**6440** *Macromolecules* **2006,** *39,* 6440−6444

# Transition Metal-Mediated Copolymerization of Diazocarbonyl Compounds with Alkyne and Isocyanide

**Eiji Ihara,* Akiko Nakada, Tomomichi Itoh, and Kenzo Inoue***

*Department of Material Science and Biotechnology, Graduate School of Science and Engineering, Venture Business Laboratory, Ehime University, 3 Bunkyo-cho, Matsuyama 790-8577, Japan*

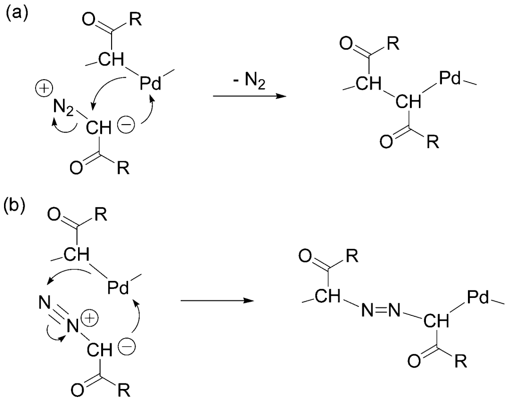
*Received April 6, 2006; Revised Manuscript Received July 12, 2006*

ABSTRACT: Transition metal-mediated copolymerizations of diazocarbonyl compounds with alkynes and an isocyanide were investigated with the following combinations of the comonomers: (*E*)-1-diazo-3-nonen-2-one (**1a**) with phenylacetylene (**2a**), (*E*)-1-diazo-4-phenyl-3-buten-2-one (**1b**) with 1-heptyne (**2b**), ethyl diazoacetate (**1c**) with **2a** and **2b**, and **1b** with *tert*-butyl isocyanide (**3**). All the copolymerizations afforded random copolymers whose GPC traces were unimodal, and $^1$H NMR spectra exhibited superposition of signals derived from the repeating units of both comonomers. In addition, the progress of the copolymerizations was supported by the DSC analyses of the products.

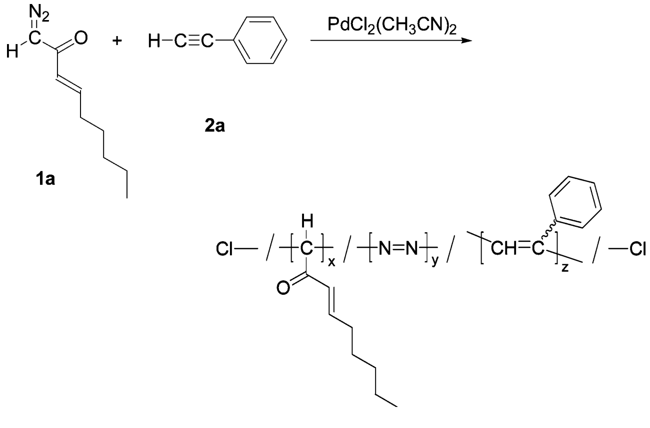
## Introduction

We have reported that Pd-mediated polymerization of diazocarbonyl compounds such as alkyl diazoacetates[1] and diazoketone[2] affords poly(alkoxycarbonylmethylene)s and poly(acylmethylene)s, respectively. The polymerization can be a unique method for preparing C−C main chain polymers, constructing the main chain from *one carbon unit*, not from *two carbon units* as in vinyl polymerization.[3] In particular, the so-called “poly(substituted methylene) synthesis (PSMS)” can be useful when the target polymers cannot be obtained by the vinyl polymerization. We have proposed that the mechanism for the Pd-mediated polymerization includes the insertion of the α-carbon of the diazocarbonyl compound into a Pd−carbon bond in the propagating chain end, as shown in Scheme 1a, releasing $N_2$ at the same time, whereas occasional incorporation of azo groups into the main chain occurs via nucleophilic attack of the propagating carbon to the terminal nitrogen of the monomers, as shown in Scheme 1b.[4] In any case, because the growing chain end contains a Pd−C *σ*-bond, it would be possible to copolymerize the diazocarbonyl compounds with substrates that can be inserted into the C−Pd bond. In addition, if such copolymerization proceeds, it would strongly support our proposed mechanism for the Pd-mediated polymerization. Herein, choosing phenylacetylene and 1-heptyne as the substrates, we examined Pd-mediated copolymerizations of diazocarbonyl compounds with the alkynes.[5] Ni-mediated copolymerization of a diazoketone with *tert*-butyl isocyanide[6] was also investigated.

**Scheme 1. Proposed Mechanism for the Propagation of Pd-Mediated Polymerization of Diazocarbonyl Compounds (a) and Incorporation of a Diazo Group into the Main Chain (b)**



**Scheme 2. Copolymerization of (*E*)-1-Diazo-3-nonen-2-one (1a) with Phenylacetylene (2a)**



## Results and Discussion

**Copolymerization of (*E*)-1-Diazo-3-nonen-2-one (1a) with Phenylacetylene (2a).** Copolymerization of (*E*)-1-diazo-3-nonen-2-one (**1a**) with phenylacetylene (**2a**) was examined by using $PdCl_2(MeCN)_2$ as an initiator in toluene at 80 °C for 17 h (Scheme 2). Under the conditions, homopolymerization of **1a** afforded poly**1a** with $M_n = 2450$ (run 6 in Table 1). As described in our previous paper,[2] azo groups (−N═N−) were incorporated into the main chain of poly**1a** in this polymerization, and the [**1a′**]/[-N═N−] (**1a′** = repeating unit derived from **1a** via the mechanism shown in Scheme 1a) ratio for the sample obtained in run 6 was 16.0:1.5, determined by the elemental analysis on the assumption that initiating Cls attached to both chain ends.[7] Calcd for Cl(**1a′**)$_{16.0}$(−N═N−)$_{1.5}$Cl ($M_n$ = 2378.3): C, 72.72; H, 9.74; N, 1.77. Found: C, 71.32; H, 8.98; N, 1.54. On the other hand, the reaction of **2a** with $PdCl_2(MeCN)_2$ gave poly**2a** with a very low molecular weight whose $^1$H NMR exhibited a broad signal at 6.0−8.0 ppm derived from

---

* Corresponding author. E-mail: ihara@eng.ehime-u.ac.jp (E.I.). Telephone and Fax: +81-89-927-8547 (E.I.).

