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Alkoxyboration Polymerization. Synthesis of Novel Poly(boronic carbamate)s

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ABSTRACT: Novel organoboron polymers were prepared by alkoxyboration polymerization of diisocyanates with mesityldimethoxyborane. The polymers obtained have boronic carbamate in their repeating units and can be expected as a novel type of reactive polymers. First, alkoxyboration polymerization between mesityldimethoxyborane and 1,6-hexamethylene diisocyanate was examined, and the best reaction condition was optimized to be 140 °C in bulk. Both aliphatic and aromatic diisocyanates gave the corresponding polymers. When aromatic diisocyanates were employed, the reactions required severe reaction conditions (150 °C). The polymers prepared from aromatic diisocyanates have a high stability toward air. Among various boron monomers, mesityldimethoxyborane was found to be the most suitable monomer for the present polymerization system.

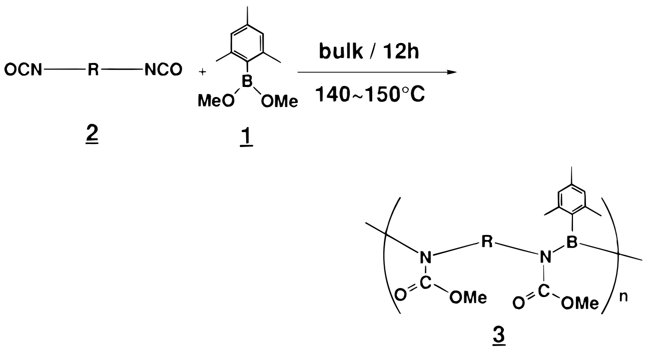
Introduction

Recently, we have reported various methodologies for the synthesis of boron-main chain polymers by hydroboration polymerization.[1] Although the polymers prepared by these methods are generally unstable toward air, these novel types of reactive polymers provide a useful approach for the synthesis of poly(alcohol)s, poly(ketone)s, and cyano group containing polymers[2] that cannot be prepared by other conventional methods. On the other hand, the polymers prepared by hydroboration or allylboration polymerization of dicyano compounds[3] or phenylboration polymerization of diyne compounds[4] show a high stability toward air, and these new groups of polymers are interesting as boron-containing materials. Very recently, it was found that boration polymerization of bis(allene) compounds also proceeded without gelation to afford poly(diallylborane)s, despite the presence of cumulated double bonds in bis(allene) monomers.[5] Accordingly, boration polymerization of other bis(cumulene) compounds should also be an attractive approach for the preparation of new organoboron polymers. We have reported haloboration−phenylboration polymerization of diisocyanates successfully gave poly(diamidoborane)s.[6] In this paper, alkoxyboration polymerization of diisocyanates was examined for the further extension of this methodology (Scheme 1). The polymers obtained having boronic carbamate in their units are expected to be a novel type of reactive polymer.

Results and Discussion

Optimization of Reaction Condition. Previously, Lappert et al. reported that a catechol type alkoxyborane underwent an alkoxyboration reaction with isocyanate to give a boronic carbamate.[7] For the use of this reaction in polymer synthesis, relatively thermally stable mesityldimethoxyborane (**1**) was employed as a boron monomer. To optimize reaction conditions, reactions between **1** and 1,6-hexamethylene diisocyanate (**2b**) were performed under various reaction conditions. The results are listed in Table 1. In each case, GPC measurement was carried out after purifying the crude polymer by precipitation into *n*-pentane. The polymer obtained (**3b**) was soluble in common organic solvents such as THF, dichloromethane, and benzene. When tetrachloroethane was used as a solvent (runs 1 and 2), the molecular weight of the polymer was relatively low even at 130 °C. On the other hand, in the reactions in bulk at 130 or 140 °C (runs 4 and 5), the relatively high molecular weights were attained. But when the reaction was performed at 160 °C (run 6), gelation was observed. This was probably due to disproportionation of boron monomer under such a severe reaction condition. From these results, the best reaction condition was optimized to be at 140 °C in bulk.

