cycloaddition copolymer having a carbon backbone by the diyne cycloaddition copolymerization with an alkene. This copolymerization necessitates an efficient transition metal-catalyzed cycloaddition reaction of two monoyne molecules with one alkene molecule to form a 1,3-cyclohexadiene as a polymer-forming elementary reaction. Extensive studies have been done on the transition metal-catalyzed alkyne cycloaddition [3–6], but examples of an efficient transition metal-catalyzed intermolecular monoyne-alkene cycloaddition reaction to afford a 1,3-cyclohexadiene are very limited [3–6,31] while some examples of the corresponding intramolecular one involving enynes and diynes are known [6].
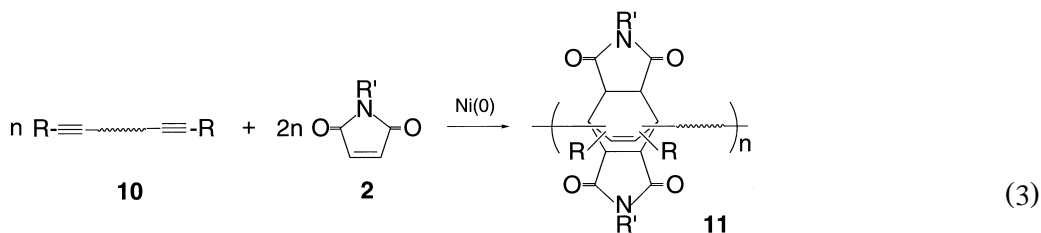
The $Ni(CO)_2(PPh_3)_2$-catalyzed single- and double-cycloaddition reactions of alkynes with *N*-substituted maleimides to form 1,3-cyclohexadienes (**3**) and/or bicyclo[2.2.2]oct-7-enes (**6** and **7**), respectively, were reported by Chalk [32] (Scheme 2). Its efficiency and/or chemoselectivity, however, is not satisfactory for its utilization in the diyne-maleimide cycloaddition copolymerization to a poly(1,3-cyclohexadiene) or a poly(bicyclo[2.2.2]oct-7-ene) (Scheme 3).

In this study, we have explored efficient and chemoselective synthesis of bicyclo[2.2.2]oct-7-enes by the nickel(0)-catalyzed double-cycloaddition of terminal and internal monoynes with *N*-substituted maleimides (Eqs. (1) and (2)) and its application to nickel(0)-catalyzed diyne-maleimide double-cycloaddition copolymerization to afford a poly(bicyclo[2.2.2]oct-7-ene) (Eq. (3)) and nickel(0)-catalyzed monoyne-dimaleimide and diyne-dimaleimide double-cycloaddition copolymerizations to afford a poly(imide) (Eqs. (4) and (5)).
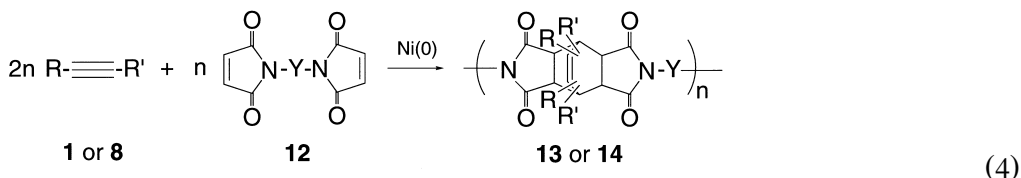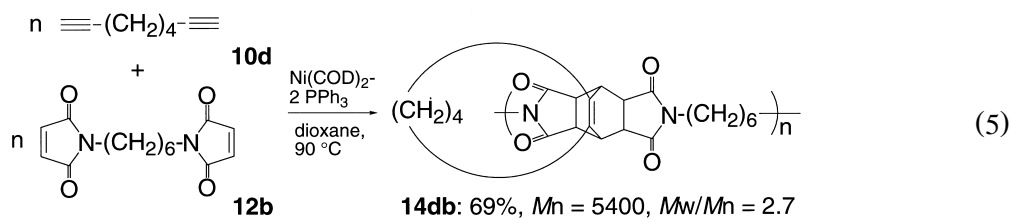

(1)

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

$$2 \ R\text{—}\equiv\text{—}R \ + \ 2 \ \mathbf{2} \xrightarrow{\text{Ni(0)}} \mathbf{9} \tag{2}$$

