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Synthesis and modification reaction of organoboron segmented block copolymer of allyl-telechelic poly(isobutylene)

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Summary

Hydroboration polymerization of low molecular weight allyl-telechelic polyisobutylene with narrow molecular weight distribution gave a novel stable organoboron segmented block copolymer by using tripylborane as a boron monomer. The chain transformation reaction of the copolymer was also examined. The reaction with α,α-dichloromethyl methyl ether (DCME) gave the corresponding poly-isobutylene segmented poly(alcohol).

Introduction

We have reported the synthesis of organoboron polymers by hydroboration polymerization of dienes [1], diynes [2], bisallenes [3] and dicyano compounds [4]. The polymers prepared by dienes and thexylborane are regarded as polymer homologues of trialkylboranes, which are useful intermediates in the field of organic chemistry with versatile reactivity. Therefore, they are used as a novel type of reactive polymers [5]. For example, poly(alcohol)s [6] and poly(ketone)s [7] are prepared by polymer reactions. Just as trialkylboranes, the boron main-chain polymers are unstable under air and the decomposition takes place in a few minutes. The instability makes the handling of these polymers difficult.

On the other hand, we reported stable organoboron polymers recently. The polymers prepared from dienes and tripylborane (tripyl = 2,4,6-triisopropylphenyl) are stable under air due to the steric hindrance of the bulky side group [8]. The tripyl group prevents the attack of oxygen to boron atom. These polymers are stable enough to be handled under air.

In this paper, we describe the preparation of a new stable segmented block copolymer by hydroboration polymerization of not a small diene molecule but a polymer with terminal double bonds, exactly allyl-telechelic polyisobutylene [9,11] using tripylborane. In addition, a chain transformation reaction of the resulting unique copolymer to poly(alcohol) is also described. According to our knowledge, this is the first example on chain extension of a telechelic polymer with vinyl termini for organoboron polymers and for the synthesis of a functional polymer with well-defined distances (number of monomer units) between functional groups by this technique.

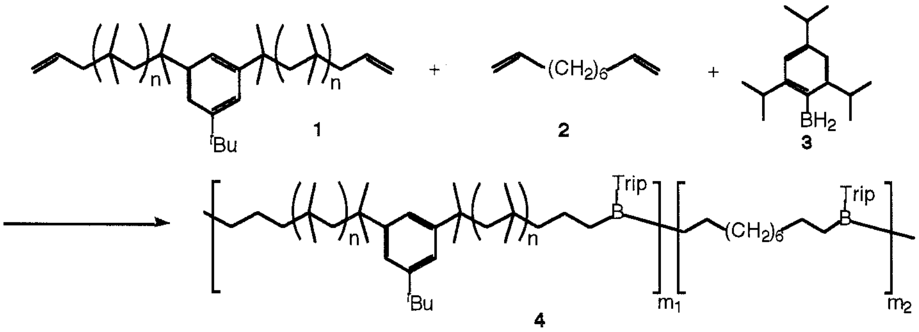
Results and discussion

Preparation of allyl-telechelic polyisobutylene

Allyl-telechelic polyisobutylene (**1** in Scheme 1) with narrow molecular weight distribution (MWD) was prepared by quasi-living carbocationic polymerization of isobutylene [9-11]. The allyl end-groups were introduced by quantitative end-quenching of the polymerization with allyltrimethylsilane (ATMS) as a functionalizing agent [11]. The resulting polymer was characterized by gel permeation chromatography (GPC) and ^{1}H NMR. According to the GPC analysis, the number-average molecular weight (M_n) of the oligomer was 1500 and the MWD was unimodal and narrow (M_w/M_n=1.05). The ^{1}H NMR spectrum of the telechelic polymer indicated that the chain ends are quantitatively functionalized by allyl groups and no other type of chain end structure was present.

