Rhodium-catalyzed copolymerization of norbornadiene derivatives with carbon monoxide

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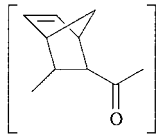
Received (in Cambridge, UK) 24th November 1999, Accepted 19th January 2000

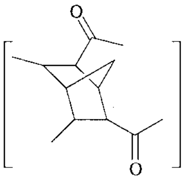
Alternate copolymerization of norbornadiene derivatives with carbon monoxide is catalyzed by a rhodium complex under water-gas shift reaction conditions selectively to give unsaturated polyketones in high yields.

Polyketones are of current interest in terms of functional materials exhibiting photo- and biodegradabilities as well as of starting materials for other classes of functionalized polymers.[1] As a useful method for the synthesis of polyketones, transition metal-catalyzed copolymerization between an olefin and carbon monoxide has been receiving much attention over the last few decades. Among transition metals, mono- and dicationic palladium complexes have predominantly been investigated and developed as excellent catalysts for the perfectly alternating copolymerization of olefins with carbon monoxide until recently.[2] The palladium catalytic system has also been extended to the copolymerization of several dienes with carbon monoxide, giving saturated poly(cyclic ketone)s.[3] Some reports described the copolymerization of norbornadiene with carbon monoxide in the presence of palladium complexes.[2a,4] but the resulting copolymers were characterized to be a mixture of structures A and B. Very recently, Novak and Safir have described a palladium-catalyzed copolymerization of 2,3-substituted norbornadiene derivatives with carbon monoxide to give alternating copolymers.[5] Other than palladium complexes, few effective catalysts are known for the copolymerization of olefins with carbon monoxide,† although the copolymerization of ethylene[7] and arylallene[8] with carbon monoxide catalyzed by rhodium complexes has been reported. In the course of our studies on the rhodium-catalyzed carbonylations of alkynes under water-gas shift reaction conditions,[9] we have now found that norbornadiene and its derivatives can smoothly be copolymerized with carbon monoxide. Here we report the first rhodium-catalyzed copolymerization of norbornadiene and its derivatives with carbon monoxide, producing perfectly alternating polyketones in which one of the two carbon–carbon double bonds of norbornadiene remains intact [eqn. (1)]. The structure has been characterized by chemical reactions as well as by spectral analyses.



A

+



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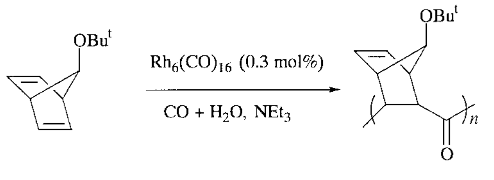


(1)

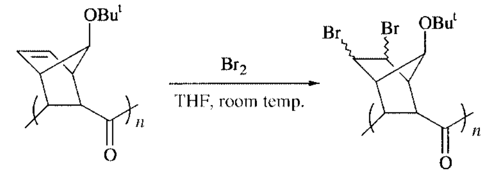
1a

2a (92% yield)

Thus, a mixture of 7-*tert*-butoxynorborna-2,5-diene **1a** (5 mmol, 0.820 g), $Rh_6(CO)_{16}$ (0.015 mmol, 15 mg), triethylamine (2 ml) and water (1 ml) in benzene (15 ml) was stirred in an autoclave at 55 °C for 24 h under 100 atm of carbon monoxide. After venting the gases from the autoclave at room temperature, the reaction solution was poured into a large amount of methanol (*ca.* 200 ml). Precipitates formed were collected by filtration, washed several times with methanol, and dried *in vacuo* at 50 °C overnight to give product **2a** as a white powder (0.883 g, 92% yield). Product **2a** is soluble in a variety of organic solvents such as acetone, chloroform, benzene and THF, and the GPC analysis (polystyrene standards) indicated **2a** to be a polymer with a molecular weight of 24 500 and a narrow molecular weight distribution (M_w/M_n = 1.38). In its IR spectrum, polymer **2a** showed a characteristic absorption at 1715 cm^{-1} typical of the carbonyl groups of polyketones.[4b,5] The weak absorption band at 1630 cm^{-1} and the stronger band at 3059 cm^{-1} indicated the presence of a carbon–carbon double bond.[10] ^1H and ^{13}C NMR ($CDCl_3$) spectra of **2a** exhibited broad signals but a very simple pattern, suggesting that the copolymer may have a regular structure. The ^1H NMR spectrum showed broad signals in the range 2.55–3.95 ppm, indicating that **2a** contains a ring structure and may be a copolymer of **1a** with CO. Furthermore, the ^1H NMR spectrum revealed that the ratio of olefinic protons to the other protons present in the copolymer is consistent with that predicted on the basis of structure **2a**, suggesting that one of the two C=C bonds of norbornadiene remains intact. Indeed, the $^{13}C\{^1H\}$ NMR spectrum exhibited a signal at 132 ppm attributable to the C=C group and a carbonyl resonance at 208 ppm. When the $^{13}C\{^1H\}$ NMR experiment was performed using an NNE (Heterogated Decoupling without Nuclear Overhauser Effect) pulse sequence, the spectrum exhibited a ratio of sp^2 to sp^3 carbons for the norbornene units consistent with the proposed structure for **2a**, corresponding to an alternating 1 : 1 copolymer of **1a** with CO. Thermogravimetric analysis (TGA) revealed that **2a** appeared to degrade by a two-step process with a mass loss of 72% at the first degradation step. This mass loss rate corresponds to the theoretical value ($C_5H_5OBu^t/C_{12}H_{16}O_2$ = 0.719) calculated for the case where all of the *tert*-butoxycyclopentadiene moieties $(C_5H_5OBu^t)_n$ of **2a** are liberated by a retro-Diels–Alder reaction.

