Notes

Reactions of Organoboron Polymers Prepared by Hydroboration Polymerization. 1. Synthesis of Poly(alcohol) by Reaction with Carbon Monoxide

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A wide variety of reactions of organoboron compounds have been investigated in organic synthesis[1] together with the progress of the chemistry of hydroboration. In the field of polymer synthesis, however, applications of these reactions have been achieved only in the oxidation of poly(olefin)s to poly(alcohol)s.[2] Recently, we reported a "hydroboration polymerization", in which organoboron polymers were produced by a polyaddition between a diene and thexylborane (Scheme I).[3]

As the organoboron polymers obtained by hydroboration polymerization are regarded as a polymer homologue of trialkylborane, these new polymeric materials should have a possible potential as a new reactive polymer.

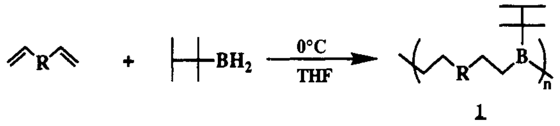
In general, poly(alcohol)s have interesting characteristics that can be applied as coatings, adhesives, and polymeric reagents.[4] However, the general synthetic methods for the preparation of poly(alcohol)s have been limited so far. Here we wish to present a novel synthetic method for the preparation of poly(alcohol) by the reaction of organoboron polymers with carbon monoxide followed by an oxidative treatment.

Results and Discussion

Organoboron compounds are known to react with carbon monoxide to produce alcohols, aldehydes, or ketones.[5] The products can be varied by changing the additional reagents and reaction conditions. To convert boron-alkyls into alcohols and ketones, their reactions with dichloromethyl methyl ether[6] and with cyanide anion[7] are also available, respectively. During the course of our studies on the reaction of organoboron polymers, the reaction with carbon monoxide was first examined here (Scheme II).

The starting organoboron polymers (**1a–i**) were obtained easily by the reaction of the corresponding diene and thexylborane under mild conditions.[3] When 1,7-octadiene was used as the diene monomer, M_n and M_w of the obtained polymer (**1a**) were 19 500 and 27 700, respectively (GPC, dry THF, polystyrene standard). In order to optimize the conditions of the reaction with carbon monoxide, this polymer (**1a**) was subjected to the reaction. The polymer obtained by hydroboration polymerization was used without further purification and was reacted directly with carbon monoxide in an autoclave. Details of the reaction conditions are described under Experimental Section. The results are summarized in Table I.

Scheme I



Scheme II

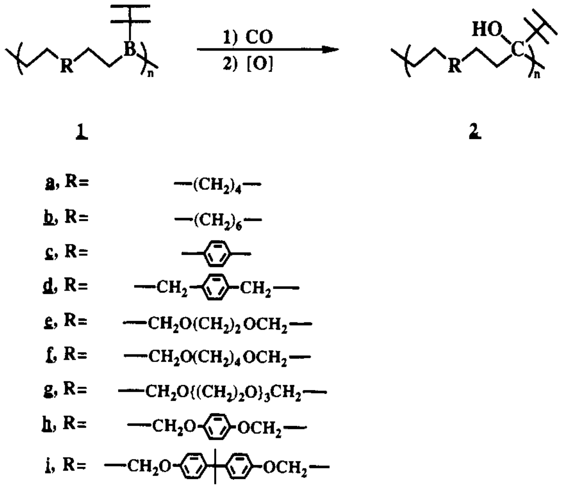


Table I
Reactions of Organoboron Polymer 1a with Carbon Monoxide

run	conditions	composition[f] alcohol	composition[f] ketone	$\bar{M}_n$[g]	yield,[h] %
1	50 °C 15 h, 120 °C 5 h[a]	100	0	4080	82
2	50 °C 15 h[b]	50	50	2500	80
3	rt 18 h[b]	32	68	2500	61
4	0 °C 15 h[b]	34	66	590	67
5	−25 °C 40 h[c]			no polymer	0
6	50 °C 15 h[d]	35	65	3900	nd[i]
7	50 °C 15 h[e]			gelation	

[a] Run 1: 50 °C 15 h (CO, 25 kg/cm^2) and then 120 °C 5 h (after CO was released). [b] Runs 2–4: CO, 20–25 kg/cm^2. [c] Run 5: CO, 30–35 kg/cm^2. [d] H_2O (1 equiv) was added at the carbonylation stage (CO, 30–35 kg/cm^2). [e] In the absence of ethylene glycol. [f] Calculated from ^1H NMR. [g] GPC (THF), polystyrene standard. [h] Isolated yields after reprecipitation into methanol/water (v/v = 2/1). [i] Not determined.

