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Reactions of organoboron polymers prepared by hydroboration polymerization

III. Synthesis of poly(alcohol)s by the reaction with α,α-dichloromethyl methyl ether*

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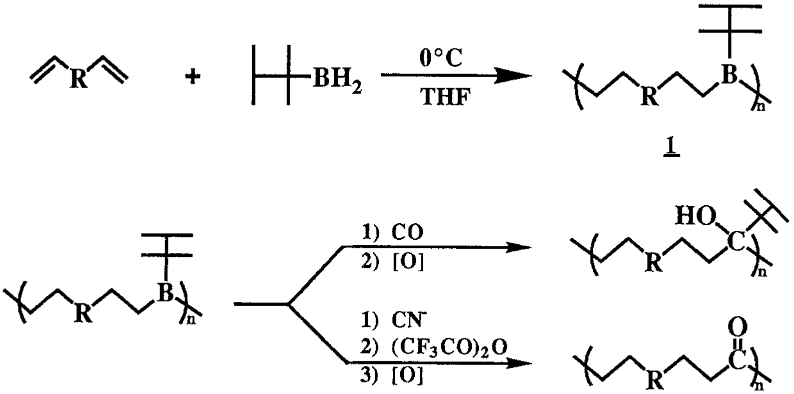
Summary

Hydroboration polymerization of diolefin gives an organoboron polymer, which can be regarded as a polymer homologue of trialkylborane. The organoboron polymers obtained were reacted with α,α-dichloromethyl methyl ether (DCME) followed by the oxidative treatment to produce the corresponding poly(alcohol)s in high yields.

Introduction

Recently, we reported the synthesis of organoboron polymers by hydroboration polymerization [2]. The organoboron polymers obtained were used as a novel type of reactive polymers. For example, these polymers were reacted with carbon monoxide or with potassium cyanide followed by the oxidative treatment to produce poly(alcohol)s [3] or poly(ketone)s [4], respectively (Scheme I).

Scheme I



Each of these transformation reactions provided a facile synthetic way to produce poly(alcohol)s or poly(ketone)s, respectively. Synthesis of these polymers are quite difficult by the conventional known methods. Here we wish to present an alternative method to convert organoboron polymers into poly(alcohol)s by using α,α-dichloromethyl methyl ether (DCME).

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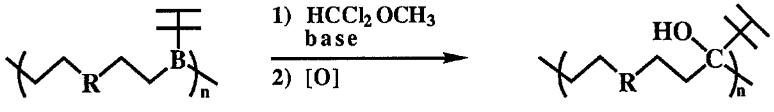
Results and Discussion

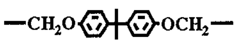
Tertiary alcohols are obtained from trialkylboranes by the reaction with α,α-dichloromethyl methyl ether (DCME) [5] as well as by the reaction with carbon monoxide [6]. The present migration reaction using DCME is known to proceed intramolecularly. Due to the high conversion of this reaction, the formation of poly(alcohol)s by the reaction of organoboron polymers with DCME can be expected (Scheme II).

Scheme II



1 2

Table I Synthesis of Poly(alcohol)s (2a-2i) from Various Organoboron Polymers (1a-1i)$^{a)}$.

Run	R		B-Polymers (1)	Poly(alcohol)s (2)	
			$\overline{M}_n$$^{b)}$	$\overline{M}_n$$^{c)}$	$\overline{M}_w$$^{c)}$
1	$-(CH_2)_4-$	(a)	12,700	3,600	10,600
2	$-(CH_2)_6-$	(b)	18,400	4,900	14,700
3		(c)	19,200	2,200	5,400
4		(d)	9,400	1,700	9,700
5	$-CH_2O(CH_2)_2OCH_2-$	(e)	1,200	780	1,600
6	$-CH_2O(CH_2)_4OCH_2-$	(f)	1,900	560	1,200
7	$-CH_2O\{(CH_2)_2O\}_3CH_2-$	(g)	1,900	550	1,300
8		(h)	5,100	1,300	2,400
9		(i)	7,600	2,300	4,700

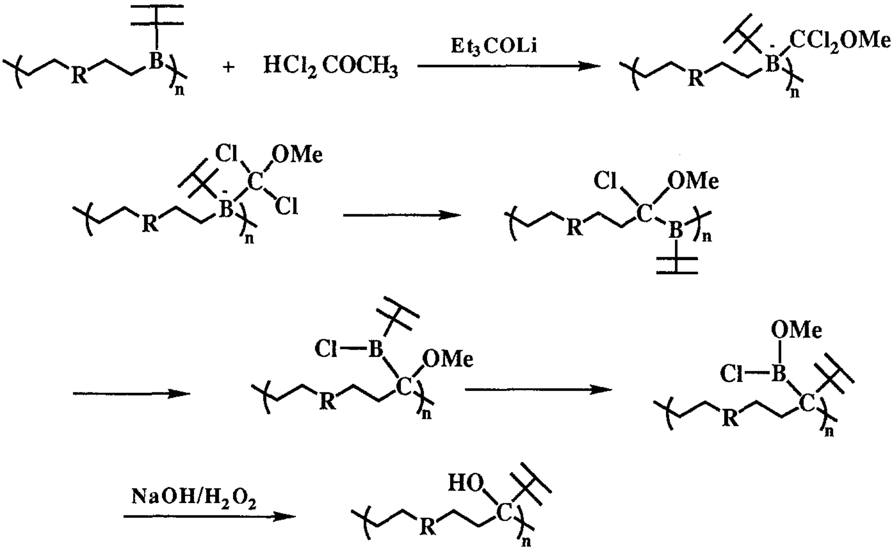
a) After adding 1.2eq. of DCME to a THF solution of organoboron polymers, 1.5eq. of Et_3COLi/n-hexane was added at 0°C.
b) GPC (dry THF, PSt, Std). c) GPC (THF, PSt, Std).