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

$$n \ R\text{-}\equiv\text{---}\equiv\text{-}R \ + \ 2n \ \mathbf{2} \xrightarrow{\text{Ni(0)}} \mathbf{11} \tag{3}$$

⌇⌇⌇ = 1,4-C_6H_4, R = H (**a**); ⌇⌇⌇ = $(CH_2)_8$, R= H (**b**); ⌇⌇⌇ = $(CH_2)_6$, R = Et (**c**)

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

$$2n \ R\text{-}\equiv\text{-}R' \ + \ n \ \mathbf{12} \xrightarrow{\text{Ni(0)}} \mathbf{13} \ \text{or} \ \mathbf{14} \tag{4}$$

R = Ph, R' = H (**1a**); R = C_8H_{17}, R' = H; (**1b**); R = EtO, R' = H (**1c**); R = R' = C_6H_{13} (**8b**)

Y = 1,1',4,4'-$C_6H_4CH_2C_6H_4$ (**a**); $(CH_2)_6$ (**b**); 1,1',4,4'-$C_6H_4OC_6H_4$ (**c**); 1,4-C_6H_4 (**d**); 1,3-C_6H_4 (**e**)

$$n \ \equiv\text{-}(CH_2)_4\text{-}\equiv \ \ \mathbf{10d} \ + \ n \ \mathbf{12b} \xrightarrow[\substack{\text{dioxane,} \\ 90\,°C}]{\substack{\text{Ni(COD)}_2\text{-} \\ 2\ PPh_3}} \mathbf{14db} \tag{5}$$

14db: 69%, M_n = 5400, M_w/M_n = 2.7

2. Experimental, results, and discussion

2.1. Synthesis of bicyclo[2.2.2]oct-7-enes

The Ni(CO)$_2$(PPh$_3$)$_2$-catalyzed cycloaddition of phenylacetylene (**1a**) with *N*-methylmaleimide reported by Chalk [32] proceeded heterogeneously due to poor solubility of the 1,3-cyclohexadiene

cycloadduct **3** (Scheme 2; R=Ph, R′=Me) in the reaction solvent of benzene. Low solubility of the cycloadduct may be inconvenient for the synthesis of a soluble diyne-maleimide cycloaddition copolymer. Therefore, the nickel(0)-catalyzed double-cycloaddition reaction of monoynes with *N*-substituted maleimides including *N*-octylmaleimide (**2b**) bearing a long *N*-alkyl substituent was studied [33]. In addition, THF, which is more polar than benzene, was used as a reaction solvent.

The results of the monoyne-maleimide double-cycloaddition reactions are summarized in Table 1. The equimolar **1a**–**2b** reaction (**2b**/**1a** = 1) proceeded homogeneously to give bicyclo[2.2.2]oct-7-ene **6ab**, which is a monoyne-maleimide double-cycloaddition product, only in ca. 50% yield. The molar ratio of **2b** to **1a** was important for the efficient formation of **6ab**: use of a two-fold excess of **2b** to **1a** (**2b**/**1a** = 2) afforded **6ab** chemo- and regioselectively in excellent yield. A typical experimental procedure is as follows. A reaction mixture consisting of $Ni(CO)_2(PPh_3)_2$ (0.032 g, 0.050 mmol), **2b** (0.21 g, 1.0 mmol), **1a** (0.055 ml, 0.50 mmol), and THF (3.0 ml) was heated at 90°C for 3 h under nitrogen in a 50-ml stainless steel autoclave. The resulting reaction mixture was concentrated under vacuum to give the residue, which was purified by preparative layer chromatography (PLC) (AcOEt/hexane = 2/1 (v/v)) to afford **6ab** (0.15 g, 97%) as a white powder. A nickel(0) catalyst generated from bis(1,5-cyclooctadiene)nickel ($Ni(COD)_2$) and two equivalents of PPh_3 was also effective. $Ni(COD)_2$ itself induced the formation of **6ab** although its efficiency was not high. PPh_3 was the most effective among various ligands examined such as tri-*o*-tolylphosphine, tricyclohexylphosphine, dppe, and dppb.

