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[16] The polyaniline-encapasulated nanotubes gave IR absorption peaks at 1514 (C=C stretching of the benzenoid rings), 1622 (C=C stretching of the quinoid rings), 1359 (C–N stretching), and 1197 cm^{-1} (electronic-like absorption of N=*Q*=N, where *Q* represents the quinoid ring), consistent with reported data.[14] XPS measurements indicated a decrease in the carbon content to 71.08% and concomitant increases to 12.11, 5.81, and 11.00% for nitrogen, sulfur, and oxygen, respectively, after the electrodeposition of polyaniline. The calculated C:N atomic ratio of 6.7 is close to that of aniline (C:N = 6), suggesting the formation of a continuous polyaniline coating with a thickness greater than the XPS detection depth (typically, 10 nm; see Figure 3). The corresponding atomic ratios of 3.8 for O:S and 4.7 for N:S indicated a high doping level of the polymer coating by H_2SO_4.[17] Further evidence for the electrodeposition of polyaniline on the nanotube surface comes from Raman scattering measurements. Whilst the Raman spectrum of the bare nanotubes shows an intense peak at 1584 cm^{-1}, attributable to the E_{2g} mode of the multiwall nanotubes, with a shoulder centered at 1322 cm^{-1} associated with the amorphous graphite,[2] the corresponding Raman spectrum for the polyaniline-coated nanotubes reveals broad bands around 1600, 1495, and 1390 cm^{-1}, typical for polyaniline.[18] An additional peak at 1330 cm^{-1} is associated with the stretching vibration of the -C-N^+- polaron groups, indicating the conducting nature of the polymer coating.

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Living Coordination Polymerization of Allene Derivatives Bearing Hydroxy Groups by π-Allylnickel Catalyst

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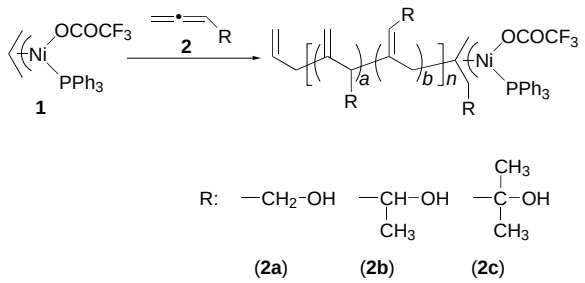
Synthetic polymers such as poly(vinyl alcohol) and poly(2-hydroxyethyl methacrylate)bearing hydroxy groups in their repeating units are, because of their unique polar character and reactivities, useful starting materials for the preparation of many functional compounds. [1] Nevertheless, with the exception of methods that involve the protection and deprotection of hydroxy groups, their use in well-defined synthesis has been limited.[2]

Living polymerization, a technique which is insensitive to polar functional groups on the monomers, is thus a suitable method to prepare well-defined polymers directly from monomers bearing hydroxy groups. The living coordination polymerization of allene derivatives by [{(π-allyl)NiO-$COCF_3$}$_2$] (**1**) is therefore attractive because this complex is able to polymerize monomers having a variety of functional groups, such as alkoxy,[3a–c] aryl,[3d] alkyl,[3e–f] amide,[3g] and carboalkoxy[3h] moieties. Herein we investigate the coordination polymerization of allenes bearing hydroxy groups (**2a**–**2c**) mediated by **1** (Scheme 1).



Scheme 1. Living coordination polymerization of allene derivatives that contain hydroxy moieties (**2a**–**2c**).

The polymerization of 2,3-butadiene-1-ol (**2a**)[4a] by **1** ([**2a**]/[**1**] = 60) was carried out in the presence of PPh_3 ([PPh_3]/[**1**] = 1.0) in EtOH at 50 °C (Table 1, entry 1). The polymerization was complete within 3 h and a white powdery polymer (poly(**2a**)) was obtained in 96% yield. The ^{1}H NMR spectrum of poly(**2a**) indicated that it consists of both the 1,2- and the 2,3-polymerized units (labeled *a* and *b* in Scheme 1) in a ratio

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Table 1. Living coordination polymerization of **2** by **1**.