Scheme 1



Polymer Structure. The structure of polymer **3b** was supported by ^{1}H-, ^{13}C-, and ^{11}B-NMR and IR spectra, shown in Figure 1a−c. In the ^{1}H NMR spectrum (Figure 1a), the peak corresponding to methylene adjacent to the B−N bond (around 3.2 ppm) is separated into two absorptions that are assigned to cis or trans isomers. This is due to the characteristics of the B−N bond as a double bond by the $p\pi-p\pi$ interaction between the boron atom and nitrogen atom.

The same phenomenon was also observed in the ^{13}C NMR spectrum (Figure 1b). The peaks of carbons near the B−N bond (a−c) are split into two absorptions, respectively, and the existence of two different chemical environments is implied.

The ^{11}B-NMR spectrum of polymer **3b** (Figure 1c) has a main peak at 31.7 ppm corresponding to the boronic

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Table 1. Alkoxyboration Polymerization between 1,6-Hexamethylene Diisocyanate (2b) and Mesityldimethoxyborane (1)

run	1/2	solvent	conc (M)	temp (°C)	time (h)	M_w	M_n	M_w/M_n	yield (%)
1	1.04	tetrachloroethane	2.0	130	12	2700	1900	1.4	20
2	1.08	tetrachloroethane	2.0	130	32	4400	2100	2.0	72
3	0.99	bulk		110	12	2000	1600	1.2	40
4	1.13	bulk		130	12	10400	4500	2.3	43
5	1.10	bulk		140	12	12000	6700	1.8	43
6	1.06	bulk		160	12		gelation		

[a] GPC (THF). Polystyrene standards. [b] Isolated yields after reprecipitation into *n*-pentane.

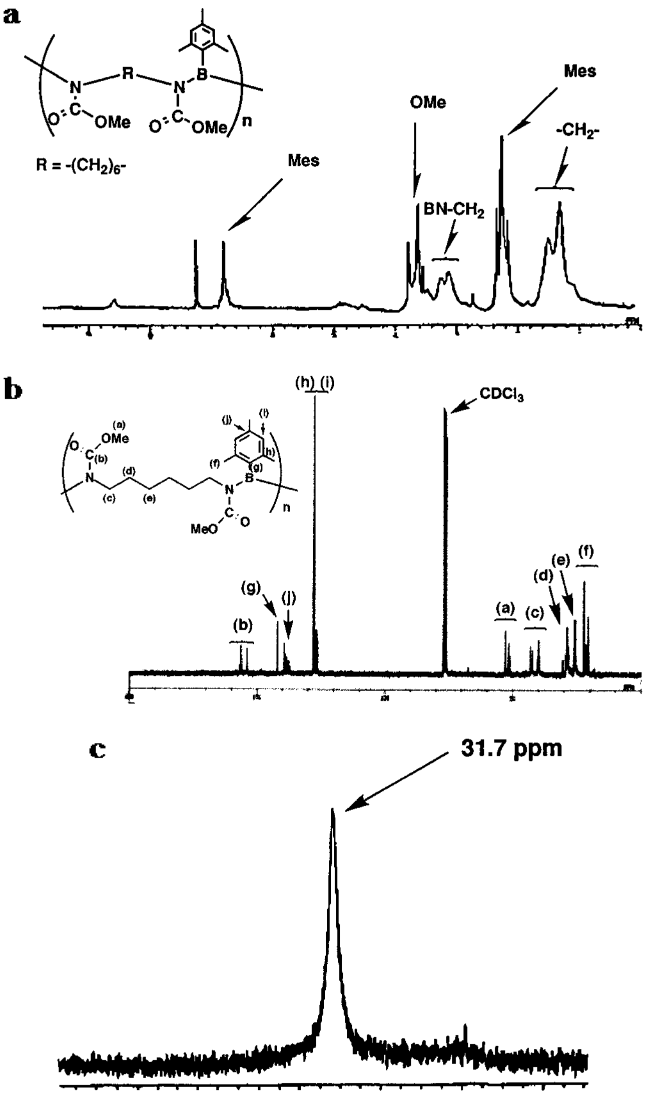


Figure 1. (a) ^{1}H-NMR spectrum of polymer **3b**. (b) ^{13}C-NMR spectrum of organoboron polymer **3b**. (c) ^{11}B-NMR spectrum of organoboron polymer **3b**.

dicarbamate unit. This result indicates that this polymer has mainly one kind of borane unit. However, the chemical shift of the peak (31.7 ppm) is rather low compared with those of polymers prepared by haloboration polymerization or phenylboration polymerization (0−10 ppm). Generally, an amidoborane group works as an electron acceptor and coordination of electron donors enriches electron density on the boron atom, which moves the chemical shift of the boron atom to a higher frequency. This result is probably because of steric hindrance around the boron atom by the bulky mesityl group. That is, interchain coordination of the carbonyl group to the boron atom might be disturbed.