In the equimolar **1a**–**2b** reaction, aromatized product **5ab** was obtained as a side reaction product in 8% yield along with the formation of **6ab** (53% yield). This result suggests that the use of a

Table 1

Nickel(0)-catalyzed double-cycloaddition of monoynes (**1** or **8**) with *N*-substituted maleimides (**2**) to form bicyclo[2.2.2]oct-7-enes (**6**, **7** and/or **9**) (Eqs. (1) and (2))[a]

1 or **8**	**2**	**2/1** or **8**[b]	Catalyst	Yield, %[c]		
				6	**7**	**9**
1a	**a**	2	$Ni(COD)_2$-2 PPh_3	**aa**, 68	n.d.[d]	
1a	**b**	1	$Ni(CO)_2(PPh_3)_2$	**ab**, 53	n.d.[d]	
		2		97	n.d.[d]	
		1	$Ni(COD)_2$-2 PPh_3	30	n.d.[d]	
		2		99	n.d.[d]	
				88[e]	n.d.[d]	
			$Ni(COD)_2$	40	n.d.[d]	
1a	**c**	2	$Ni(COD)_2$-2 PPh_3	**ac**, 20[f]	n.d.[d]	
1b	**a**	2	$Ni(COD)_2$-2 PPh_3	**ba**, 55	**ba**, 44	
1b	**b**	1	$Ni(CO)_2(PPh_3)_2$	**bb**, 36	**bb**, 26	
		2		52	35	
			$Ni(COD)_2$-2 PPh_3	51	45	
			$Ni(COD)_2$	54	0	
8a	**a**	2				**aa**, 100[g]
8a	**c**	2				**ac**, 88[g]

[a] **1** or **8**, 0.5 mmol; Ni/**1** or **8** = 0.10; solvent, THF, 3 ml; temperature, 90°C; time, 3 h.
[b] Molar ratio.
[c] Isolated yield by PLC based on 100% conversion of **1** or **8** to **6**, **7** and/or **9**.
[d] Not determined.
[e] Ni/**1a** = 0.02.
[f] Heterogeneous reaction.
[g] Temperature, 110°C.

two-fold excess of **2b** to **1a** promoted non-catalyzed Diels–Alder cycloaddition of **3ab** with **2b** to afford **6ab** suppressing the formation of **5ab** (Scheme 2).

Phenylacetylene (**1a**) also reacted with *N*-phenylmaleimide (**2a**) homogeneously in THF to produce bicyclo[2.2.2]oct-7-ene **6aa** in 68% yield (Table 1). In contrast, the reaction of **1a** with *N*-ethylmalei-mide (**2c**) was heterogeneous in THF to give bicyclo[2.2.2]oct-7-ene **6ac** only in 20% yield (Table 1). Thus, the use of **2b** having a long alkyl substituent was significant to the efficient monoyne-malei-mide double-cycloaddition. Two regioisomeric bicyclo[2.2.2]oct-7-enes **6bb** and **7bb** were produced in the reaction of 1-pentyne (**1b**) with **2b**. It is noteworthy that Ni(COD)$_2$ itself produced **6bb** without **7bb** although its yield was not high. Monoyne **1b** also underwent the non-regioselective cycloaddition with **2a** to give two regioisomers **6ba** and **7ba** efficiently. 3-Hexyne (**8a**) reacted with **2a** to afford bicyclo[2.2.2]oct-7-ene **9aa** in excellent yield at the elevated reaction temperature of 110°C while the reaction at 90°C gave **9aa** only in 51% yield. Increase of the substrate concentration raised the yield of **9aa** up to 91% at 90°C. The **8a**–**2c** reaction in THF was homogeneous to afford **9ac** in high yield, but the corresponding one in benzene was heterogeneous. Thus the use of the THF solvent was also important.