Entry	Monomer	[**2**]/[**1**]	*a*:*b*[a]	Yield [%][b]	M_n ($\times 10^3$)[c]	M_w/M_n[c]
1	**2a**	60	40:60	96	9.6[d]	1.13[d]
2	**2b**	60	50:50	98	4.6	1.13
3	**2c**	50	35:65	94	6.4	1.08

[a] The ratio of 1,2- and 2,3-polymerized units, determined by ^{1}H NMR spectroscopy. [b] Yields after precipitation with hexane. [c] GPC (THF, polystyrene standard). [d] Determined by GPC measurement performed after the reaction with ethyl vinyl ether.

of about 40:60. Poly(**2a**) is soluble in polar organic solvents such as MeOH, EtOH, DMSO, and DMF but insoluble in hexane, benzene, CH_2Cl_2, THF, and water. In the reaction with ethyl vinyl ether, the hydroxy group attached to the polymer was converted quantitatively to acetal moieties and the resulting polymer was soluble in MeOH, THF, benzene, hexane, and CH_2Cl_2.[5] Gel permeation chromatographic (GPC) analysis of the acetal-containing polymer revealed that the number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) are 9.6×10^3 and 1.13, respectively (THF, polystyrene standard; see Table 1). The living nature of the present system was confirmed by polymerization reactions with different ratios of [**2a**]/[**1**] (Figure 1). That is, the molecular weight of the polymers obtained after conversion of the hydroxy groups to the acetal moieties increased linearly as the ratio of [**2a**]/[**1**] increased, and M_w/M_n remained narrow ($\cong$1.13).

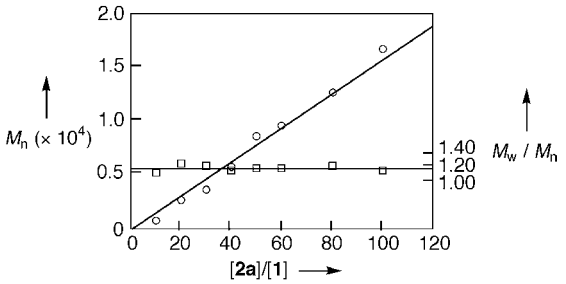

Figure 1. Dependence of M_n (○) and M_w/M_n (□) of poly(**2a**) on the ratio of monomer to initiator ([**2a**]/[**1**]).

The coordination polymerization of allenes bearing secondary and tertiary hydroxy groups (**2b**[4b] and **2c**,[4b] respectively) also proceeds smoothly to give narrowly dispersed polymers in high yields (Table 1, entries 2 and 3).[6]

The block copolymerization of **2a** with 1,2-heptadiene ((**3**) *n*-butylallene)[4c] by the sequential addition of monomers to **1** further confirmed the living nature of the polymerization. That is, after the polymerization of **2a** ([**2a**]/[**1**] = 40), **3** was added to the polymer solution ([**3**]/[**1**] = 50) and the postpolymerization was conducted at 50 °C for 3 h; a block copolymer was obtained quite effectively, as confirmed by GPC measurements (Figure 2).[7]

These results show that well-defined poly(alcohol)s can be prepared without a multiple-step protection–deprotection process, and that the polymerization of allene derivatives by **1** can yield polymers bearing a variety of functional groups. This suggests that the designed synthesis of macromolecules, such as block copolymers with a versatile combination of functional blocks, should be possible. To the best of our knowledge, this is the first example of a living polymerization reaction capable of the polymerization of a wide variety of functionalized monomers.

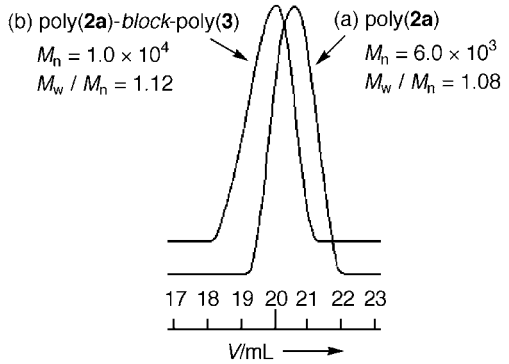

Figure 2. GPC traces a) before, and b) after postpolymerization with **3**.

