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Reactions of organoboron polymers prepared by hydroboration polymerization

II. Selective synthesis of poly(ketone) by the reaction with cyanide anion

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Summary

This paper describes a novel methodology for the preparation of poly(ketone). An organoboron polymer was prepared by polyaddition between thexylborane and 1,7-octadiene, which was reacted with potassium cyanide in the presence of trifluoroacetic anhydride. After oxidation of the reaction mixture, the corresponding poly(ketone) was obtained.

Introduction

Reactions of organoboron compounds with cyanide anion in the presence of acylating reagents such as trifluoroacetic anhydride (TFAA) are reported to produce the corresponding ketons [1]. Numerous numbers of reports have dealt with this reaction [2]. Recently, we reported a novel synthetic method to obtain organoboron polymers by polyaddition between thexylborane and dienes (i.e., "Hydroboration Polymerization") [3]. As the obtained organoboron polymers having trialkylborane unit in their main chains can be considered to be a novel type of reactive polymers, we have reported the reaction of organoboron polymers with carbon monoxide to produce the corresponding poly(alcohol)s [4]. In this report, the direct use of the migration reaction of organoboron polymers with cyanide anion to produce a polymeric ketone was examined.

Results and Discussion

The starting organoboron polymer (**1**) was obtained easily by the reaction of 1,7-octadiene and thexylborane under mild conditions (Scheme I) [3]. As a preliminary experiment, **1** was subjected to the reaction with potassium cyanide (Scheme II). Details of the reaction conditions are described in the experimental section.

After the oxidation of the reaction mixture followed by the coagulation with methanol, the desired poly(ketone) (**2**) was obtained in a yield of 39%. The obtained poly(ketone) (**2**) was a white solid,

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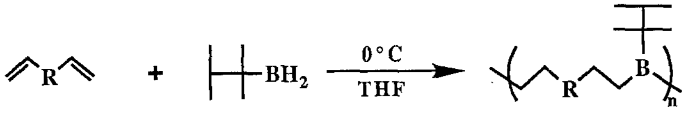
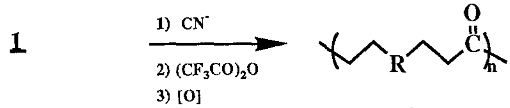
Scheme I



1

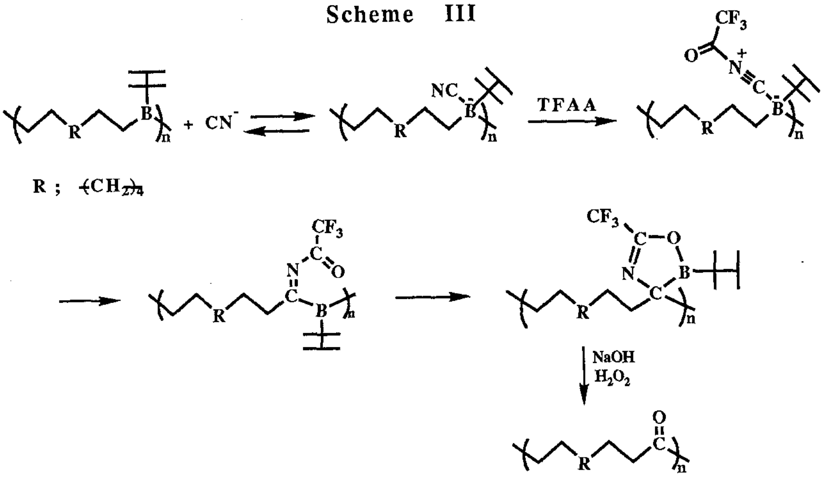
Scheme II



2

and was soluble in chloroform. **2** was stable enough under air. This stability indicates no C-B bonds in the main chain of the resulting polymer. The number average molecular weight of **2** was estimated to be 1,300 from GPC ($CHCl_3$ as an eluent) by using polystyrene calibration curves. This value is somewhat lower than that of poly(alcohol)s obtained by the reaction of the organoboron polymer with carbon monoxide [4]. According to the proposed mechanism for the reaction of organoborane with cyanide anion [1], the present polymer reaction can be described to proceed as shown in Scheme III.

Scheme III



Primary alkyl group is known to be more reactive than tertiary alkyl group in this intramolecular rearrangement [1]. Thus, it is possible to make a poly(ketone) by the exclusive migration of main chains of organoboron polymer (consisting of primary alkyl groups). Although the difference of reactivity between methylene group and thexyl group seems to be large enough, the molecular weight of the obtained poly(ketone) was lower than expected. The reaction for thexyl dialkylborane has been reported to be not quantitative (76-85%) [1].