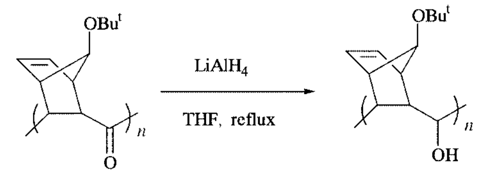
In order to characterize further and prove the structure of **2a**, we tried to convert it into functionalized polymers. Since **2a** has one C=O group and one C=C bond in the repeat unit, it may be easily modified chemically. Thus, as shown in eqn. (2), treatment of **2a** with an excess of bromine at room temperature gave dibromide **3a** in 84% yield. In the ^1H NMR spectrum of **3a**, the signal due to the olefinic protons of **2a** at 6.2 ppm disappeared completely and a new signal appeared at higher field around 4.5 ppm, while the IR spectrum showed that the absorption at 1715 cm^{-1} due to a carbonyl group remained, indicating that the polyketone structure was not affected.‡ In addition, the reaction of **2a** with $LiAlH_4$ in THF at 65 °C selectively gave polyol **4a** in 90% yield [eqn. (3)]. The IR spectrum of **4a** showed the disappearance of the C=O band at 1715 cm^{-1} of polyketone **2a** and the appearance of a new broad band at 3395 cm^{-1} attributable to a hydroxy group. The ^{13}C

NMR spectrum displayed the complete disappearance of the carbonyl carbon at 208 ppm, and the ^1H NMR spectrum is also consistent with the structure of **4a**.



2a **3a** (84% yield)

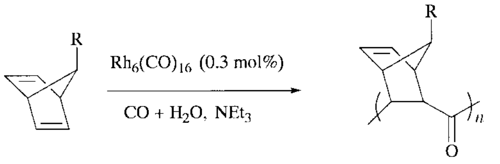
(2)



2a **4a** (90% yield)

(3)

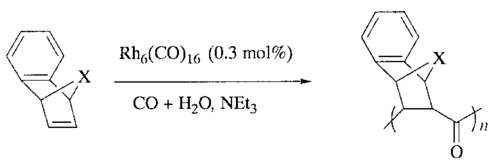
Besides 7-*tert*-butoxynorborna-2,5-diene **1a**, norbornadiene and its derivatives smoothly reacted with carbon monoxide in the presence of $Rh_6(CO)_{16}$ under the same reaction conditions to give the corresponding copolymers in good yields. As shown in eqn. (4), the reaction of norbornadiene **1b** (R = H) gave copolymer **2b** which is almost insoluble in organic solvents. The high-resolution solid-state ^{13}C NMR (CPMAS) spectrum of **2b** suggested that **2b** has the same structure as **2a**. 7-Phenylnorbornadiene **1c** (R = Ph), which was prepared by treatment[11] of 7-*tert*-butoxynorbornadiene with PhMgBr, also reacted with carbon monoxide to give copolymer **2c** in good yield with a molecular weight of M_w = 9000 (M_w/M_n = 1.38). Interestingly, 1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene **1d** having a norbornadiene skeleton was copolymerized with carbon monoxide to give copolymer **2d** with a high molecular weight (M_w = 25 500) in a high yield [eqn. (5)]. In contrast to **1d**, the reaction of **1e** gave the corresponding copolymer in good yield but with lower molecular weight (M_w = 2570, M_w/M_n = 1.24). Similarly, 2,3-substituted norbornadiene **1f** gave copolymer **2f** in 81% yield, but also with low molecular weight (M_w = 2530, M_w/M_n = 1.20), as shown in eqn. (6). Different electron densities on the C=C bonds of monomers **1d**, **1e** and **1f** could be considered to be a factor affecting the chain growth of the copolymers. In the present reaction system, the steric effect of the substituents on the norbornadiene skeleton might be another factor.



1b R = H **2b** (95% yield)

1c R = Ph **2c** (85% yield)

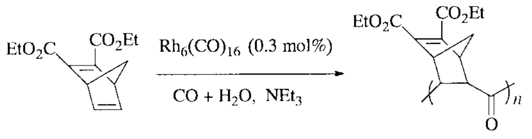
(4)



1d X = C=CMe$_2$ **2d** (90% yield)

1e X = O **2e** (81% yield)

(5)



1f **2f** (81% yield)

(6)

It should be noted that the copolymerization did not occur in the absence of water and amine, suggesting that the copolymerization could be catalyzed by an active rhodium species formed from the reaction of rhodium carbonyl species with water and amine.[7d,9] Detailed investigations are now in progress.

We thank Dr Kenji Wada, Kyoto University, for the measurement of solid-state ^{13}C NMR spectra, and are grateful to the Material Analysis Center of ISIR, Osaka University, for elemental analyses.

Notes and references

† The first transition metal-catalyzed copolymerization of ethylene with carbon monoxide was performed using nickel cyanide complexes in aqueous medium with carbon monoxide pressures as high as 200 atm and at a temperature up to 250 °C to form 'high molecular weight polyketones' (ref. 6). The subsequent advances made using a variety of nickel complexes were outlined in a review [ref. 2(*c*)].

‡ In fact the C, H and Br analyses of polymer **3a** gave a satisfactory result: calc. for $[C_{11}H_{16}OBr_2{\cdot}CO]_n$: C, 40.94; H, 4.58; Br, 45.39. Found: C, 40.81; H, 4.30; Br, 45.24%).

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Communication a909287k