In the IR spectrum of **3b**, the C=O stretching of the carbamate moiety was observed at 1715 cm^{-1}.

Dependence of Molecular Weight on the Feed Ratio of Monomers. In general, stoichiometry is very important in polyaddition reactions. The dependence of molecular weight on the feed ratio between **1** and **2b** was investigated. As shown in Table 2, the molecular weight of the polymer increased when the feed ratio of the two monomers approached unity. This result supports the fact that the present polymerization proceeds in a polyaddition manner.

Alkoxyboration Polymerization of Various Aliphatic Diisocyanates. The results of alkoxyboration polymerization of various aliphatic diisocyanates with **1** are summarized in Table 3. All the reactions were carried out in bulk at 140 °C for 12 h. When 1,4-tetramethylene diisocyanate (**2a**) or isophorone diisocyanate (**2d**) was used (runs 1 and 4), the molecular weights of the polymers were relatively low. This might be due to some cyclization during the reaction. The relatively high molecular weight observed in run 3 is probably due to the high unit molecular weight of the polymer prepared from 1,12-diisocyanatododecane (**2c**) having a long methylene linker and relatively high hydrophobicity of the monomer. In each case, isolated yields of polymers were lower than for haloboration−phenylboration polymerization or phenylboration polymerization, in which isolated yields of polymers obtained were almost quantitative. The yield can probably be improved by optimization of the procedure for purification, because thermal degradation of monomer seems not to be a problem. Since no deviation of the stoichiometry was observed in Table 2.

The ^{1}H NMR spectra of organoboron polymers prepared from various aliphatic diisocyanates are shown in Figure 2. As mentioned before, in the ^{1}H NMR spectrum of **3b**, the methylene proton adjacent to the B−N bond was separated into two peaks corresponding to cis and trans isomers, owing to the double bond nature of the B−N bond. But it should be noted that the peak intervals of isomers differ depending on the length of the methylene linkers [$-(CH_2)_m-$]. For example, in the case of **3a** ($m = 4$), the peak interval was significantly wider than that of **3b** ($m = 6$). On the other hand, in the spectrum of **3c** ($m = 12$), no such peak separation was observed. These results might be due to the difference in the mobility of polymer units, which depends on the methylene chain length. That is, in the case of $m = 4$, the mobility of the main chain is not so high that rotation around the B−N bond is slower than the NMR time scale. However, when $m = 12$, the mobility of polymer units is high enough to suppress the rotational hindrance around the B−N bond, and the change of configuration becomes faster than the NMR time scale.

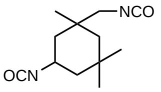
Alkoxyboration Polymerization of Various Aromatic Diisocyanates. The results of alkoxyboration polymerization of various aromatic diisocyanates are shown in Table 4. The reactions were also carried out in bulk, above the melting points of diisocyanates. In

Table 2. Dependence of Molecular Weight on the Feed Ratio of 1/2b[a]

run	amt of **2b** (mmol)	amt of **1** (mmol)	**1/2b**	M_n[b]	M_w[b]	M_w/M_n[b]	yield (%)[c]
1	1.37	0.99	0.73	2800	2100	1.4	27
2	1.15	0.97	0.85	4100	2900	1.4	37
3	0.88	0.97	1.10	6700	12000	1.8	43
4	0.72	0.97	1.33	3600	10100	2.8	40
5	0.54	0.99	1.82	2300	8900	3.8	20

[a] Reactions were carried out in bulk at 140 °C. [b] GPC (THF), polystyrene standards. [c] Isolated yields after reprecipitation into *n*-pentane.