Experimental Section

Typical living polymerization reaction: EtOH (2.0 mL), a solution of **1** (0.10 M, 0.2 mL, 0.020 mmol) in toluene, a solution of PPh_3 (1.0 M, 20 μL, 0.020 mmol) in toluene, and **2a** (0.084 g, 1.2 mmol, [**2a**]/[**1**] = 60) at 0 °C were placed under a nitrogen atmosphere in a test tube equipped with a three way tap and a magnetic stirrer bar. The mixture was stirred at 50 °C for 3 h. After the complete conversion of **2a** (monitored by gas chromatography), the solution was precipitated with hexane and dried in vacuo to give poly(**2a**) (0.081 g; 96 %). ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 1.96 (br, 2H × *b*; =C-CH$_2$-C=), 2.75 (br, 1H × *a*; -CH<), 3.34 (br, 2H × *a*; >C-CH$_2$-O-), 3.48 (br, 2H × *b*; =C-CH$_2$-O-), 4.03 (br, 1H; OH), 4.80 (br, 2H × *a*; >C=CH$_2$), 5.42 (br, 1H × *b*; >C=CH-O-); *a* and *b* are shown in Scheme 1; *a*:*b* = 0.40:0.60; ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 24.0, 24.9 (-CH$_2$-), 30.1, 31.6 (>CH-), 60.0 (>CH$_2$-*C*H$_2$-OH), 69.1 (=CH-*C*H$_2$-OH), 129.5, 129.8, 130.0 (=CH$_2$), 132.4, 133.0, 133.1, 134.6, 134.8, 139.4 (=*C*H-CH$_2$-OH, >*C*=CH$_2$, and >*C*=CH-CH$_2$-OH); IR (CHCl$_3$): $\tilde{\nu}$ = 3389 (O–H), 2966, 2928, 1452, 1369 (C–H), 1682, 1633 (C=C), 1053 cm^{-1} (C–O).

Block copolymerization reaction: EtOH (2.0 mL), a solution of **1** (0.10 M, 0.2 mL, 0.020 mmol) in toluene, a solution of PPh_3 (1.0 M, 20 μL, 0.020 mmol) in toluene, and **2a** (0.056 g, 0.80 mmol, [**2a**]/[**1**] = 40) at 0 °C, were placed under a nitrogen atmosphere in a test tube equipped with a three way tap and a magnetic stirrer bar. The mixture was stirred at 50 °C for 3 h. After the complete conversion of **2a** (monitored by gas chromatography), a portion of the solution (ca. 50 μL) was removed, and **3** (0.096 g, 1.0 mmol, [**3**]/[**1**] = 50) was added to the remaining solution. After postpolymerization at 50 °C for 3 h, the product was precipitated with water and dried in vacuo to give the block copolymer (0.137 g, 90 %). GPC measurements of both poly(**2a**) sampled before the addition of **3** and the block copolymer were performed after the treatment with ethyl vinyl ether. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): δ = 0.82 (br, 3H × *n*; -CH$_3$), 1.12 (br, 4H × *n* + 2H × *n* × *c* + 2H × *n* × *d*; -CH$_2$-, >C-CH$_2$-, and =C-CH$_2$-), 1.96 (br, 2H × *m* × *b* + 2H × *n* × *d*, =C-CH$_2$-C=), 2.55 (br, 1H × *m* × *a* + 1H × *n* × *c*; -CH<), 3.40 (br, 2H × *m* × *a*; >C-CH$_2$-O-), 3.53 (br, 2H × *m* × *b*; =C-CH$_2$-O-), 4.07 (br, 1H × *m*; OH), 4.76 (br, 2H × *m* × *a* + 2H × *n* × c; >C=CH$_2$), 5.18 (br, 2H × *m* × *b* + 2H × *n* × *d*; >C=CH-O-,); *a* and *b* are shown in Scheme 1 *a*:*b* = 0.43:0.57, *c* and *d* represent the 2,3- and the 1,2-polymerized units, respectively, in poly (**3**) segment *c*:*d* = 0.10:0.90, *m* and *n* represent the ratio of poly (**2a**) and poly (**3**), respectively, in the block copolymer *m*:*n* = 0.39:0.61; ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 14.0 (-CH$_3$), 22.5, 24.0, 27.5 (-CH$_2$-), 30.1, 31.6, 35.6 (>CH-), 60.0 (>CH$_2$-*C*H$_2$-OH), 69.1 (=CH-*C*H$_2$-OH), 110.3, 128.4, 128.6, 130.0 (=CH$_2$), 132.2, 132.1, 134.6, 134.8 (=*C*H-CH$_2$-OH, >*C*=CH$_2$, and >*C*=CH-CH$_2$-OH); IR (CHCl$_3$): $\tilde{\nu}$ = 3395 (O–H), 2957, 2928, 2858, 1464, 1379 (C–H), 1674, 1637 (C=C), 1095 cm^{-1} (C–O).