The nickel(0)-catalyzed **1a**–**2b** double-cycloaddition reaction afforded 1,8-diphenyl-substituted bicyclo[2.2.2]oct-7-ene **6ab** regioselectively. This regiochemistry is unusual [4,5] and suggests that the reaction does not proceed predominantly via a usual 2,5-diphenylnickelacyclopentadiene intermediate, which produces a 1,4-diphenyl-substituted bicyclo[2.2.2]oct-7-ene after its reaction with **2b**. There-fore, it is reasonable to assume initial monoyne-alkene coupling to generate a nickelacyclopentene intermediate (Scheme 4) [5]: **1a**, **2b**, and the nickel(0) catalyst form first a nickelacyclopentene intermediate, in which a phenyl group takes the position adjacent to the nickel atom by carbon–carbon bond formation involving an unsubstituted carbon atom. Subsequent insertion of **1a** into the nickelacyclopentene proceeds so as to diminish steric interaction between the two phenyl groups to
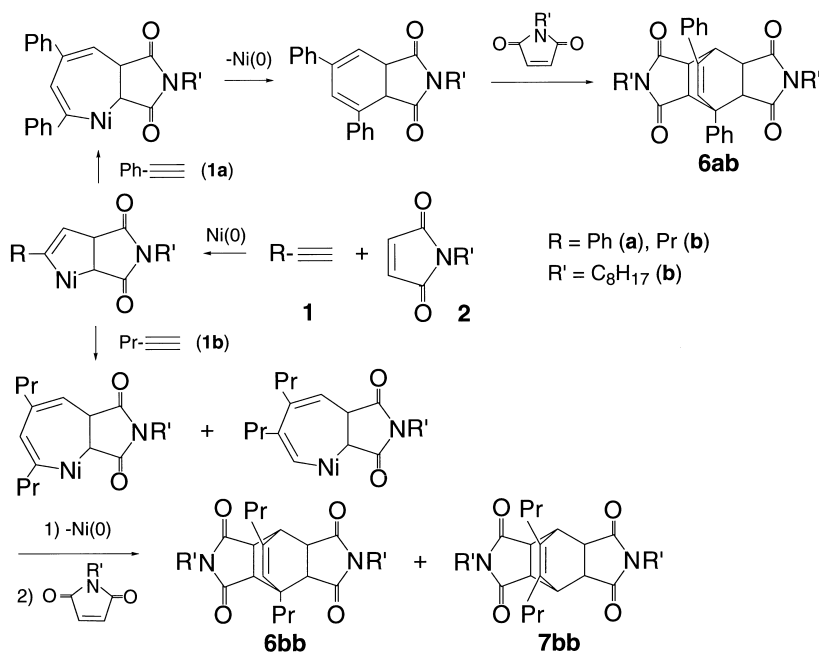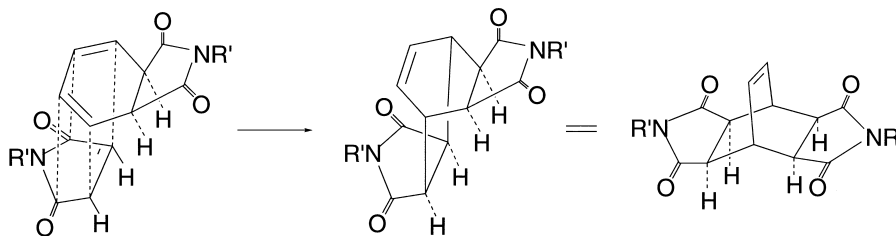

Scheme 4.

produce a seven-membered nickelacycle intermediate having the 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 **6ab** regioselectively. In contrast, 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 insertion of **1b** into the nickelacyclopentene takes place non-regioselectively to afford the two regioisomers **6bb** and **7bb** because a Pr group is less sterically demanding than a phenyl group.

Colorless prismatic crystals of **9ac** were obtained from its diethyl ether-hexane solution at 0°C. X-ray structural analysis confirmed an *exo*, *exo*-stereochemistry of its bicyclo[2.2.2]oct-7-ene ring. Other bicyclo[2.2.2]oct-7-enes are reasonably assumed to have the same stereochemistry on the basis of their ^{1}H and ^{13}C NMR spectral data and the *exo*, *exo*-stereochemistry of **9ac**. A reasonable explanation for this stereochemistry is given in Scheme 5, in which the cycloaddition of acetylene with an *N*-substituted maleimide is represented as the simplest example: cycloaddition of the second maleimide molecule to a 1,3-cyclohexadiene intermediate proceeds from an opposite side to an imide group according to *endo*-selectivity of the Diels–Alder reaction to produce an *exo*, *exo*-fused bicyclo[2.2.2]oct-7-ene ring.

Thus, we have developed an efficient, chemo-, and stereoselective nickel(0)-catalyzed monoyne-maleimide double-cycloaddition reaction to afford a bicyclo[2.2.2]oct-7-ene by using a highly soluble *N*-substituted maleimide, an excess amount of the maleimide to the monoyne, and a THF solvent. A variety of bicyclo[2.2.2]oct-7-enes were prepared in high to excellent yields from aromatic and aliphatic terminal monoynes along with an aliphatic internal monoyne and *N*-alkyl- and *N*-aryl-substituted maleimides. This reaction is the first example of an efficient transition metal-catalyzed intermolecular monoyne-alkene double-cycloaddition reaction involving a 1,3-cyclohexadiene intermediate.