10.1021/ma0607822 CCC: $33.50

**Table 1. Copolymerization of (*E*)-1-Diazo-3-nonen-2-one (1a) with Phenylacetylene (2a) Mediated with $PdCl_2(MeCN)_2$[a]**

| run | **1a**, mmol | **2a**, mmol | [**1a**]/[**2a**] | yield (%) | $M_n$[b] | $M_w/M_n$[b] | copolymer composition[c] [**1a′**]/[**2a′**] |
|---|---|---|---|---|---|---|---|
| 1 | 4.22 | 12.8 | 1:3 | 42.7 | 1030 | 1.49 | 0.86:1 |
| 1−1[d] | | | | 4.7 | 3110 | 1.45 | 1.20:1 |
| 1−2[d] | | | | 17.8 | 1520 | 1.30 | 0.88:1 |
| 1−3[d] | | | | 19.1 | 670 | 1.28 | 0.56:1 |
| 2 | 1.93 | 1.99 | 1:1 | 52.2 | 1110 | 1.64 | 1.97:1 |
| 3 | 2.89 | 0.96 | 3:1 | 57.9 | 1450 | 1.55 | 4.48:1 |
| 4 | 3.21 | 0.66 | 5:1 | 62.5 | 1640 | 1.71 | 8.22:1 |
| 5 | 3.37 | 0.48 | 7:1 | 30.7 | 3060 | 1.47 | 11.5:1 |
| 6[e] | 3.86 | | 1:0 | 35.0 | 2450 | 1.69 | |
| 7[f] | | 3.92 | 0:1 | 15.3 | 670 | 1.15 | |

[a] In toluene (10 mL) at 80 °C for 17h; $[PdCl_2(MeCN)_2] = ([\mathbf{1a}] + [\mathbf{2a}])/12.5$ (run 1), $([\mathbf{1a}] + [\mathbf{2a}])/50$ (runs 2−7). [b] $M_n$ and $M_w/M_n$ were obtained by GPC calibration using standard PMMAs and dibutyl sebacate in THF solution. [c] Copolymer compositions were determined by $^1H$ NMR. [d] These samples were fractionated with respect to their molecular weights by using preparative recycling GPC. [e] Homopolymerization of **1a**. [f] Homopolymerization of **2a**.

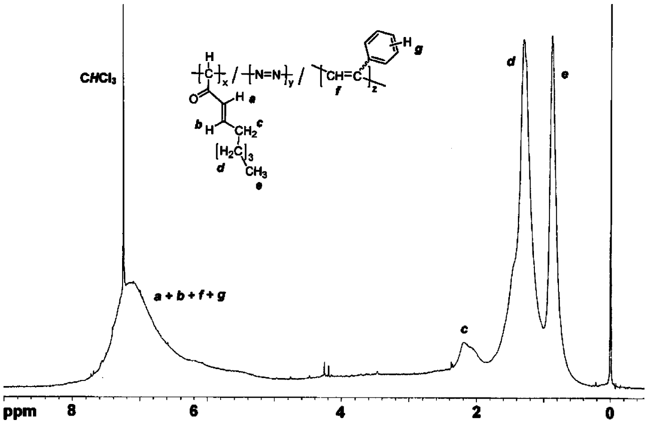


**Figure 1.** $^1H$ NMR spectrum of a copolymer of **1a** and **2a** (run 1−1 in Table 1).

both the phenyl and vinyl protons as reported in the literature (run 7).[5]

When a mixture of **1a** and **2a** in a ratio of [**1a**]/[**2a**] = 1:3 with 8 mol % (with respect to the total concentration of [**1a**] and [**2a**]) of $PdCl_2(MeCN)_2$, a product obtained after purification using preparative recycling GPC showed a unimodal GPC trace with $M_n = 1030$ and $M_w/M_n = 1.49$, and $^1H$ NMR spectrum of the product showed signals assignable to the repeating units derived from both monomers (run 1). The composition of the two repeating unit [**1a′**]/[**2a′**] = 0.86:1 was determined by relating the integral of $CH_3$ signal at 0.88 ppm belonging to the **1a′** repeating unit to the broad signal for Ph-H and vinyl-H at 6.0−8.0 ppm for the **2a′** repeating unit. To confirm that the product is not a mixture of homopolymers (poly**1a** and poly**2a**), fractionation with respect to molecular weights by using the preparative recycling GPC was carried out. As listed in runs 1−1 to 1−3, the product was separated into three fractions whose $M_n$s were 3110, 1520, and 670, respectively, and the composition of each fraction was determined from their $^1H$ NMR spectra. As a result, it was found that the [**1a′**]/[**2a′**] ratio in the copolymer gradually decreased with the decrease of $M_n$, which suggests that $M_n$ of the copolymer with higher **2a′** content tends to be relatively low, or low-molecular-weight poly**2a** might be contained in the product. However, on the basis of the observation that the composition of the fraction with the highest $M_n$ was 1.20:1 ([**1a′**]/[**2a′**]) as determined from the $^1H$ NMR spectrum in Figure 1 and the GPC trace of the fraction does not overlap so much with the GPC trace of poly**2a** obtained with the homopolymerization (Figure 2), it is reasonable to assume that the copolymerization of the two monomers actually proceeded. The results of the elemental analysis for the sample obtained in run 1−1 agreed well with the values expected from the structure with the NMR-determined composition of [**1a′**]/[**2a′**] Calcd for $Cl(\mathbf{1a'})_{9.6}(-N{=}N-)_{1.0}(\mathbf{2a'})_{8.0}Cl$ ($M_n = 2296.9$): C, 78.65; H, 8.27; N, 1.22. Found: C, 76.57; H, 7.25; N, 1.17.