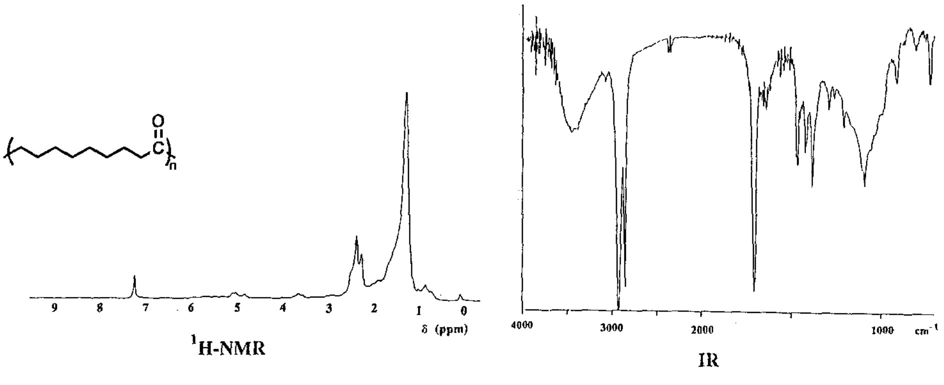
The present reaction proceeds stepwise, i.e., the formation of poly(anion) followed by the migration. Accordingly, before adding TFAA, it is necessary to form a poly(anion) completely. This step may require the severe condition due to the repulsion of the charge in the poly(anion). The remained neutral boron should result in the scission of the expected polymer after the oxidation of C-B bonds. This point is entirely different from the reaction with carbon monoxide in which the migration reaction does not proceed stepwise. These may be the reasons of low molecular weight of poly(ketone) obtained. Table I summarizes the results of preparation of poly(ketone) under various conditions.

^{1}H-NMR and IR spectra of **2** are represented in Figure 1. In its IR spectrum, a strong peak due to the stretching of C=O was observed around 1710cm^{-1}. In its ^{1}H-NMR, the integral ratio between the protons of inner methylenes and methylene protons adjacent to carbonyl group was in good agreement to the calculated value.

Table I Synthesis of Poly(ketone) by the Reaction of 1 with KCN and TFAA.[a)]

Run	Reaction Conditions KCN	Reaction Conditions TFAA	Yield(%)[b)]	$\overline{M}$n[c)]
1	60°C 1.5h	50°C 4h	29	1,800
2	40°C 1h	50°C 3h	39	1,300
3	rt 1h	50°C 1h	10	-
4	rt	rt	6	-

a) Reactions were carried out in THF.
b) Isolated yields after reprecipitation into methanol.
c) GPC ($CHCl_3$, Polystyrene standard).



^{1}H-NMR

IR

Figure 1 ^{1}H-NMR and IR spectra of poly(ketone) (2).

The fact that this migration reaction proceeds intramolecularly [1] supports the formation of polymeric organoboron species by hydroboration polymerization. Although the molecular weight of the obtained polymer is not enough high at the present time, the present conversion reaction of organoboron polymers provides a new synthetic method to prepare poly(ketone)s.

Experimental Section

Materials and Instruments Tetrahydrofuran was dried over lithium aluminum hydride and distilled before use. TFAA was purified as usual technique. Potassium cyanide, sodium hydroxide, hydrogen peroxide (30%), and methanol were used without further purification.

^{1}H-NMR spectrum was recorded in $CDCl_3$ on a Hitachi R-600 instrument. IR spectrum was obtained on a Perkin Elmer 1600 spectrometer. Gel permeation chromatographic analysis was carried out on a Jasco Triroter (Shodex AC803, $CHCl_3$) after calibration with standard polystyrene samples.

Synthesis of Poly(ketone) (2) from Organoboron Polymer (1). The organoboron polymer (**1**) was prepared as reported [3] and used without isolation. To well dried KCN (0.36g, 5.5mmol) was added a 5ml THF solution of **1** (prepared from 0.55g, 5.0mmol of 1,7-octadiene and 0.49g, 5.0mmol of thexylborane) under nitrogen. This reaction mixture was stirred for 1 hour at 40°C. TFAA (1.26g, 6mmol) was added and the mixture was allowed to keep for 3 hours at 50°C. The reaction mixture was treated with aqueous NaOH (6N, 3ml) and hydrogen peroxide (30%, 8ml) at 50°C for 4 hours. The organic layer was dried over Na_2SO_4, and concentrated. After precipitation into methanol, **2** was obtained as a white solid (0.27g, 39% yield). ^{1}H-NMR and IR spectra are shown in Figure 1.

References and Notes

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