Under forced reaction conditions, e.g., at 120 °C, the obtained polymer (**2a**) after oxidation was found to consist exclusively of alcohol segment (run 1). In contrast, under milder conditions, e.g., at 50 °C, the obtained polymer was found to consist of both alcohol and ketone segments (run 2), from their ^1H NMR and IR analyses. Typical examples of ^1H NMR and IR spectra of poly(alcohol) and poly(alcohol)–poly(ketone) are illustrated in Figures 1 and 2, respectively.

As shown in Figure 1, no peak due to the stretching of C=O is observed around 1700 cm^{-1} in the IR, and the integral area ratio between thexyl protons and methylene protons in the ^1H NMR is in good agreement with the calculated value. In Figure 2, however, the stretching band of C=O at 1702 cm^{-1} is observed in the IR, and new peaks at 2.38 ppm assignable to the methylene protons adjacent to C=O are observed accompanied by a decrease of protons of thexyl groups in the ^1H NMR. The compositions of alcohol segments and ketone segments can be estimated

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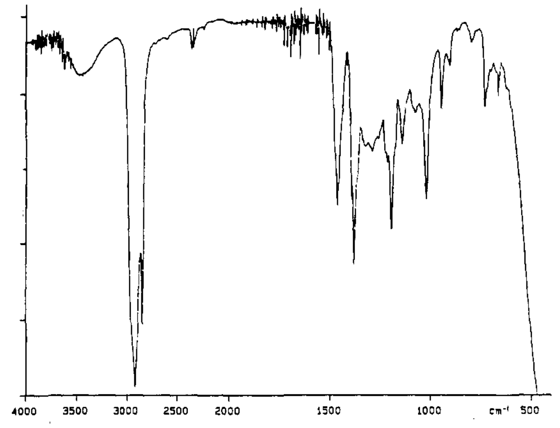
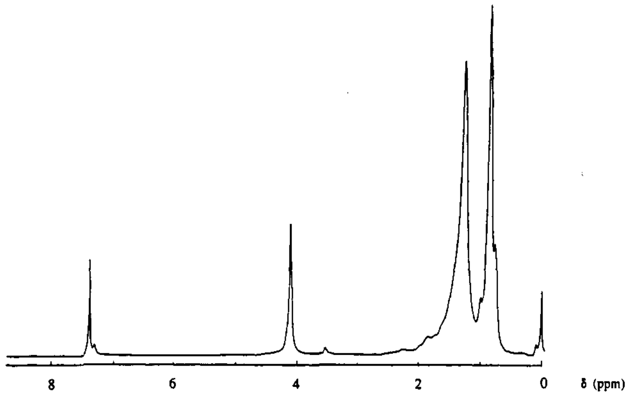


IR



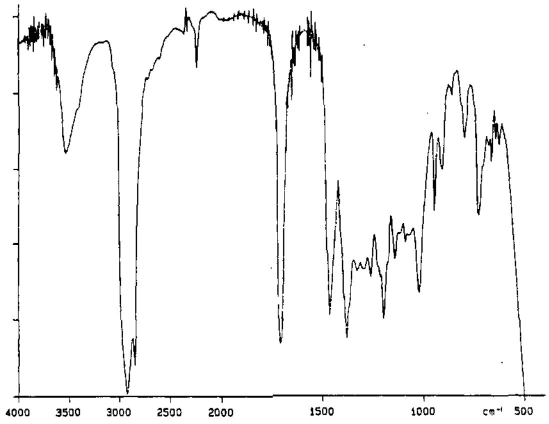
^{1}H-NMR

Figure 1. IR and ^{1}H NMR spectra of a poly(alcohol) (**2a**, Table I, run 1).

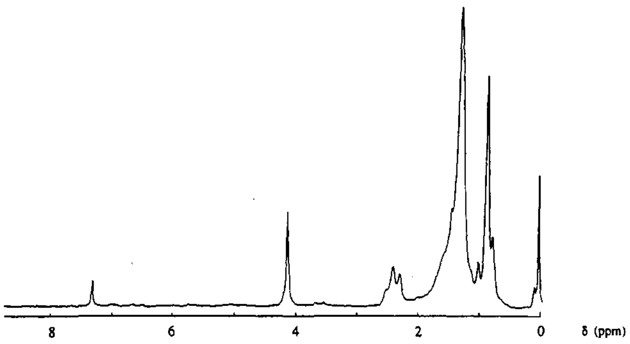
from the integral ratio between thexyl protons and methylenes. These values are also listed in Table I. According to the proposed mechanism for the reaction of organoboron compounds with carbon monoxide,[5c] the present polymer reaction can be considered to proceed as shown in Scheme III. A primary alkyl group is known to be more reactive than a tertiary alkyl group in this intramolecular rearrangement reaction.[5d] Thus, it is reasonable to suppose that the migration of the main-chain methylene group of the organoboron polymer (mostly consisting of a primary alkyl group) is more likely to occur than that of the thexyl group. This different reactivity made it possible to include ketone segments without obvious scission of the polymer chain, though the molecular weight of the obtained polymer was decreased due to the unreacted unit of boron–methylene linkage, as the reaction condition became milder. Under much milder condition, e.g., at −25 °C (run 5), this migration reaction did not occur and resulted only in the decomposition of the starting polymer.