Table 3. Methoxyboration Polymerization of Aliphatic Diisocyanates with Mesityldimethoxyborane (1)[a]

run	diisocyanates	**1/2b**	M_w[b]	M_n[b]	M_w/M_n[b]	yield (%)[c]
1	$OCN(CH_2)_4NCO$ (**2a**)	1.06	4400	2800	1.6	30
2	$OCN(CH_2)_6NCO$ (**2b**)	1.10	12000	6700	1.8	43
3	$OCN(CH_2)_{12}NCO$ (**2c**)	1.02	22400	10200	2.2	41
4	 (2d)	1.09	1900	1500	1.3	76

[a] Reactions were carried out at 140 °C for 12 h. [b] GPC (THF), polystyrene standards. [c] Isolated yields after reprecipitation into *n*-pentane.

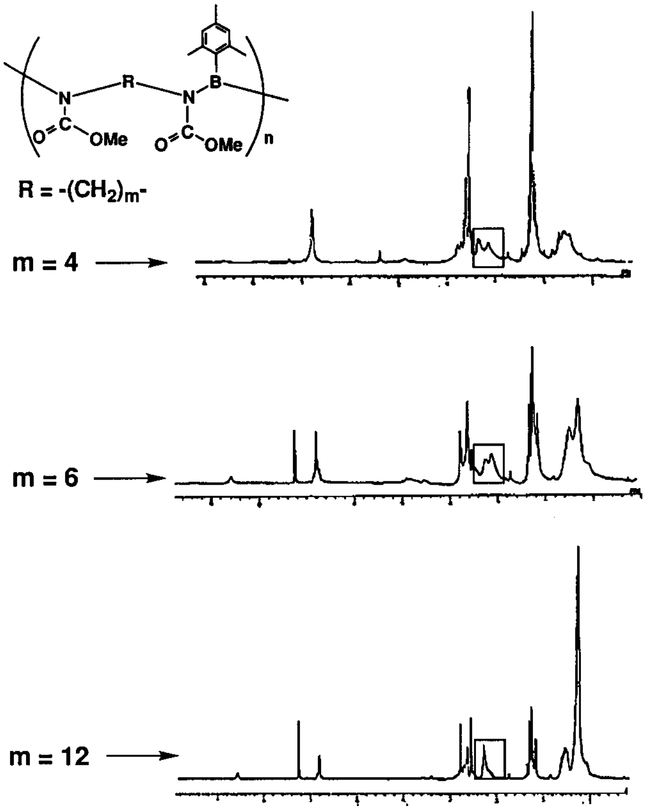


Figure 2. ^{1}H-NMR spectra of organoboron polymers prepared by alkoxyboration polymerization of various aliphatic diisocyanates.

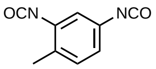
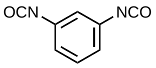
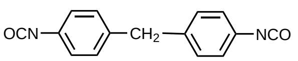
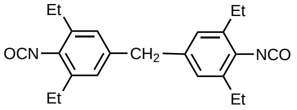
these cases, a slightly higher reaction temperature (150 °C) was needed compared with polymerization of aliphatic diisocyanates (140 °C) due to the lower reactivity of aromatic monomers. When tolylene 2,4-diisocyanate (**2e**) was used (run 1), the number-average molecular weight of the obtained polymer was estimated to be 3800. On the other hand, in the case of 1,3-phenylene diisocyanate (**2f**) (run 2), the molecular weight of the obtained polymer was 1200, due to lower reactivity of this monomer in comparison with **2e**. Polymerization of diphenylmethane diisocyanate (**2g**) (run 3) gave a relatively high molecular weight polymer (M_n 4100). However, when 4,4-diisocyanato-3,3,5,5-tetraethyldiphenylmethane (**2h**) was used, no polymerization was observed. In this case, steric hindrance might be critical.

