

NOTES

Reactions of Organoboron Polymers Prepared by Hydroboration Polymerization V.[†] Synthesis of Polymers Having Cyano Groups by the Reaction with 2-Bromo-6-lithiopyridine

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We have recently explored a novel methodology of hydroboration polymerization,¹ in which the organoboron polymers (**3**) were obtained by polyaddition reaction between thexylborane (**1**) and various dienes (**2**). The polymers prepared by this hydroboration polymerization can be regarded as a polymer homologue of trialkylborane. Generally, organoboron compounds are known as very versatile reagents or reaction intermediates for the preparation of a wide variety of functional compounds.² Similarly, the organoboron polymers can be expected as precursor polymers for the preparation of various functional groups. In other words, these polymers are expected to have a potential as a novel reactive polymer. From this point of view, we reported some transformation reactions from these organoboron polymers to polyalcohols or polyketones by the reaction with carbon monoxide,³ cyanide anion,⁴ or α,α -dichloromethyl methyl ether,⁵ respectively. Very recently, we also explored a conversion from organoboron polymers to diol-containing polymers by the reaction with α -furyllithium

followed by the treatment with acetic acid and then by the oxidative treatment.⁶

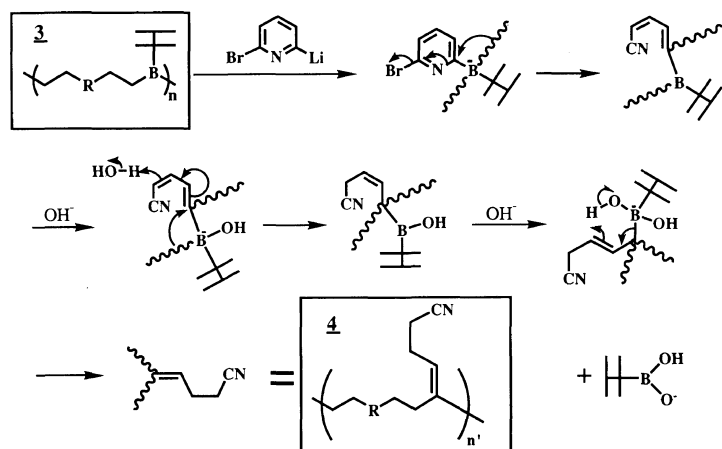
On the other hand, Chung *et al.* reported the synthesis of polymers having organoboron moieties in the branches by means of ring-opening metathesis polymerization⁷ or Ziegler–Natta polymerization.⁸ In these studies, organoboron polymers obtained were transformed to various polyalcohols by the oxidative treatments. This study provides a useful methodology for the functionalization of commodity polymers, especially of polyolefins.

The ring-opening reaction of pyridine ring can be performed *via* pyridinium salt.⁹ The reaction of trialkylborane with 2-bromo-6-lithiopyridine followed by the treatment with sodium hydroxide was also reported to give the corresponding nitrile.¹⁰ In a series of our studies on versatile reactions of organoboron polymers prepared by hydroboration polymerization, the present paper describes the reaction with 2-bromo-6-lithiopyridine to afford the corresponding polymers having cyano groups.

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[†] For Parts I, II, III, and IV, see ref 3, 4, 5, and 6, respectively.



Scheme 2.

was observed around 5.1 ppm and the integral ratios between olefinic protons and others were in good agreement with the calculated values for the expected structure. Small peak around 1.0 ppm was also observed probably due to the remained hexyl protons at polymer ends. From the results of spectroscopic analyses, other polymers (**4b**, **4d–g**) had the similar structures as **4a**. In the case of **2c**, however, hydroboration polymerization proceeded insufficiently due to cyclization, which caused low yield and low molecular weight of the product polymer. In IR spectrum of **4a**, two absorption bands assignable to $C\equiv N$ and $C=C$ stretching vibrations were observed around 2246 and 1665 cm^{-1} , respectively.

Referred to the proposed mechanism for the reaction of trialkylborane with 2-bromo-6-lithiopyridine,¹⁰ the present polymer reaction can be considered to proceed as shown in Scheme 2. Generally, a primary alkyl group is said to be more reactive than a tertiary alkyl group in this intramolecular migration. Accordingly, in the present reaction, it is reasonable to suppose that the migration of the polymer chains is easier than that of hexyl group, since polymer chains of organoboron polymer consist of primary alkyl groups. In this mechanism, the reaction of **2** with 2-

bromo-6-lithiopyridine affords lithium (6-bromo-2-pyridyl)trialkylborate, where one polymer chain migrates from boron atom to α -carbon of pyridine ring, followed by the ring-opening of pyridine ring and then the elimination of bromide anion. The following generations of borate anions and migrations of alkyl groups give rise to the polymer having olefins and cyano groups.

Generally, the synthesis of the polymers having cyano groups has been very limited so far except for polyacrylonitrile. Thus, the present study provides a useful and convenient method for the preparation of polymers having such functional groups. In other words, organoboron polymers prepared by hydroboration polymerization can be expected as a novel type of reactive polymers.

EXPERIMENTAL

Materials and Instruments

Hexylborane (**1**) was prepared by the reaction of borane-dimethylsulfide complex with 2,3-dimethyl-2-butene¹² and was purified by distillation. Tetrahydrofuran (THF) was dried over sodium and distilled before use. 2,6-Dibromopyridine was purified by recrystallization from THF/*n*-hexane. *n*-Bu-

tyllithium, sodium hydroxide, hydrogen peroxide (30%), benzene, diethyl ether, *n*-hexane, and methanol were used without further purification.