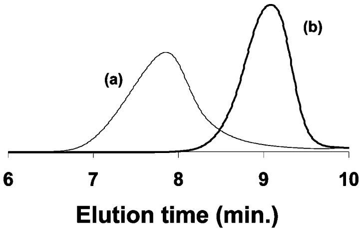


**Figure 2.** GPC traces for the copolymer of **1a** and **2a** (run 1−1, Table 1) (a) and poly**2a** (run 7 in Table 1) (b).

As summarized in runs 2−5 in Table 1, the copolymerizations with various feed ratios of **1a** and **2a** were conducted with 2.5 mol % of $PdCl_2(MeCN)_2$. Although the efficiency of the incorporation of **2a** was generally low, the [**1a′**]/[**2a′**] ratio in the copolymer varied corresponding to the feed ratio.

Thermal behavior of the copolymers was investigated by DSC analysis. Compared to $T_g = 33$ °C of poly**1a** ($M_n = 2560$, $M_w/M_n = 1.57$), decrease of the transition temperature was observed by incorporating a **2a′** unit in the main chain ($T_g = 15$ °C for the sample in run 2 with [**1a′**]/[**2a′**] = 1.97:1), probably because the closely packed rigid structure of poly**1a** would be disturbed. On the other hand, the copolymer obtained in run 1 with [**1a′**]/[**2a′**] = 0.86:1 exhibited $T_g$ at 40 °C, of which the increase from that of the sample in run 2 could be interpreted as regaining of the rigidity that should be inherent to the poly**2a** framework. Thus, poly**2a** with $M_n = 550$, $M_w/M_n = 1.15$ did not exhibited $T_g$ until the temperature (100 °C) at which decomposition would start. In any case, along with the absence of the $T_g$ of poly**2a**, the results of the DSC measurement for the copolymers strongly suggest that the copolymerization actually occurred.

**Copolymerization of (*E*)-1-Diazo-4-phenyl-3-buten-2-one (1b) with 1-Heptyne (2b).** Next, as a diazocarbonyl compound, the use of (*E*)-1-diazo-4-phenyl-3-buten-2-one (**1b**) was examined (Scheme 3). For **1b**, 1-heptyne (**2b**) was employed as an acetylene comonomer because determination of the repeating unit composition of the resulting copolymer by $^1H$ NMR is convenient for the combination. As we reported previously,[2] polymerization of **1b** mediated by $PdCl_2(MeCN)_2$ at 60 °C for 17 h in toluene gave poly**1b** ($M_n = 1640$, $M_w/M_n = 1.40$) in a 55.1% yield (run 6, Table 2). Elemental analysis of the poly**1b** indicated the presence of N in 0.35%, which should be ascribed to the incorporation of azo groups (−N=N−) in the main chain as in the aforementioned case for poly**1a**. The observed results of elemental analysis (C, 78.45; H, 5.60; N, 0.35) agree well with the calculated values based on the structure $Cl(\mathbf{1b'})_{11.0}(N{=}N)_{0.2}Cl$ ($M_n = 1662.4$): C, 79.48; H, 5.34; N, 0.34. Under the same conditions, 1-heptyne (**2b**) gave poly**2b** in a very low yield (run 7), although the GPC-estimated $M_n$ based on standard PMMAs was much higher than that of the poly**2a** described above. As expected from the different reactivity between **1b** and **2b**, the incorporation of **2b** into the copolymer is not efficient. For example, the copolymerization with [**1b**]/[**2b**] = 3:1 or 1:1, the products isolated using preparative recycling GPC exhibit much lower incorporation of **2b** than that expected from the feed ratio (runs 1 and 2). However, by increasing the amount of **2b** in feed, it is possible to prepare copolymers with higher

**Scheme 3. Copolymerization of (*E*)-1-Diazo-4-phenyl-3-buten-2-one (1b) with 1-Heptyne (2b)**

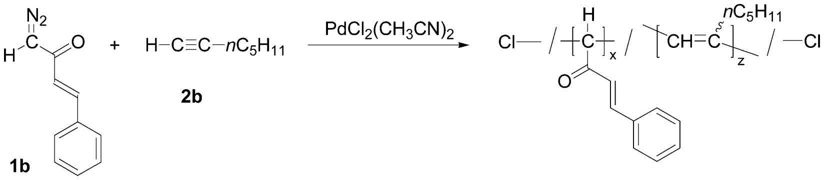


**Table 2. Copolymerization of (*E*)-1-Diazo-4-phenyl-3-buten-2-one (1b) with 1-Heptyne (2b) Mediated with $PdCl_2(MeCN)_2$**[a]