Organoboron polymers (**1a-1i**) were prepared by hydroboration polymerization starting from various diolefins and thexylborane as reported previously [2] and were used without isolation. As a typical example, an organoboron polymer (**1a**) was prepared from thexylborane and 1,7-octadiene. The number-average molecular weight of the obtained polymer (**1a**) was 12,700, which was determined by GPC on the basis of polystyrene standard samples.

Conversions of the organoboron polymers into poly(alcohol)s were examined by adding 1.2eq. of DCME to the THF solution of **1a-1i** followed by the treatment with 1.5eq. of Et_3OLi in n-hexane. After oxidative treatment with $NaOH/H_2O_2$, the corresponding poly(alcohol)s were obtained. The obtained poly(alcohol)s, however, became insoluble when the solvents were completely removed, due to the crosslinking reaction with contaminated boronic acid. Thus, after careful treatment with hot methanol, these poly(alcohol)s could be successfully isolated as THF-soluble materials in almost quantitative yields based on the starting dienes.

Table I (see the preceding page) summarizes the results of reactions of various organoboron polymers with DCME to produce the corresponding poly(alcohol)s. The molecular weights of the starting organoboron polymers are also shown in this table. According to the reaction mechanism of trialkylborane reported previously [5], the present reaction can be taken to proceed as shown in Scheme III.

Scheme III



That is, carbanion having three leaving groups (generated *in situ* by means of hindered base) attacks boron atom, and then triple migration takes place intramolecularly. In the case of incomplete migration, the boron atom is remained in the main chain, which causes a scission of the polymer. $\overline{M}_n$ of poly(alcohol) (**2a**) obtained from **1a** was estimated to be 3,600 (GPC, based on polystyrene calibration curves). Although the direct comparison of molecular weights between the starting organoboron polymers and the obtained poly(alcohol)s seems to have little meanings (both of these are calculated from the standard polystyrene samples), only small amounts of scission at C-B bond in the main chain of the starting polymers (1 or 2 points per polymer chain) might take place under the examined reaction conditions.

The reaction with DCME as well as that with carbon monoxide may offer a useful synthetic way to obtain poly(alcohol)s. Because the reaction with carbon monoxide requires relatively severe conditions (120°C, 30kg/cm^2), the reaction with DCME provides more facile way for the conversion of organoboron polymers into poly(alcohol)s under mild conditions.

Experimental Section

Materials and Instruments Tetrahydrofuran was dried over lithium aluminum hydride and was distilled before use. Commercially available DCME was distilled before use. Sodium hydroxide, hydrogen peroxide (30%), benzene, and methanol were used without further purification.

^{1}H-NMR spectrum was recorded in $CDCl_3$ on a Hitachi R-600 instrument (60MHz). 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) (2a) from Organoboron Polymer (1a) A typical procedure is as follows. To a THF solution of **1a** prepared from 1,7-octadiene (0.189g, 1.72mmol) and thexylborane (0.173g, 1.76mmol), was added DCME (0.228g, 1.98mmol) and Et_3OLi in n-hexane (1.36N, 2.2ml) at 0°C under nitrogen. The reaction mixture was stirred for 1 day at room temperature. After the treatment with aqueous NaOH (6N, 6ml) and H_2O_2 (30%, 6ml) at 50°C for 3 hours, the reaction mixture was extracted with three 50ml portions of THF and dried over Na_2SO_4. After evaporation with methanol/benzene (10 times) under normal pressure, freeze-drying with benzene gave **2a** in a quantitative yield. When this crude product was reprecipitated into ethanol/water (v/v=1/1), 0.200g (51%) of **2a** was isolated as a colorless gum. Spectral data for poly(alcohol)s (**2a**-**2i**) were identical with those reported previously by us [3].

References and Notes

1. For part II, see ref (4).
2. Y. Chujo, I. Tomita, Y. Hashiguchi, H. Tanigawa, E. Ihara, T. Saegusa, *Macromolecules*, 24, 345 (1991).
3. Y. Chujo, I. Tomita, Y. Hashiguchi, T. Saegusa, *Macromolecules,* 24, in press, (1991).
4. Y. Chujo, I. Tomita, Y. Hashiguchi, T. Saegusa, *Polym. Bull.,* 25, 1 (1991).
5. A. Pelter, K. Smith, H. C. Brown, In *Borane Reagents;* Academic Press: London, 1988, p272 and references cited therein.
6. See ref (3), and references cited therein.

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