Alkoxyboration Polymerization Using Various Borane Reagents. Alkoxyboration polymerization of **2b** with various alkoxyborane reagents was performed, and the results are listed in Table 5. All the reactions were carried out in bulk for 12 h. First, trimethoxyborane was examined (run 1) and the corresponding polymer was obtained. However, the molecular weight of the polymer obtained was relatively low compared with **1** (Table 1) due to a low reaction temperature, limited by the boiling point of trimethoxyborane (68−69 °C). Accordingly, triethoxyborane, having a higher boiling point (117−118 °C) was examined next. But in this case, gelation was observed at 100 °C, which shows the difficulty in controlling the polymerization using a trifunctional boron monomer. Then, the aliphatic bifunctional boron monomer cyclohexyldialkoxyborane was employed (runs 3−6). When the reaction was carried out at 60 °C (run 3), no polymerization was observed. In the reaction at 80 °C or 100 °C (runs 4−5), the corresponding oligomer was obtained. But when the reaction temperature was raised to 120 °C (run 6), gelation was observed. This is probably due to disproportionation of the aliphatic boron monomer, which is relatively unstable upon thermal treatment. To improve the thermal stability, the aromatic bifunctional monomer, phenyldimethoxyborane was also examined (runs 7−9). When the reaction was carried out at 60 °C (run 7), no polymerization was observed. Although oligomerization was observed at 80 °C (run 8), gelation took place at 100 °C (run 9). This result implies that phenyldimethoxyborane does not work as a bifunctional monomer. In other words, the phenylboration reaction also takes place during the reaction, which results in a highly cross-linked structure of the resulting polymer.

From the results described above, a conclusion is that the bulky and aromatic mesityl group in the boron monomer is indispensable for alkoxyboration polymerization. The aromatic mesityl group increases the thermal stability of the boron monomer so as to withstand the severe reaction conditions (140−150 °C), and steric hindrance prevents the migration of the mesityl group itself.

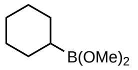
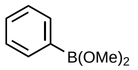
Mechanism of Boronic Carbamate Formation. There are two different pathways considerable for the formation of diamidoborane (Scheme 2). One is that the lone pair of nitrogen attacks the boron atom to form a borate intermediate. After that, one of the methoxy substituents migrates to the next carbonyl carbon atom. This pathway might be more predominant when aliphatic diisocyanates are used. In this case the electron density on the nitrogen atom is relatively high, so the nucleophilicity of nitrogen is increased. Furthermore, steric hindrance with the mesityl group is not so much

Table 4. Methoxyboration Polymerization of Aromatic Diisocyanates with Mesityldimethoxyborane (1)[a]

run	diisocyanates	**1**/**2b**	M_w[b]	M_n[b]	M_w/M_n[b]	yield (%)[c]
1	 (**2e**)	1.08	5800	3800	1.5	37
2	 (**2f**)	1.06	2800	1200	2.4	42
3	 (**2g**)	1.02	7300	4100	1.8	49
4	 (**2h**)	1.09		no polymerization		

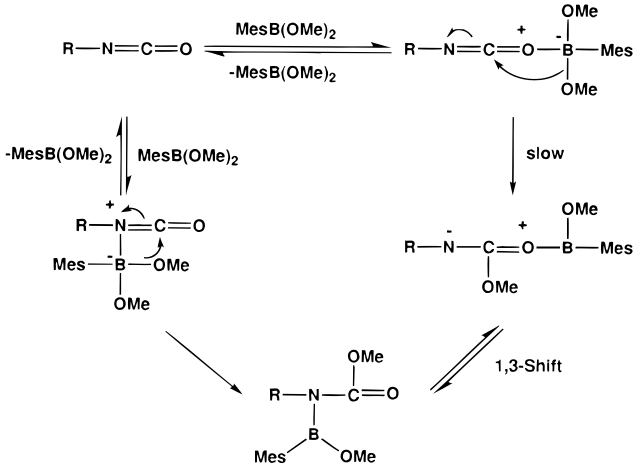
[a] Reactions were carried out at 150 °C for 12 h. [b] GPC (THF), polystyrene standards. [c] Isolated yields after reprecipitation into *n*-pentane.

Table 5. Alkoxyboration Polymerization of 1,6-Hexamethylene Diisocyanate (2b) with Various Borane Reagents[a]

run	borane	borane/**2b**	temp (°C)	M_w[b]	M_n[b]	M_w/M_n[b]	yield (%)[c]
1	$B(OMe)_3$	1.16	60	3800	2700	1.4	28
2	$B(OEt)_3$	1.11	100			gelation	
3		1.08	60			no polymerization	
4		1.10	80	2000	1300	1.5	31
5		0.97	100	2100	1100	1.9	21
6		1.05	120			gelation	
7		1.06	60			no polymerization	
8		1.14	80	1700	1100	1.6	24
9		1.15	100	1800	1400	1.3	(gelation also observed)

[a] Reactions were carried out in bulk for 12 h. [b] GPC (THF), polystyrene standards. [c] Isolated yields after reprecipitation into *n*-pentane.