| run | **1b**, mmol | **2b**, mmol | [**1b**]/[**2b**] | yield (%) | $M_n$[b] | $M_w/M_n$[b] | copolymer composition[c] [**1b′**]/[**2b′**] |
|---|---|---|---|---|---|---|---|
| 1 | 2.89 | 0.97 | 3:1 | 46.6 | 1670 | 1.41 | 6.78:1 |
| 2 | 1.93 | 1.91 | 1:1 | 31.5 | 1740 | 1.33 | 4.40:1 |
| 3 | 0.97 | 2.90 | 1:3 | 20.3 | 1350 | 1.46 | 2.52:1 |
| 4 | 0.64 | 3.20 | 1:5 | 19.1 | 1280 | 1.29 | 1.11:1 |
| 5 | 0.48 | 3.36 | 1:7 | 11.2 | 1520 | 1.30 | 0.88:1 |
| 6[d] | 3.85 | | 1:0 | 55.1 | 1640 | 1.40 | |
| 7[e] | | 3.96 | 0:1 | 5.0 | 1470 | 1.48 | |

[a] In toluene (10 mL) at 60 °C for 17h; $[PdCl_2(MeCN)_2] = ([\mathbf{1b}] + [\mathbf{2b}])/50$. [b] $M_n$ and $M_w/M_n$ were obtained by GPC calibration using standard PMMAs and dibutyl sebacate in THF solution. [c] Copolymer compositions were determined by $^1H$ NMR. [d] Homopolymerization of **1b**. [e] Homopolymerization of **2b**.

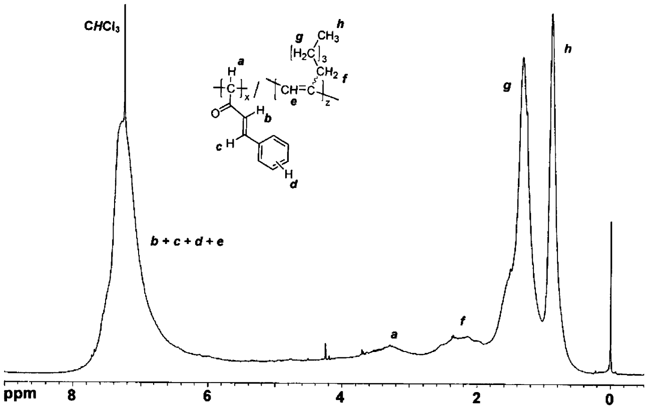


**Figure 3.** $^1H$ NMR spectrum of a copolymer of **1b** and **2b** (run 4 in Table 2).

**Scheme 4. Copolymerization of Ethyl Diazoacetate (1c) with Phenylacetylene (2a) and 1-Heptyne (2b)**

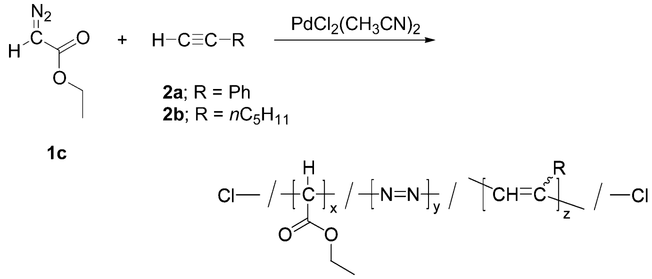


**Table 3. Copolymerization of Ethyl Diazoacetate (1c) with Phenylacetylene (2a) and 1-Heptyne (2b) Mediated with $PdCl_2(MeCN)_2$**[a]

| run | **1c**, mmol | **2a** or **2b**, mmol | [**1b**]/[**2a** or **2b**] | yield (%) | $M_n$[b] | $M_w/M_n$[b] | copolymer composition[c] [**1c′**]/[**2a′** or **2b′**] |
|---|---|---|---|---|---|---|---|
| 1 | 3.21 | **2a**, 0.68 | 5:1 | 33.7 | 870 | 1.22 | 4.20:1 |
| 2 | 2.31 | **2a**, 0.82 | 3:1 | 31.1 | 500 | 1.20 | 2.86:1 |
| 3 | 1.50 | **2a**, 1.37 | 1:1 | 25.6 | 480 | 1.16 | 1.09:1 |
| 4 | 1.22 | **2a**, 3.46 | 1:3 | 39.4 | 700 | 1.27 | 1.35:1 |
| 5 | 2.92 | **2b**, 0.95 | 3:1 | 17.0 | 1040 | 1.28 | 3.26:1 |
| 6 | 1.90 | **2b**, 1.93 | 1:1 | 20.1 | 900 | 1.32 | 1.85:1 |
| 7 | 1.01 | **2b**, 2.86 | 1:3 | 8.5 | 1280 | 1.29 | 0.78:1 |
| 8[d] | 3.93 | | 1:0 | 25.2 | 750 | 1.24 | |

[a] In toluene (10 mL) at 80 °C (runs 1−4) or 60 °C (runs 5−8) for 17h; $[PdCl_2(MeCN)_2] = ([\mathbf{1c}] + [\mathbf{2a}\text{ or }\mathbf{2b}])/50$. [b] $M_n$ and $M_w/M_n$ were obtained by GPC calibration using standard PMMAs and dibutyl sebacate in THF solution. [c] Copolymer compositions were determined by $^1H$ NMR. [d] Homopolymerization of **1c**.