Preparation of segmented block copolymer

Hydroboration polymerization using tripylborane (**3**) was carried out by a reported way [8]. Here, the copolymerization using various ratios of the allyl-telechelic oligoisobutylene (**1**) and 1,9-decadiene (**2**) was investigated (Scheme 1). The oligoisobutylene **1** or the mixture of the oligomer **1** and 1,9-decadiene **2** dissolved in THF was added to tripylborane (**3**) in THF. Though the oligomer **1** is less soluble in methanol than 1,7-octadiene or **2**, the obtained polymer was purified by repeated reprecipitation into methanol. The effectiveness of the copolymerization is shown by the comparison of the GPC traces of the polymer before and after the repeated reprecipitation. The results of the polymerizations are summarized in Table 1. The molecular weights of the polymers increased as the ratio of the oligomer to decadiene. This is due to the similar reactivity of vinyl group of **1** and **2**.



Scheme 1.

Table 1. Copolymerization of **1**, **2** and **3** with different diene ratios[a]

Ratio (**1**: **2**)	M_n[b]	M_w[b]	M_w/M_n[b]	Yield (%)[c]
only **1**	16400	21100	1.28	71
1:1	15400	20900	1.35	88
1:5	9000	13200	1.46	91
1:10	3400	4900	1.44	88

[a] Reactions were carried out in THF for 2 days. [b] GPC (THF) polystyrene standards. [c] Isolated yield after reprecipitation into methanol.

Characterization of the polymers

The structures of the polymers were supported by ^{1}H and ^{11}B NMR spectra. The ^{1}H NMR spectrum of **4** (prepared from only **1**) showed the characteristic peaks assignable to the protons of the tripyl unit and aryl unit of the oligomer, and no peaks for unreacted olefinic protons (Figure 1). The structure of **4** is supported by the observation of an equal ratio of boron unit to oligomer unit (r[B/oligomer]=1), determined by the integral ratio of the corresponding aromatic protons (found: r=1.07). The ^{11}B NMR spectrum showed one main peak at 31.4 ppm.

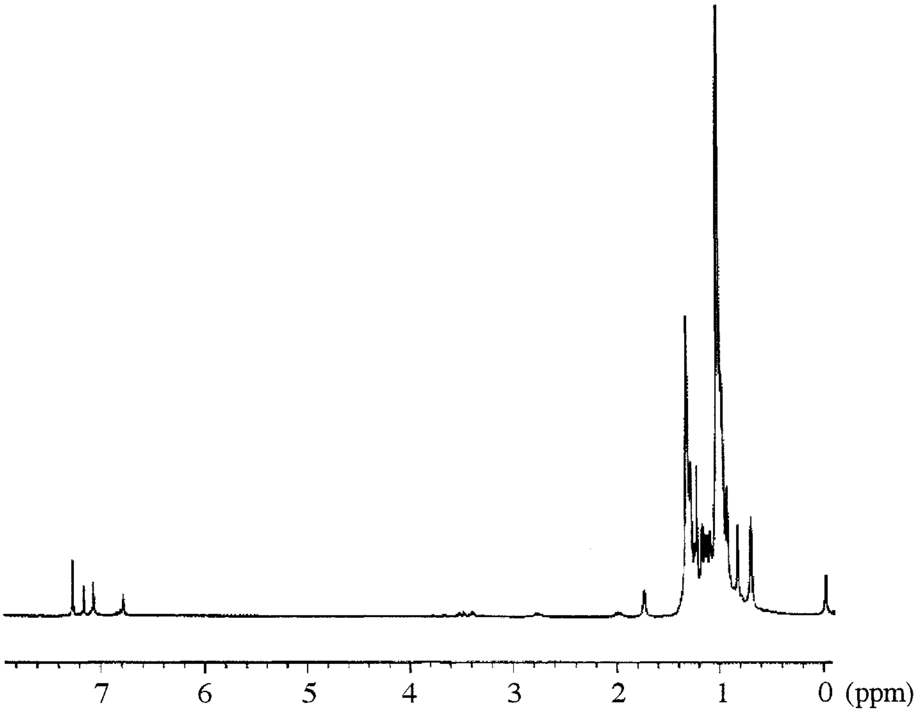


Figure 1. ^{1}H NMR spectrum of **4** (only **1**) (in $CDCl_3$).