2.2. Synthesis of poly(bicyclo[2.2.2]oct-7-ene)s

On the basis of the efficient nickel(0)-catalyzed monoyne-maleimide double-cycloaddition reaction (Eqs. (1) and (2)), we have developed a nickel(0)-catalyzed diyne-maleimide double-cycloaddition copolymerization to afford a poly(bicyclo[2.2.2]oct-7-ene) (Scheme 3, Eq. (3)) [33,34]. The results of the diyne-maleimide double-cycloaddition copolymerization by the Ni(CO)$_2$(PPh$_3$)$_2$ catalyst are summarized in Table 2. An experimental procedure of the 1,4-diethynylbenzene (**10a**)–**2b** copolymerization is as follows. A mixture of **10a** (0.25 mmol), **2b** (0.50 mmol), Ni(CO)$_2$(PPh$_3$)$_2$ (0.025 mmol), and THF (5.0 ml) was heated at 90°C for 20 h under nitrogen in a 50-ml stainless steel autoclave. Poly(bicyclo[2.2.2]oct-7-ene) **11ab** with M_n (GPC) = 27200 and M_w/M_n = 2.1 was obtained in 51% yield as a pale yellow powder by concentration of the resulting reaction mixture under vacuum and by

Scheme 5.

Table 2

Nickel(0)-catalyzed double-cycloaddition copolymerization of diynes (**10**) with *N*-substituted maleimides (**2**) to form poly(bicyclo[2.2.2]oct-7-ene)s (**11**) (Eq. (3))[a]

10	2	2/10[b]	Catalyst	Temp., °C	11		
					Yield, %[c]	M_n[d]	M_w/M_n[d]
a	**b**	4	Ni(CO)$_2$(PPh$_3$)$_2$	90	**ab**, 50	19,800	1.9
		2			51	27,200	2.1
					50[e]	26,800	3.5
				110	60	34,600	1.9
			Ni(COD)$_2$-2 PPh$_3$	90	50	16,000	2.4
b	**a**	4	Ni(CO)$_2$(PPh$_3$)$_2$	110	**ba**, 70[f]	15,900	1.3
		2			75[f]	12,400	2.3
	b	4	Ni(CO)$_2$(PPh$_3$)$_2$	90	**bb**, 96[f]	9300	1.8
		2			70[f]	12,400	2.4
	c	4	Ni(CO)$_2$(PPh$_3$)$_2$	110	**bc**, 78[f]	5000	1.6
c	**a**	4	Ni(CO)$_2$(PPh$_3$)$_2$	110	**ca**, 75[f]	6300	2.8

[a] **10**, 0.25 mmol; Ni/**10** = 0.1; solvent, THF, 5 ml; time, 20 h.
[b] Molar ratio.
[c] Based on 100% conversion of **10** to **11**.
[d] Determined by GPC with polystyrene standards in CHCl$_3$.
[e] Ni/**10a** = 0.05.
[f] Solvent, THF, 2 ml.

precipitation with methylene chloride–ethyl acetate. Raising the reaction temperature to 110°C increased the copolymer molecular weight to 34600. Ni(COD)$_2$ alone gave an insoluble copolymer, the formation of which may be ascribed to copolymer branching and/or cross-linking originating from formation of diyne trimerization units in the copolymer [20,21]. Copolymerizations of **10a** with **2a** and **2c** gave insoluble copolymers. Thus, in the **10a**–**2** copolymerization, introduction of a long *N*-alkyl substituent such as an octyl group into the maleimide was necessary for the preparation of a soluble poly(bicyclo[2.2.2]oct-7-ene) **11**. 1,11-Dodecadiyne (**10b**) copolymerized with **2b** to give copolymer **11bb** as a colorless resinous solid with the molecular weight as high as 12,400. The **10b**–**2a**, **c** copolymerizations produced soluble poly(bicyclo[2.2.2]oct-7-ene)s. The thermal stability of **11ab** was examined by thermogravimetric analysis (TGA) in air: T_{10} (the temperature causing a 10% weight loss) was 322°C.