**2b** contents in low yields (runs 3−5). As the $^1H$ NMR spectrum for the sample in run 4 in Figure 3 indicates, the [**1b′**]/[**2b′**] composition in the copolymer can be determined from the integral ratio between the broad signal for Ph-H and vinyl-H at 6.0−8.0 ppm (**1b′**) and the terminal $CH_3$ signal at 0.90 ppm for **2b′**. The calculated values for the C, H content based on the [**1b′**]/[**2b′**] ratio agreed well with the values obtained by elemental analysis Calcd for $Cl(\mathbf{1b'})_{4.8}(\mathbf{2b'})_{4.0}Cl{\cdot}4H_2O$ ($M_n$ = 1219.7): C, 74.80; H, 7.80. Found C, 73.46; H, 7.25. It is interesting to note that nitrogen was not detected at all in the analysis for the sample, which suggests that the presence of **2b** in the polymerization system somehow suppresses the propagation, leading to the incorporation of the diazo group described in Scheme 1b.

DSC analyses for the copolymers provide the supporting evidence for the progress of the copolymerization. As for homopolymers, whereas the sample of poly**2b** ($M_n$ = 1950, $M_w/M_n$ = 1.62) exhibited $T_g$ at 8 °C, poly**1b** ($M_n$ = 1990, $M_w/M_n$ = 1.25) did not show the transition until 100 °C, at which temperature decomposition of the sample starts. The copolymer samples with [**1b′**]/[**2b′**] = 0.75 ($M_n$ = 1560, $M_w/M_n$ = 1.25) exhibited $T_g$ at 62 °C, from which the rise of the transition temperature from that of poly**1b** would be caused by the flexibility imparted by the incorporation of **2b′** unit. On the other hand, copolymers with [**1b′**]/[**2b′**] ratio higher than 0.9 did not exhibit $T_g$ until they started decomposition.

**Copolymerization of Ethyl Diazoacetate (1c) with Phenylacetylene (2a) and 1-Heptyne (2b).** The Pd-mediated copolymerizations ethyl diazoacetate (**1c**) with phenylacetylene (**2a**) and 1-heptyne (**2b**) were investigated (Scheme 4). As summarized in runs 1−3 in Table 3, the copolymerization of **1c** with **2a** in the feed ratios [**1c**]/[**2a**] = 5:1−1:1 afforded copolymers with the composition nearly expected from the feed ratio. However, the incorporation of **2a** was not efficient for the copolymerization with [**1c**]/[**2a**] = 1:3, which resulted in the formation of the product with much higher content of **1c′** than expected from the feed ratio (run 4). All the copolymers exhibited unimodal GPC traces, and their $^1H$ NMR spectra consisted of the signals derived from each repeating unit, as shown in Figure 4. The composition was determined from the integral ratio between the $-OCH_2-$ signal at 4.20 ppm for **1c′** and the broad signal for Ph-H and vinyl-H at 6.0−8.0 ppm for **2a′**. The composition [**1c′**]/[**2a′**] = 1.35:1.0 for the sample in Figure 4 (run 4 in Table 3) was confirmed by a good agreement between the calculated and observed values in elemental analysis Calcd for $Cl(\mathbf{1c'})_{5.4}(-N{=}N-)_{0.1}(\mathbf{2a'})_{4.0}Cl$ ($M_n$ = 947.1): C, 67.90; H, 6.00; N, 0.30. Found: C, 68.83; H, 5.85; N, 0.34.

The Pd-mediated copolymerization of **1c** with **2b** proceeded in a similar manner, as summarized in runs 5−7 in Table 3. Although the polymer yields and efficiency of the incorporation of **2b** were much lower than those with **2a**, copolymers with

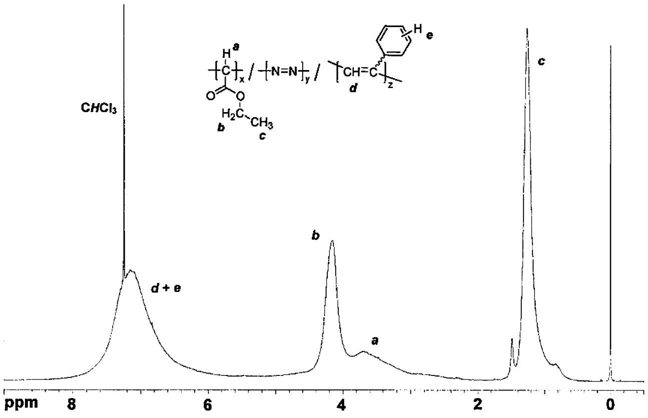


**Figure 4.** $^1$H NMR spectrum of a copolymer of **1c** and **2a** (run 4 in Table 3).

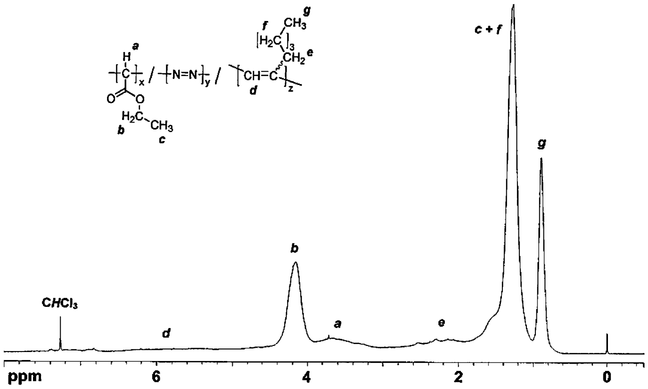


**Figure 5.** $^1$H NMR spectrum of a copolymer of **1c** and **2b** (run 6 in Table 3).

various compositions and unimodal GPC traces were obtained. Figure 5 shows $^1$H NMR spectrum for the sample in run 6, whose composition [**1c′**]/[**2b′**] = 1.85:1.0 was determined from the integral ratio between the OCH$_2$ signal (**1c′**) and terminal Me signal of the **2b′** side chain and confirmed from elemental analysis Calcd for Cl(**1c′**)$_{6.0}$(−N=N−)$_{0.1}$(**2b′**)$_{3.0}$Cl·3H$_2$O ($M_n$ = 932.8): C, 57.94; H, 8.42; N, 0.30. Found: C, 57.16; H, 7.26; N, 0.32.