^1H NMR spectrum was recorded in CDCl_3 on a Hitachi R-600 instrument or LEOL LNM-GX400 instrument. ^{13}C NMR spectrum was recorded in CDCl_3 on a Hitachi R-900 instrument. IR spectrum was obtained on a Perkin Elmer 1600 spectrometer. Gel permeation chromatographic analysis was carried out on a Tosoh HLC-8020 (TSK gel G4000) after calibration with standard polystyrene samples.

Synthesis of Polymers Having Cyano Groups from Organoboron Polymers

A typical procedure is described as follows: The organoboron polymer (**3a**) was prepared by the polyaddition between **1** and **2a**, according to the reported method.¹ To a THF solution (1 ml) of **2a** (0.145 g, 1.31 mmol), **1** (0.127 g, 1.30 mmol) was added at 0°C under nitrogen. The resulting mixture was stirred for 1 h. The solution of **3a** was used for the following reaction without isolation. 2-Bromo-6-lithiopyridine was prepared according to the previous report.¹⁰ To a slurry of 2,6-dibromopyridine (0.370 g, 1.56 mmol) in diethyl ether (3.0 ml) cooled below -60°C , 1.6*N* *n*-butyllithium (0.98 ml, 1.57 mmol) in *n*-hexane was added at such a rate that the temperature of the reaction mixture did not exceed -60°C . After addition was completed, the reaction mixture was allowed to warm to -40°C for 30 min which resulted in a clear yellow solution. To the solution of 2-bromo-6-lithiopyridine, a THF solution (3 ml) of **3a** was added at -60°C under nitrogen. The mixture was gradually warmed to room temperature and was stirred overnight, followed by the addition of 1*N* NaOH (6 ml). After stirring another overnight, this mixture was extracted with diethyl ether, dried over sodium sulfate, and concentrated. The resulting solution was reprecipitated into diethyl ether/*n*-hexane (*v/v* = 1/4). **4a** was obtained as a brown gum, which was followed

by freeze-drying to remove solvents. Yield 72%; ^1H NMR (δ , CDCl_3) 1.07–1.46 (CH_2 , m, 12H), 1.89–2.11 ($\text{CH}=\text{C}-\text{CH}_2$, m, 4H), 2.28–2.44 ($\text{CH}_2\text{CH}_2\text{CN}$, m, 4H), 5.04–5.16 ($\text{C}=\text{CH}$, m, 1H); ^{13}C NMR (δ , CDCl_3) 17.4, 23.9, 28.2, 29.4, 30.2, 36.8, 119.1, 119.8, 143.8; IR (film) 2921, 2856, 2246, 1665, 1572, 1464, 1425, 1365, 1071, 755 cm^{-1} .

Various polymers having cyano groups were prepared in a similar manner as mentioned above. **4f** and **4g** were precipitated into MeOH/ H_2O (*v/v* = 1/1). **4b**: Yield 57%; ^1H NMR (δ , CDCl_3) 0.97–1.67 (CH_2 , m, 16H), 1.67–2.17 ($\text{CH}=\text{C}-\text{CH}_2$, m, 4H), 2.17–2.47 ($\text{CH}_2\text{CH}_2\text{CN}$, m, 4H), 4.87–5.27 ($\text{C}=\text{CH}$, m, 1H); IR (film) 2921, 2856, 2246, 1665, 1583, 1464, 1262, 1164, 1066, 799 cm^{-1} . **4d**: Yield 59%; ^1H NMR (δ , CDCl_3) 1.27–2.17 (CH_2 , m, 12H), 2.17–2.52 ($\text{CH}_2\text{CH}_2\text{CN}$, m, 4H), 2.92–4.11 (OCH_2 , m, 8H), 4.87–5.33 ($\text{C}=\text{CH}$, m, 1H); ^{13}C NMR (δ , CDCl_3) 17.3, 23.4, 25.7, 27.6, 69.5, 118.8, 120.2, 141.7; IR (film) 3019, 2965, 2921, 2867, 2246, 1660, 1578, 1453, 1431, 1376, 1262, 1218, 1158, 1088 cm^{-1} . **4e**: Yield 80%; ^1H NMR (δ , CDCl_3) 1.30–2.15 (CH_2 , m, 8H), 2.15–2.47 ($\text{CH}_2\text{CH}_2\text{CN}$, m, 4H), 2.80–4.07 (OCH_2 , m, 16H), 4.87–5.25 ($\text{C}=\text{CH}$, m, 1H). **4f**: Yield 71%; ^1H NMR (δ , CDCl_3) 1.03–1.62 (CH_3 , d, 6H), 1.65–2.45 (CH_2 , m, 8H), 2.45–3.35 (CH , m, 2H), 4.81–5.58 ($\text{C}=\text{CH}$, m, 1H), 6.65–7.20 (ArH, m, 4H); IR (film) 3019, 2965, 2246, 1660, 1600, 1578, 1453, 1371, 1218, 1093, 891, 755 cm^{-1} . **4g**: Yield 79%; ^1H NMR (δ , CDCl_3) 1.37–2.87 (CH_2 , m, 12H), 3.48–4.15 (OCH_2 , m, 4H), 4.77–5.32 ($\text{C}=\text{CH}$, m, 1H), 6.30–6.95 (ArH, m, 4H); IR (film) 3052, 2921, 2867, 2246, 1583, 1551, 1507, 1464, 1420, 1229, 1109, 1055, 913, 826 cm^{-1} .

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