The ^{13}C NMR C=O and C=C signals of **11ab** were similar to those of **6ab**, which is a model bicyclo[2.2.2]oct-7-ene compound of the copolymer repeat unit, and the ^{13}C NMR C=O and C=C signals of **11bb** were a superposition of those of **6bb** and **7bb** (Fig. 1). These spectral results indicate that the diyne-maleimide double-cycloaddition copolymerization occurred efficiently to produce poly(bicyclo[2.2.2]oct-7-ene) **11**, which has the *exo, exo*-fused bicyclo[2.2.2]oct-7-ene ring in its repeat unit.

In the nickel(0)-catalyzed **1a**–**2b** and **1b**–**2b** cycloaddition reactions (Eq. (1), Table 1), the maleimide-monoyne molar ratio was important for the efficient formation of 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 two-fold excess of the maleimide to the monoyne was necessary for its effective formation. In contrast, in the diyne-maleimide copolymerization, the use of a two-fold excess of the maleimide (maleimide/diyne = 4) did not influence significantly the yield and molecular weight of the poly(bicyclo[2.2.2]oct-7-ene) in comparison to the stoichiometric copolymerization (maleimide/diyne = 2) (Table 2). These results are understandable because copolymer growth reaction of the nickel(0)-catalyzed diyne-maleimide double-cycloaddition copolymerization is 1,3-cyclohexadiene ring formation
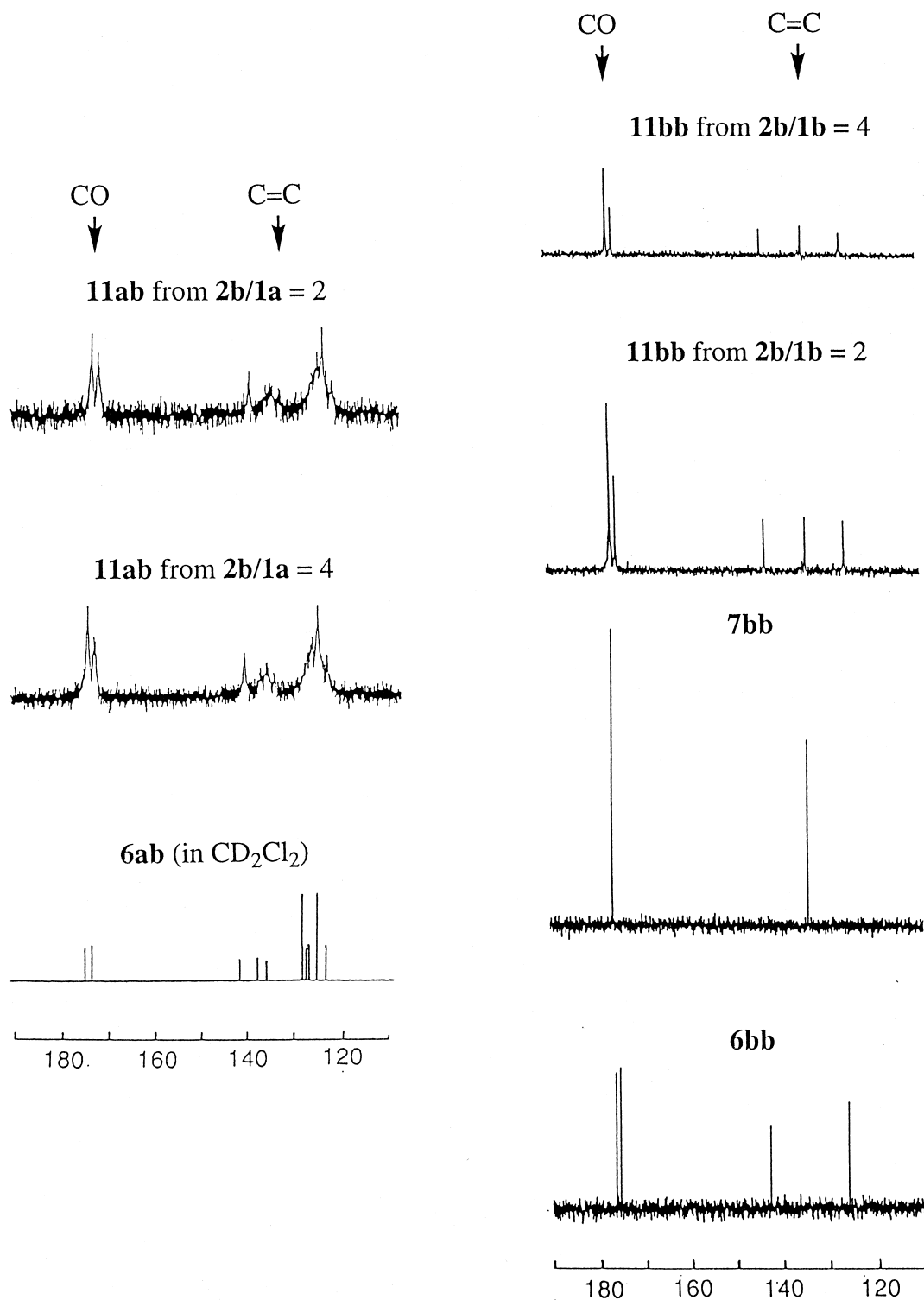
Fig. 1. ^{13}C NMR C=C and C=O signals of bicyclo[2.2.2]oct-7-enes (**6ab**, **6bb**, and **7bb**) and poly(bicyclo[2.2.2]oct-7-ene)s (**11ab** and **11bb**) (CDCl$_3$, δ-ppm).