DSC analyses of the copolymers suggested the progress of the copolymerization. Whereas $T_g$ of poly**1c** ($M_n$ = 710, $M_w/M_n$ = 1.23) was observed at −27 °C, incorporation of the rigid **2a′** framework resulted in the raise of $T_g$ as expected: $T_g$ = −5 °C for the sample with [**1c′**]/[**2a′**] = 6.19:1.0, $M_n$ = 810, $M_w/M_n$ = 1.18; $T_g$ = 26 °C, [**1c′**]/[**2a′**] = 1.09:1.0, $M_n$ = 480, $M_w/M_n$ = 1.16. Similar behavior was also observed for the copolymers of **1c** with **2b**: $T_g$ = −13 °C for the sample with [**1c′**]/[**2b′**] = 6.98:1.0, $M_n$ = 960, $M_w/M_n$ = 1.33; $T_g$ = −9 °C, [**1c′**]/[**2a′**] = 1.51:1.0, $M_n$ = 1260, $M_w/M_n$ = 1.42.

**Ni-Mediated Copolymerization of (*E*)-1-Diazo-4-phenyl-3-buten-2-one (1b) with *tert*-Butyl Isocyanide (3).** Finally, copolymerization of **1b** with *tert*-butyl isocyanide (**3**) was investigated (Scheme 5). After examining various initiating systems based on Ni complex following the literature[6a−e] on the polymerization of alkyl or aryl isocyanides, we have found that Ni(acac)$_2$·2H$_2$O in conjunction with (*S*)-(−)-1-phenylethylamine was able to afford low-molecular-weight copolymers. As shown in Table 4, the reaction of **1b** with **3** in the presence of 2 mol % of Ni(acac)$_2$·2H$_2$O and 4 mol % of (*S*)-(−)-1-phenylethylamine in 2-propanol gave copolymers, whose composition roughly corresponded to the feed ratio of **1b** and **3**. Although the $M_n$s were very low (∼500), GPC traces of the products were unimodal and broad signals derived from both repeating units are observed in their $^1$H NMR. Under the same condition, homopolymerization of **3** afforded poly**3** in a very low yield (run 4), which suggests that copolymerization of **1b** with **3** actually proceeded in runs 1−3. For the sample obtained in run 2 in Table 4, the composition [**1b′**]/[**3′**] = 1.20:1.0, calculated based on the integral ratio between the broad signal for Ph-H and vinyl-H for **1b′** at 6.5−8.0 ppm and *t*Bu signal at 0.5−2.0 ppm for **3′**, was confirmed by the result of elemental analysis, where the presence of amino groups at the α-chain is assumed, Calcd for MePhCHNH(**1b′**)$_{3.6}$(−N=N-)$_{1.0}$(**3′**)$_{3.0}$H ($M_n$ = 972.7): C, 72.80; H, 7.65; N, 8.64. Found: C, 71.57; H, 6.50; N, 8.03. These results indicate that the diazocarbonyl compounds can be inserted into the Ni−C bond in the propagating chain end for the isocyanide polymerization and isocyanide can insert into the resulting Ni−C bond.

**Table 4. Copolymerization of (*E*)-1-Diazo-4-phenyl-3-buten-2-one (1b) with *tert*-Butyl Isocyanide (3) Mediated with Ni(acac)$_2$·2H$_2$O[a]**

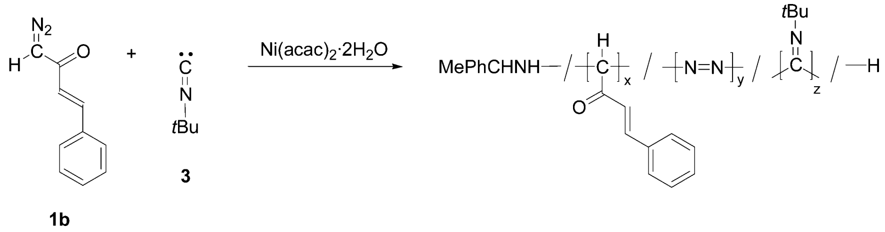
| run | **1b**, mmol | **3**, mmol | [**1b**]/[**3**] | yield (%) | $M_n$[b] | $M_w/M_n$[b] | copolymer composition[c] [**1b′**]/[**3′**] |
|---|---|---|---|---|---|---|---|
| 1 | 1.47 | 4.24 | 1:3 | 28.2 | 510 | 1.18 | 1:2.04 |
| 2 | 1.77 | 1.81 | 1:1 | 22.5 | 530 | 1.26 | 1.20:1 |
| 3 | 2.56 | 0.84 | 3:1 | 50.3 | 780 | 1.46 | 2.85:1 |
| 4[d] | 3.42 |  | 1:0 | 37.8 | 1110 | 1.44 |  |
| 5[e] |  | 3.40 | 0:1 | 8.1 | 810 | 1.13 |  |

[a] In 2-propanol (10 mL) at 60 °C for 17h; [Ni(acac)$_2$·2H$_2$O] = ([**1b**] + [**3**])/50; [(*S*)-(−)-1-phenylethylamine] = 2 × [Ni(acac)$_2$·2H$_2$O]. [b] $M_n$ and $M_w/M_n$ were obtained by GPC calibration using standard PMMAs and dibutyl sebacate in THF solution. [c] Copolymer compositions were determined by $^1$H NMR. [d] Homopolymerization of **1b**. [e] Homopolymerization of **3**.