TGA traces of the polymers

TGA traces of the polymer **4** (prepared from only **1**) and the oligomer **1** are shown in Figure 2. The temperature at which 10% weight loss occurred (T_{10}) is listed in Table 2. T_{10} of the polymers are lower than that of the oligomer (**1**). These results show that the polymer containing more boron atoms in the polymer chain was less stable toward oxidation. After the pyrolysis of the boron containing polymer, a black solid remained in a cell.

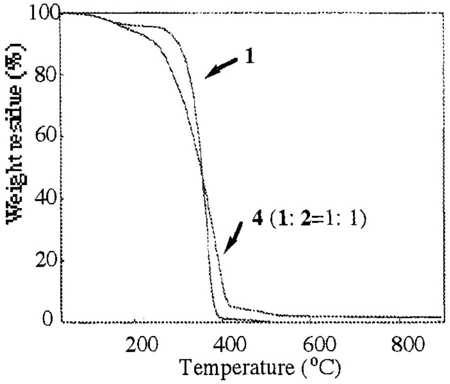


Figure 2. TGA traces of the oligomer (**1**) and the polymer **4**.

Table 2. T_{10}[a] of polymers **4**

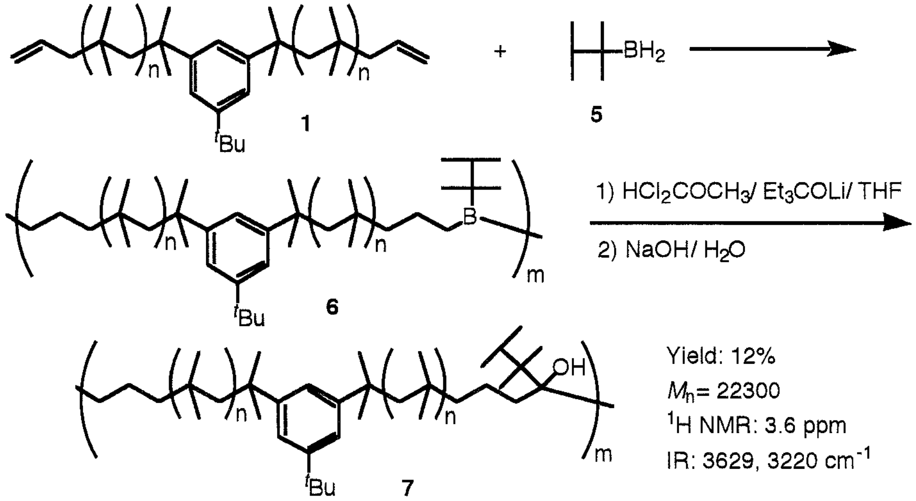
polymer (**1**: **2**)	T_{10} (°C)
(1)	(303)
4(only **1**)	267
4(1:1)	252

[a] 10% weight loss temperature.

In the previous works, we reported TGA results of analogous polymers prepared from thexylborane [1] or mesitylborane [12]. While the polymers prepared from mesitylborane are more stable than those prepared from thexylborane, the thermal stability of **4** exceeds both of them. It should also be noted that the organoboron copolymer (**4**) obtained can be handled under air without decomposition.

Polymer analogous reaction of segmented block copolymer

The preparation of a new functional segmented block copolymer was also investigated. To obtain a reactive boron polymer, thexylborane was used as a borane monomer. First hydroboration polymerization of the oligomer using thexylborane (**5**) was carried out in a reported way (Scheme 2) [1]. Then the obtained polymer **6** was subjected to a chain transformation reaction (DCME rearrangement) [3,13]. Dichloromethyl methyl ether (DCME) and lithium alkoxide of 3-ethyl-3-pentanol in hexane was added to a THF solution of the polymer at 0 °C. The reaction mixture was stirred at room temperature for 24h followed by oxidative treatment with H_2O_2/NaOH to give the corresponding poly(alcohol) (Scheme 2). The yield of the product polymer was relatively low due to the repeated reprecipitations and column purification. The structure of **7** was supported by ^{1}H NMR and IR spectra. In the ^{1}H NMR spectrum, a peak due to hydroxyl proton was observed at 3.6 ppm. In the IR spectrum, absorptions were observed at 3629 cm^{-1} and 3220 cm^{-1}. No peak was observed in the ^{11}B NMR spectrum, which indicates no boron atom remained in the resulting polymer (**7**). This transformation reaction can be considered to proceed in a similar mechanism as in the case of organoboron homopolymer reported previously [13].