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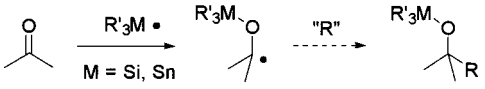
[5] The reaction of poly(**2a**) with ethyl vinyl ether (twofold excess with respect to the hydroxy moieties) was carried out in the presence of *p*-toluenesulfonic acid (1.0 mol%) in DMSO at 50 °C for 10 min. Addition to water precipitated a polymer in 98% yield whose acetal content was confirmed to be quantitative by ^{1}H NMR spectroscopy. The polymer thus obtained is soluble in various organic solvents including MeOH, THF, benzene, hexane, and CH_2Cl_2.
[6] Both poly(**2b**) and poly(**2c**) have high solubility in THF, a poor solvent for poly(**2a**). Thus, the GPC measurements were performed without treatment with ethyl vinyl ether.
[7] Since the block copolymer is soluble in THF, benzene, and CH_2Cl_2 which reflects the solubility of poly(**3**) segment, the GPC measurement was also performed directly without treatment with ethyl vinyl ether, and gave a unimodal elution peak ($M_n = 8.3 \times 10^3$, $M_w/M_n = 1.12$).

Novel Group-Transfer Three-Component Coupling of Silyltellurides, Carbonyl Compounds, and Isocyanides**

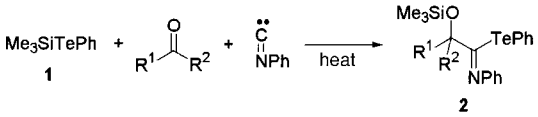
Hiroshi Miyazoe, Shigeru Yamago,* and Jun-ichi Yoshida*

Silyl and stannyl radicals add to the carbonyl oxygen atom to generate α-alkoxy radicals, and this is an elemental step in the radical-mediated reduction of carbonyl compounds with silyl and stannyl hydride reagents.[1, 2] Addition of the α-alkoxy radicals to radical acceptors would form a new C–C bond [Eq. (1)].[3] Indeed, α-stannyloxy radicals thus



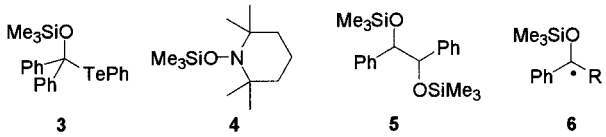
(1)

formed have been utilized for intramolecular C–C bond formation,[4] but there is no report on the intermolecular version, probably because reduction of the α-alkoxy radical by the metal hydride competes with C–C bond formation. Since organotellurium compounds are excellent precursors for carbon-centered radicals,[5, 6] we envisaged that silyl tellurides would act as silyl radical precursors which do not contain reducing hydrido groups.[7] We examined reactions of silyl tellurides in the presence of several radical acceptors and found a new coupling reaction of phenyl trimethylsilyl telluride (**1**), carbonyl compounds, and phenyl isocyanide [Eq. (2)]. Here we report on this new three-component coupling reaction, which is of both mechanistic and synthetic interest.



(2)

The coupling reaction of **1**,[8] benzophenone, and phenyl isocyanide proceeded under mild thermal conditions, and the group-transfer product **2a** ($R^1 = R^2 = Ph$) was formed in 82% yield after heating at 100 °C for 12 h in propionitrile. The tellurium atom plays a crucial role in this reaction, and the use of the corresponding silyl selenide or sulfide led to complete recovery of the starting materials. In addition, various silyl and stannyl hydrides did not promote C–C bond formation, and either the recovery of the starting materials or the reduction of the carbonyl group was observed. Monitoring the reaction in CD_3CN by ^{1}H NMR spectroscopy indicated that the formation of the α-silyloxytelluride **3** competed with that of **2a** and that the amount of **3** gradually decreased with the progress of the reaction. Indeed, isolated **3** reacted with



phenyl isocyanide at 100 °C to give **2a** in 92% yield. The coupling reaction was inhibited by the addition of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) radical (1.0 equiv) and mainly afforded silylated TEMPO **4** (63%); this suggests the intermediacy of trimethylsilyl radicals. The reaction proceeded faster in polar solvents such as propionitrile, DMF, and pyridine than in nonpolar solvents such as toluene, and the smooth reaction in basic media also ruled out the involvement of carbocation intermediates.[9]

The present reaction is generally applicable to a variety of ketones and aldehydes, and its scope and efficiency are summarized in Table 1. Aromatic ketones reacted smoothly and gave the desired adducts in high yields when almost equimolar quantities of each reagent were used (entries 1 – 6). Aliphatic ketones and aldehydes also gave the desired adducts in good yields (entries 7 and 8), but they were slightly less reactive than aromatic ketones. The reaction of benzaldehyde

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