## Conclusions

We have demonstrated that transition metal-mediated copolymerizations of diazocarbonyl compounds with alkynes and an isocyanide proceed to give random copolymers with various compositions. The structures of the resulting copolymers are unique and cannot be obtained by any other polymerization methodologies. The results described here will extend the utility of our “poly(substituted methylene) synthesis” based on the polymerization of diazocarbonyl compounds and support our proposed mechanism for the polymerization, where the propagation is the insertion of the monomers into the Pd−C bond at the growing end.

**Scheme 5. Copolymerization of (*E*)-1-Diazo-4-phenyl-3-buten-2-one (1b) with *tert*-Butyl Isocyanide (3)**



## Experimental Section

**Materials.** Toluene was dried over sodium and distilled before use. (*E*)-1-Diazo-3-nonen-2-one (**1a**),[2] (*E*)-1-diazo-4-phenyl-3-buten-2-one (**1b**),[8] ethyl diazoacetate (**1c**),[9] and $PdCl_2(MeCN)_2$[10] were prepared according to the literature. 2-Propanol (Nacalai, >99.0%), phenylacetylene (**2a**) (Aldrich, 98%), and 1-heptyne (**2b**) (Aldrich, 98%) were dried over $CaH_2$ and used without further purification. *tert*-Butyl isocyanide (**3**), (*S*)-(−)-1-phenylethylamine, and $Ni(acac)_2{\cdot}2H_2O$ (Kanto Chemical, >97.0%) was used as received.

**Measurements.** $^1H$ (400 MHz) NMR spectra were recorded on a Bruker Avance 400 spectrometer using tetramethysilane as an internal standard in chloroform-*d* ($CDCl_3$) at 50 °C.

Molecular weights ($M_n$) and molecular weight distributions ($M_w/M_n$) were measured by means of gel permeation chromatography (GPC) on a Jasco−Bowin system (version 1.50) equipped with a differential refractometer detector using tetrahydrofuran as eluent at a flow rate of 1.0 mL/min at 40 °C, calibrated with poly(MMA) standards (Shodex M-75, $M_n = 5220$, $M_w/M_n = 1.06$, $M_n = 2190$, $M_w/M_n = 1.08$) and dibutyl sebacate (MW = 314.5). The column used for the GPC analyses was a Styragel HR2 (Waters; 300 mm × 7.8 mm i.d., 5 $\mu$m average particle size, exclusion molecular weight of 20 K for polystyrene).

Purification by preparative recycling GPC was performed on a JAI LC-918R equipped with a combination of columns of a JAIGEL-3H (600 mm × 20 mm i.d., exclusion molecular weight of 70 K for polystyrene) and a JAIGEL-2H (600 mm × 20 mm i.d., exclusion molecular weight of 20 K for polystyrene) using $CHCl_3$ as eluent at a flow rate of 3.8 mL/min at 25 °C. The sample solution (3 mL, containing ca. 0.3 g of the crude product) was injected and recycled before fractionation.

Thermal properties of the polymers were measured using a differential scanning calorimeter (DSC), Seiko DSC 6200, under nitrogen atmosphere at a 10 °C/min heating rate.

Elemental analyses were performed on a YANAKO MT-5 analyzer at Integrated Center for Science (INCS) in Ehime University.

**Pd-Mediated Copolymerization of Diazocarbonyl Compounds (1a, b) with Alkynes (2a, b).** As a typical procedure, the copolymerization of **1a** with **2a** for run 1 in Table 1 is described as follows. Under a nitrogen atmosphere, a suspension of $PdCl_2(MeCN)_2$ (87.5 mg, 0.337 mmol) in 5 mL of toluene was placed in a Schlenk tube. After a toluene solution (5 mL) of a mixture of **1a** (0.702 g, 4.22 mmol) and **2a** (1.40 mL, 12.8 mmol) was added to the suspension at room temperature, the resulting mixture was heated to 80 °C and stirred for 17 h at the temperature. After the volatiles were removed under reduced pressure, 8 mL of 1 N HCl/MeOH, 8 mL of 1 N HCl aqueous solution, and 15 mL of $CHCl_3$ were added to the residue. The $CHCl_3$ phase was separated using a separatory funnel, and the aqueous phase was extracted with 35 mL of $CHCl_3$. The combined $CHCl_3$ phase was washed with 150 mL of 1 N HCl aqueous solution and 50 mL of water, dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure to afford a crude product. Purification with preparative recycling GPC gave the copolymer (0.805 g, 42.7%) as a dark-brown solid.

Other copolymerizations were carried out in similar procedures. As shown in the figures, $^1H$ NMR spectra for these copolymers were basically superposition of the spectra of each homopolymer reported in the literature; poly**1a**,[1] poly**1b**,[1] poly**1c**,[2] poly**2a**.[5] Poly**2b**: $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 5.0−6.5 (br, 1H, $-CH{=}$), 1.9−3.0 (br, 2H, $=C-CH_2-$), 1.33 (br, 6H, $-(CH_2)_3-$), 0.90 (br, 3H, $-CH_3$). Poly**3**: $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 1.0−2.0 (br, 9H, $-C(CH_3)_3$).