Scheme 2



a problem. The other mechanism is one where the oxygen atom in the carbonyl group coordinates to the boron atom to form a borate intermediate. In this case, migration of one methoxy group takes place slowly, and then the boron atom migrates from oxygen to nitrogen by a 1,3-shift. This pathway might be more predominant when aromatic diisocyanates are used. In this case, the electron density on the nitrogen atom is low and, accordingly, the nucleophilicity is decreased due to delocalization of the lone pair into the benzene ring. Furthermore, steric hindrance between the mesityl group and the benzene ring in diisocyanates is severe in this case. These reaction mechanisms are supported by the different reactivities of the monomers. Polymerization of aromatic diisocyanates requires a higher reaction temperature than for aliphatic diisocyanates. This result is in accord with the mechanism described above, that is, boronic carbamate formation of aromatic diisocyanate requires a thermally undesirable 1,3-shift during the migration.

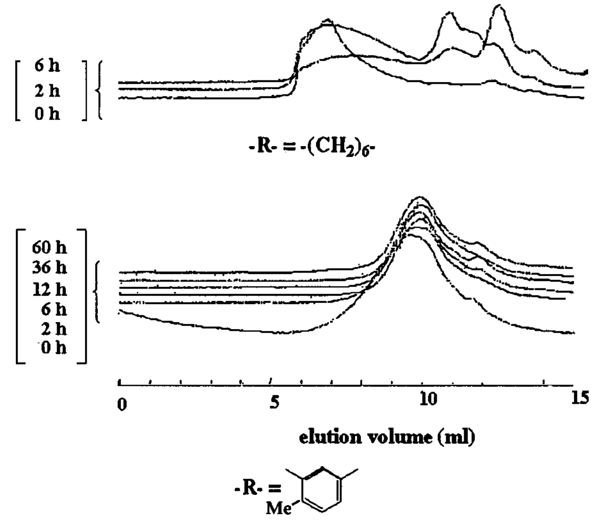


Figure 3. Air stability of organoboron polymers.

Air Stability of Organoboron Polymers. To examine the air stability of polymers prepared from aliphatic or aromatic diisocyanates, air bubbling was performed on THF solutions of polymers. The decomposition of polymers was followed by GPC measurement. The results are shown in Figure 3. The polymer **3b** prepared from 1,6-hexamethylene diisocyanate was considerably decomposed by air-bubbling for 6 h. On the other hand, the polymer **3e** prepared from tolylene 2,4-diisocyanate showed unusually high stability. This is probably due to the highly rigid structure of the polymer having an aromatic backbone.

Thermal Stability of the Polymer. To investigate the thermal stability of **3b**, a TGA measurement was made under nitrogen. As shown in Figure 4, the weight loss of the polymer accelerated around 200 °C and was almost complete around 500 °C. About 15% of the residue remained after heating to 900 °C, and after the

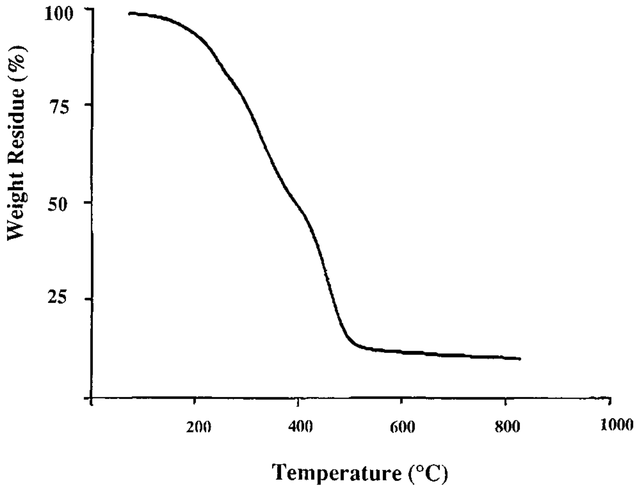


Figure 4. TGA (10 °C/min) trace of organoboron polymer **3b** under nitrogen.

measurement, a black solid remained in the cell. This result indicates that the polymer prepared here might be utilized as precursors for boron-containing inorganic materials.