Scheme 2.

Conclusion

Stable organoboron segmented block copolymer was obtained by hydroboration polymerization of allyl-telechelic polyisobutylene and tripylborane. The polymerization using thexylborane also gave a segmented block copolymer, which was converted to the corresponding poly(alcohol) by DCME rearrangement.

Experimental section

Materials and instruments

Methylene chloride was purified by reflux and distillation over calcium hydride. Hexane was stored over cc. H_2SO_4 for 2 weeks in order to remove double bond containing impurities, then passed through basic alumina, refluxed and distilled over calcium hydride. Tetrahydrofuran was dried over sodium and distilled before use. Methanol was dried and distilled from magnesium methoxide. 1,9-Decadiene was purified by distillation. Tripylborane [14] and thexylborane were prepared according to the reported methods.

^1H and ^{11}B NMR spectra were recorded in $CDCl_3$ on a JEOL EX-270 instrument (270 MHz). IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. Gel permeation chromatographic (GPC) analyses were carried out on a Tosoh HLC-8200 (TSK gel G3000H_{XL}) by using THF as an eluent after calibration with polystyrene standards. Thermogravimetric analyses (TGA) were made on a Seiko TG/DTA 6200 (10 °C/min).

Preparation of allyl-telechelic polyisobutylene

1.722 g (6 mmol) of 1,3-bis(2-chloroisopropyl)-5-*t*-butylbenzene initiator [15] was dissolved in the mixture of 720 ml *n*-hexane and 480 ml methylene chloride under nitrogen. The solution was cooled to -80 °C during stirring, then 1.395 g (12 mmol) *N,N,N',N'*-tetramethylethylenediamine (TMEDA), 10.28 g (184 mmol) liquid isobutylene, 36.42 g (192 mmol) titanium tetrachloride and 2.743 g (24 mmol) allyltrimethylsilane were added, respectively. The reaction was quenched with methanol after 40 minutes reaction time. The polymer was purified by precipitating into methanol and by passing its hexane solution through neutral alumina. M_n (GPC) = 1500 g/mol, M_w/M_n=1.05. ^{1}H NMR (δ, ppm): 0.90-1.80 (CH_2, CH_3 in polymer chain), 2.00 ($CH_2CH{=}CH_2$), 5.00 ($CH{=}CH_2$), 5.85 ($CH{=}CH_2$), 7.07 (*H*-Ar).

*Hydroboration polymerization of **1** (preparation of **4**)*

To a THF solution (0.2 M) of tripylborane (**3**) (47.7 mg, 0.221mmol) was added a THF solution (0.2 M) of **1** (323.6 mg, 0.210 mmol) dropwise at room temperature under nitrogen. The reaction mixture was stirred for 2 days. Evaporation of the solvent gave a colorless gum and the resulting polymer was purified by reprecipitation into methanol. Yield 71%. ^{1}H NMR (δ, ppm): 0.70-1.73 (CH_2, CH_3 in polymer chain), 1.97-2.01 (C*H* (tripyl)), 2.78-2.80 (C*H* (tripyl)), 6.78 (*H*-Ar (tripyl)), 7.07 (*H*-Ar (oligomer)). ^{11}B NMR (δ, ppm): 31.4.

*DCME rearrangement of copolymer **6** (Preparation of poly(alcohol))*

To a THF solution of **4** prepared from 286.0 mg (0.1857 mmol) of **1** and 31.1 mg (0.319 mmol) of 5, DCME (34.49 mg, 0.30 mmol) and Et_3COLi in hexane (1.56 M, 0.2 ml) were added at 0 °C under nitrogen. The reaction mixture was stirred at room temperature for 2 days. After the treatment with aqueous sodium hydroxide solution (6 N, 1 ml) and hydrogen peroxide (30%) at 50 °C for 6h, the reaction mixture was extracted with THF and dried with sodium sulfate. After evaporation with methanol and benzene (ten times) under normal pressure, a freeze drying with benzene gave **7**.

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