**Ni-Mediated Copolymerization of 1-Diazo-4-phenyl-3-buten-2-one (1b) with *tert*-Butyl Isocyanide (3).** As a typical procedure for the copolymerization, the procedure for run 2 in Table 4 is described as follows. Under a nitrogen atmosphere, a solution of $Ni(acac)_2{\cdot}2H_2O$ (20.9 mg, 0.0714 mmol) in 5 mL of 2-propanol was placed in a Schlenk tube. After a 2-propanol solution (5 mL) of a mixture of **1b** (0.305 g, 1.77 mmol) and **3** (0.205 mL, 1.81 mmol) was added to the solution at room temperature, (*S*)-(−)-1-phenylethylamine (0.0165 g, 0.136 mmol) was added to the resulting mixture. The mixture was heated to 60 °C and stirred for 17 h at the temperature. The aforementioned workup procedure gave the copolymer (91.2 mg, 22.5%) as a dark-brown solid. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 6.5−8.0 (br, Ph-*H*, $-CH{=}$), 2.5−4.5 (br, $-CH-$), 0.5−2.0 (br, 6H, $-CH_3$).

**Acknowledgment.** This research was supported by Mitsubishi Chemical Corporation Fund, the Inamori Foundation, the Kurata Memorial Hitachi Science and Technology Foundation, and Grants-in-Aid (nos. 16655047, 18350066, and 15036251) for Scientific Research on Priority Areas “Reaction Control of Dynamic Complexes” from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

## References and Notes

(1) Ihara, E.; Haida, N.; Iio, M.; Inoue, K. *Macromolecules* **2003**, *36*, 36−41.

(2) Ihara, E.; Fujioka, M.; Haida, N.; Itoh, T.; Inoue, K. *Macromolecules* **2005**, *38*, 2101−2108.

(3) (a) Shea, K. J.; Walker, J. W.; Zhu, H.; Paz, M.; Greaves, J. *J. Am. Chem. Soc.* **1997**, *119*, 9049−9050. (b) Shea, K. J.; Busch, B. B.; Paz, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1391−1393. (c) Shea, K. J.; Lee, S. Y.; Busch, B. B. *J. Org. Chem.* **1998**, *63*, 5746−5747. (d) Shea, K. J.; Staiger, C. L.; Lee, S. Y. *Macromolecules* **1999**, *32*, 3157−3158. (e) Zhou, X.-Z.; Shea, K. J. *J. Am. Chem. Soc.* **2000**, *122*, 11515−11516. (f) Busch, B. B.; Paz, M. M.; Shea, K. J.; Staiger, C. L.; Stoddard, J. M.; Walker, J. R.; Zhou, X.-Z.; Zhu, H. *J. Am. Chem. Soc.* **2002**, *124*, 3636−3646. (g) Busch, B. B.; Staiger, C. L.; Stoddard, J. M.; Shea, K. J. *Macromolecules* **2002**, *35*, 8330−8337. (h) Wagner, C. E.; Kim, J.-S.; Shea, K. J. *J. Am. Chem.* Soc. **2003**, *125*, 12179−12195. (i) Wagner, C. E.; Rodriguez, A. A.; Shea, K. J. *Macromolecules* **2005**, *38*, 7286−7291.

(4) We have confirmed the presence of the azo groups in the main chain of the polymers obtained by the Pd-mediated polymerization of phenyldiazomethane by using Raman spectroscopy. The details will be reported elsewhere.

(5) (a) Simionescu, C. I.; Percec, V.; Dumitrescu, S. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2497−2509. (b) Trumbo, D. L., Marvel, C. S. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 1027−1034. (c) Li, K.; Wei, G.; Darkwa, J.; Pollack, S. K. *Macromolecules* **2002**, *35*, 4573−4576.

(6) (a) Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* **1974**, *13*, 438−443. (b) Beijnen, A. J. M. v.; Nolte, R. J. M.; Drenth, W.; Hezemans, A. M. F.; Coolwijk, P. J. F. M. v. d.; *Macromolecules* **1980**, *13*, 1386−1391. (c) Beijnen, A. J. M. v.; Nolte, R. J. M.; Naaktgeboren, A. J.; Zwikker, J. W.; Drenth, W.; Hezemans, A. M. F. *Macromolecules* **1983**, *16*, 1679−1689. (d) Kamer, P. C. J.; Cleij, M. C.; Nolte, R. J. M.; Harada, T.; Hezemans, A. M. F.; Drenth, W. *J. Am. Chem. Soc.* **1988**, *110*, 1581−1587. (e) Kamer, P. C. J.; Nolte, R. J. M.; Drenth, W. *J. Am. Chem. Soc.* **1988**, *110*, 6818−6825. (f) Ito, Y.; Ihara, E.; Murakami, M.; Shiro, M. *J. Am. Chem.* Soc. **1990,** *112*, 6446−6447. (g) Ohshiro, N.; Shimizu, A.; Okumura, R.; Takei, F.; Onitsuka, K.; Takahashi, S. *Chem. Lett.* **2000**, 786−787. (h) Onitsuka, K.; Yabe, K.-I.; Ohshiro, N.; Shimizu, A.; Okumura, R.; Takei, F.; Takahashi, S. *Macromolecules* **2004**, *37*, 8204−8211.

(7) Although we have not obtained any direct evidence for the chain end structure so far, we have demonstrated that it is reasonable to evaluate the elemental analyses results assuming the presence of Cls at both polymer chain ends. For details, see ref 2.

(8) Danheiser, R. L.; Miller, R. F.; Brisbois, R. G.; Park, S. Z. *J. Org. Chem.* **1990**, *55*, 1959−1964.

(9) Searle, N. E. Organic Synthesis; Rabjohn, N., Ed.; John Wiley & Sons: New York, 1963; Collected Vol. 4, pp 424−426.

(10) Hegedus, L. S. *Organometallics in Synthesis: A Manual*; Schlosser, M., Ed.; John Wiley & Sons: West Sussex, U.K., 2002; p 1126.

MA0607822