by cycloaddition involving each one terminal C≡C bond of the two growing poly(bicyclo[2.2.2]oct-7-ene)s and a C=C bond of the maleimide (Scheme 3), in which the excess maleimide, i.e., maleimide/diyne = 4, may not be necessary.

In the equimolar **1a**–**2b** reaction, aromatized cycloadduct **5ab** was formed as a side product. This type of aromatization reaction is one possible side reaction of the diyne-maleimide double-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 monomer feed ratio did not influence the poly(bicyclo[2.2.2]oct-7-ene) structure: the poly(bicyclo[2.2.2]oct-7-ene)s obtained from the maleimide-diyne monomer feed ratios of 2 and 4 showed almost identical IR, ^{1}H, and ^{13}C NMR spectra (Fig. 1). This fact indicates that the aromatization of the intermediate 1,3-cyclohexadiene unit of the copolymer is not significant in the stoichiometric diyne-maleimide copolymerization. The difference between the aromatization reactivity of the 1,3-cyclohexadiene ring in the copolymer and that of the intermediate 1,3-cyclohexadiene cycloadduct may partly be ascribed to sterically suppressed dehydrogenation reaction of the internal 1,3-cyclohexadiene moiety in the poly(bicyclo[2.2.2]-oct-7-ene).

The poly(bicyclo[2.2.2]oct-7-ene) prepared in this study is a novel polymer and cannot easily be prepared by other known methods of polymer synthesis. The poly(bicyclo[2.2.2]oct-7-ene) **11ab** having two long alkyl side chains per repeat unit is potentially interesting because it has a rigid fence-like structure. Structurally related comb-like polymers are well-known and attract much attention on account of their specific properties [35,36].

2.3. Synthesis of poly(imide)s

Another application of the nickel(0)-catalyzed monoyne-maleimide double-cycloaddition reaction (Eqs. (1) and (2)) to polymer synthesis is a nickel(0)-catalyzed monoyne-dimaleimide double-cycloaddition copolymerization to afford a poly(imide) (Eq. (4)) [37]. The copolymerization results are summarized in Table 3. An experimental procedure of the 1-decyne (**1b**)-*N,N*′-1,1′-(4,4′-methylenediphenylene)dimaleimide (**12a**) copolymerization is as follows. A mixture of **1b** (1.0 mmol), **12a** (0.50 mmol), a nickel(0) catalyst generated from Ni(COD)$_2$ (0.050 mmol) and two equivalents of PPh$_3$, and dioxane (10 ml) was heated at 90°C for 20 h under nitrogen in a 50-ml stainless steel autoclave. Poly(imide) **13ba** with $M_n = 8500$ and $M_w/M_n = 1.9$ was obtained in 68% yield by concentration of the resulting reaction mixture under vacuum and by precipitation with methylene chloride-diethyl ether. Monoynes with a relatively long alkyl group such as **1b** and **8b** copolymerized with various dimaleimides **12** to give soluble poly(imide)s (Eq. (4)).