The obtained poly(alcohol) was a white gum and was soluble in organic solvents such as THF and chloroform. These polymers were obviously air stable. This migration reaction is known to proceed intramolecularly. Thus, it can be mentioned that the molecular weight of the starting organoboron polymers should be higher than (or the same as) that of poly(alcohol)s.

Poly(alcohol)s from Various Organoboron Polymers. As mentioned above, selective conversion of an organoboron polymer to the corresponding poly(alcohol) was possible under forced reaction condition. When other organoboron polymers (**1b–i**) were subjected to this reaction at 120 °C, the corresponding poly(alcohol)s were obtained. The results are summarized in Table II. These conversions may offer a new synthetic method for poly(alcohol)s from the corresponding dienes.



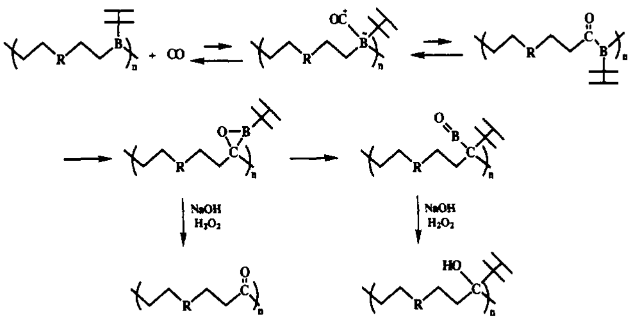
IR



^{1}H-NMR

Figure 2. IR and ^{1}H NMR spectra of a poly(alcohol)-*co*-poly(ketone) (Table I, run 2).

Scheme III



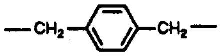
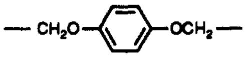
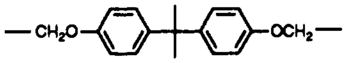
Experimental Section

Materials and Instruments. Tetrahydrofuran was dried over lithium aluminum hydride and distilled before use. Ethylene glycol was dried over sodium and distilled under reduced pressure. Sodium hydroxide, hydrogen peroxide (30%), benzene, and methanol were used without purification.

The ^{1}H NMR spectrum was recorded in $CDCl_3$ on a Hitachi R-600 instrument. The IR spectrum was obtained on a Perkin-Elmer 1600 spectrometer. Gel permeation chromatographic analysis was carried out on a Tosoh HLC-8020 (TSK gel G3000) after calibration with standard polystyrene samples.

Synthesis of Poly(alcohol)s from Organoboron Polymers. A Typical Procedure (Table I, Run 1). The organoboron polymer **1a** was prepared as previously described[3] and was used without isolation. To a nitrogen-purged autoclave (30 mL) equipped with a magnetic stirrer tip were added a THF solution (5 mL) of **1a** (prepared from 0.189 g, 1.72 mmol, of 1,7-octadiene and 0.172 g, 1.75 mmol, of thexylborane) and ethylene glycol (0.2 mL). Carbon monoxide was charged (20–25 kg/cm^2) from a cylinder. After the mixture was heated at 50 °C for 15 h, carbon

Table II
Synthesis of Poly(alcohol)s (2a–i) from Various Organoboron Polymers (1a–i)[a]

run	R		B polymers (1)	poly(alcohol)s (2)		
			$\bar{M}_n$[b]	$\bar{M}_n$[c]	$\bar{M}_w$[c]	yield,[d] %
1	$-(CH_2)_4-$	(a)	19500	4080	13500	82
2	$-(CH_2)_6-$	(b)	20500	4200	9600	60
3		(c)	14600	2990	7650	74
4		(d)	9300	5400	12300	77
5	$-CH_2O(CH_2)_2OCH_2-$	(e)	1520	1280	2200	24
6	$-CH_2O(CH_2)_4OCH_2-$	(f)	2280	1620	2800	59
7	$-CH_2O\{(CH_2)_2O\}_3CH_2-$	(g)	3200	2200	3720	47
8		(h)	6800	1940	3700	39
9		(i)	11700	2320	4400	89

[a] Reactions were carried out in the presence of 0.1 mL of ethylene glycol under carbon monoxide (20–25 kg/cm^2) in an autoclave. [b] GPC (dry THF, polystyrene standard). [c] GPC (THF, polystyrene standard). [d] Isolated yield after reprecipitation into methanol/water ($v/v = 2/1$).