N,N′-1,6-hexylenedimaleimide (**12b**) with a relatively long alkylene group connecting two maleimide moieties was found to be a versatile dimaleimide component and copolymerized with **1a** to form soluble poly(imide) **13ab** while **1a**–**12a,d** copolymerizations produced insoluble copolymers. Ethoxyacetylene (**1c**) copolymerized with **12b** to produce **13cb** with a vinyl ether moiety. Poly(imide) **13cb** had a repeat unit containing a regioselectively formed 1,8-diethoxy-substituted bicyclo[2.2.2]oct-7-ene ring. In contrast, 3-butyn-2-one, i.e., a monoyne with an electron-withdrawing group, did not undergo the copolymerization.

Poly(imide)s were identified spectroscopically using model bicyclo[2.2.2]oct-7-ene compounds prepared by the nickel(0)-catalyzed double-cycloaddition of monoynes with *N*-substituted maleimdes (Eqs. (1) and (2)). The nickel(0)-catalyzed monoyne-dimaleimide double-cycloaddition copolymerization provides a new method of poly(imide) synthesis and affords a variety of new poly(imide)s with

Table 3
Nickel(0)-catalyzed double-cycloaddition copolymerization of monoynes (**1** or **8**) with dimaleimides (**12**) to form poly(imide)s (**13** or **14**) (Eq. (4))[a]

1 or **8**	**12**	**13** or **14**	Yield, %[b]	M_n[c]	M_w / M_n[c]
1b	**a**	**13ba**	68	8500	1.9
8b	**a**	**14ba**	49[d]	12,100	2.2
1a	**b**	**13ab**	33	4500	1.9
1b	**b**	**13bb**	53	15,000	1.4
1c	**b**	**13cb**	41	5000	1.7
1b	**c**	**13bc**	92	7400	2.3
1b	**d**	**13bd**	71	8800	1.7
8b	**d**	**14bd**	23[d]	7700	1.8
1b	**e**	**13be**	91	8300	1.9

[a]**1** or **8** = 1 mmol; **1** or **8**/**12** = 2; Ni(COD)$_2$-2 PPh$_3$ /**1** or **8** = 0.05; solvent, 1,4-dioxane, 10 ml; temperature, 90°C; time, 20 h.
[b]Based on 100% conversion of **1** or **8** to **13** or **14**.
[c]Determined by GPC with polystyrene standards in CHCl$_3$.
[d]Temperature, 150°C.

complex structures by various combinations of monoynes and dimaleimides. T_{10} determined by TGA analysis in air was 341, 362, and 343°C for **13ba**, **13bd**, and **13be**, respectively.

A diyne-dimaleimide double-cycloaddition copolymerization was also possible (Eq. (5)). 1,7-Octadiyne (**10d**) acted as two monoyne molecules to produce soluble poly(imide) **14db** containing pendant cyclohexene rings formed by a regioselective intramolecular cyclization of **10d** [37].

3. Conclusions

In this study, we have developed an efficient, chemo-, and stereoselective nickel(0)-catalyzed monoyne-maleimide double-cycloaddition reaction to afford a bicyclo[2.2.2]oct-7-ene. On the basis of this bicyclo[2.2.2]oct-7-ene synthesis along with the transition metal-catalyzed diyne cycloaddition copolymerization, which we found previously, we have further developed three types of transition metal-catalyzed alkyne (monoyne and diyne) double-cycloaddition copolymerizations as a new variation of the diyne cycloaddition copolymerization, i.e., (1) a diyne-maleimide double-cycloaddition copolymerization to form a poly(bicyclo[2.2.2]oct-7-ene), (2) a monoyne-dimaleimide double-cycloaddition copolymerization to afford a poly(imide), and (3) a diyne-dimaleimide double-cycloaddition copolymerization to afford a poly(imide).

A remarkable feature of the transition metal-catalyzed alkyne double-cycloaddition copolymerization is one-step construction of a copolymer repeat unit with a complex structure using cycloaddition connecting three moieties. The transition metal-catalyzed diyne cycloaddition copolymerization and alkyne double-cycloaddition copolymerization have demonstrated usefulness of the transition metal-catalyzed alkyne cycloaddition reaction as a polymer-forming elementary reaction. The exploitation of a new transition metal-catalyzed cycloaddition reaction along with the improvement of efficiency and regiocontrol of the known cycloaddition reaction, therefore, is expected to increase remarkably the effectiveness of the transition metal-catalyzed alkyne cycloaddition copolymerization as a new method of polymer synthesis.

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