monoxide was purged out and the temperature was raised to 120 °C for an additional 5 h. The reaction mixture was treated with aqueous NaOH (6 N, 4 mL) and hydrogen peroxide (30%, 4 mL) at 50 °C for 3 h. This mixture was extracted with diethyl ether, dried with Na_2SO_4, and concentrated. To remove contaminated boronic acid, the obtained polymer was subjected to 10× evaporation with methanol/benzene under normal pressure.[8] After precipitation into $MeOH/H_2O$ ($v/v = 2/1$), **2a** was obtained as a colorless gum (0.319 g, 82% yield). ^1H NMR and IR data are given in Figure 1. Poly(alcohol)–poly(ketone)s from **1a** (in Table I, runs 2–7) were prepared in a similar manner to this, except the reaction conditions were as follows: Table I, run 2, 15 h at 50 °C with 20–25 kg/cm^2 of carbon monoxide; run 3, 15 h at ambient temperature with 20–25 kg/cm^2 of carbon monoxide; run 4, 18 h at 0 °C with 20–25 kg/cm^2 of carbon monoxide; run 5, 40 h at −25 °C with 30–35 kg/cm^2 of carbon monoxide; run 6, 15 h at 50 °C with 30–35 kg/cm^2 of carbon monoxide in the presence of an equivalent molar of water; run 7, 15 h at 50 °C with 30–35 kg/cm^2 of carbon monoxide without ethylene glycol.

Various poly(alcohol)s were prepared in the same manner as described above. **2b**: ^1H NMR δ ($CDCl_3$) 0.55–1.06 (CH_3, 12 H), 1.06–2.01 (CH, CH_2, 21 H); IR (neat) 3447, 2852, 1465, 1383, 1196, 1022 cm^{-1}. **2c**: ^1H NMR δ ($CDCl_3$) 0.59–1.15 (CH_3, 12 H), 1.15–2.31 (CH, CH_2, 5 H), 2.36–3.13 ($PhCH_2$, 4 H), 7.20 (C_6H_4, s, 4 H); IR (neat) 3482, 2961, 1513, 1465, 1382, 1042, 909, 734 cm^{-1}. **2d**: ^1H NMR δ ($CDCl_3$) 0.55–1.15 (CH_3, 12 H), 1.25–2.85 (CH, CH_2, 13 H), 7.07 (C_6H_4, 4 H); IR (cell, $CHCl_3$) 3616, 2960, 1463, 1384, 1020, 906 cm^{-1}. **2e**: ^1H NMR δ ($CDCl_3$) 0.63–1.19 (CH_3, 12 H), 1.33–2.17 (CH, CH_2, 9 H), 3.17–3.91 (OCH_2, 8 H); IR (neat) 3474, 2959, 1465, 1381, 1120 cm^{-1}. **2f**: ^1H NMR δ ($CDCl_3$) 0.55–1.15 (CH_3, 12 H), 1.33–2.37 (CH, CH_2, 13 H), 3.15–3.97 (OCH_2, 8 H); IR (neat) 3446, 2945, 1471, 1367, 1111 cm^{-1}. **2g**: ^1H NMR δ ($CDCl_3$) 0.59–1.13 (CH_3, 12 H), 1.31–2.35 (CH, CH_2, 9 H), 3.09–3.91 (OCH_2, 16 H); IR (neat) 3465, 2868, 1464, 1382, 1115 cm^{-1}. **2h**: ^1H NMR δ ($CDCl_3$) 0.63–1.13 (CH_3, 12 H), 1.13–2.35 (CH, CH_2, 9 H), 3.66–4.27 (OCH_2, 4 H), 6.83 (C_6H_4, s, 4 H); IR (neat) 3508, 2957, 1506, 1471, 1382, 1228, 1030, 824 cm^{-1}. **2i**: ^1H NMR δ ($CDCl_3$) 0.57–1.11 (CH_3, 12 H), 1.33–2.38 (CH, CH_2, CH_3, 15 H), 3.58–4.36 (OCH_2, 4 H), 6.57–7.30 (C_6H_4, 8 H); IR (neat) 3510, 2965, 1608, 1510, 1472, 1248, 1181, 1011, 910, 829, 735 cm^{-1}.

References and Notes

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(6) In ref 1a, p 272.

(7) In ref 1a, p 280.

(8) If this procedure was omitted, the obtained poly(alcohol) became insoluble due to the cross-linking reaction of alcohol moieties with boronic acid.

Registry No. **1a** (copolymer), 128967-04-4; **1b** (copolymer), 130934-20-2; **1c** (copolymer), 130934-21-3; **1d** (copolymer), 130934-22-4; **1e** (copolymer), 130934-23-5; **1f** (copolymer), 130934-24-6; **1g** (copolymer), 130934-25-7; **1h** (copolymer), 130934-26-8; **1i** (copolymer), 130934-27-9.