Conclusion

In conclusion, novel organoboron polymers having boronic carbamate units in their main chain were prepared by alkoxyboration polymerization between **1** and various diisocyanates. The polymers obtained have mesityl groups in their side chain and those prepared from aromatic diisocyanates showed high air stability. It is found that the mesityl group in the boron monomer plays a very important role in the present polymerization.

Experimental Section

Materials and Instruments. Tetrachloroethane was dried over calcium chloride and distilled under nitrogen before use. Tetrahydrofuran and *n*-pentane were dried over sodium and distilled before use. Trimethoxyborane (trimethylborate) and triethoxyborane (triethylborate) were dried over calcium hydride and distilled. Mesityldimethoxyborane (**1**) was prepared by the method reported before.[5] Other dimethoxyboranes were prepared by the same method using chlorobenzene (for phenyldimethoxyborane) or cyclohexyl bromide (for cyclohexyldimethoxyborane), instead of mesityl bromide. Diisocyanates were purified by distillation.

^{1}H-, ^{13}C-, and ^{11}B-NMR spectra were recorded in $\mathrm{CDCl_3}$ on a JEOL EX-270 instrument. Gel permeation chromatographic analysis was carried out on a TOSOH G3000HXI by using THF as an eluent after calibration with standard polystyrene samples. The IR spectrum was obtained on a Perkin-Elmer 1600 spectrometer. Thermogravimetric analysis (TGA) was made on a Shimadzu DT-30 instrument (10 °C/min).

Polyaddition between Mesityldimethoxyborane and 1,6-Hexamethylene Diisocyanate. As a typical example of polymerization, **1** (189.0 mg, 0.984 mmol) was added to **2b** (151.3 mg, 0.900 mmol) at room temperature under a nitrogen atmosphere. Then the resulting mixture was heated to 140 °C and stirred for 12 h. After the crude product was dissolved in THF, reprecipitation was carried out into *n*-pentane. The polymer was obtained as a yellow gum, but after reprecipitation as a brown solid. Yield: 172.9 mg, 53%. ^{1}H NMR (δ, ppm): 1.32 (4H, N−C−C−$\mathrm{CH_2}$), 1.51 (4H, N−C−$\mathrm{CH_2}$), 2.24 (9H, Ar−$\mathrm{CH_3}$), 3.15, 3.29 (4H, B−N−$\mathrm{CH_2}$), 3.65 (6H, $\mathrm{OCH_3}$), 6.81 (2H, Ar−H). ^{13}C NMR (δ, ppm): 21.1 (Ar−$\mathit{CH_3}$), 25.7 (B−N−C−C−*C*), 28.9 (B−N−C−*C*), 39.9, 43.2 (B−N−C), 51.6, 52.9 (OMe), 126.6, 127.8 (B−C−*C*−*CH*), 139.0 (B−C−C−C−*C*−Me), 142.0 (B−C), 153.8, 156.3 (C═O). ^{11}B-NMR (δ, ppm): 31.7 ppm.

Polymerization between Various Aliphatic Diisocyanates and Mesityldimethoxyborane. The following organoboron polymers were prepared by using the procedure similarly to that described for **3b**.

3a: yield 30%; ^{1}H NMR (δ, ppm) 1.59 (4H, N−C−$\mathrm{CH_2}$), 2.25 (9H, Ar−$\mathrm{CH_3}$), 3.15, 3.36 (4H, B−N−$\mathrm{CH_2}$), 3.61 (6H, $\mathrm{OCH_3}$), 6.78 (2H, Ar−H). **3c**: yield 41%; ^{1}H NMR (δ, ppm) 1.25 (16H, −$\mathrm{CH_2}$−), 1.52 (4H, N−C−$\mathrm{CH_2}$), 2.23 (9H, Ar−$\mathrm{CH_3}$), 3.26 (4H, B−N−$\mathrm{CH_2}$), 3.62 (6H, $\mathrm{OCH_3}$), 6.80 (2H, Ar−H). **3d**: yield 76%; ^{1}H NMR (δ, ppm) 0.91 (15H, −$\mathrm{CH_2}$−, Me), 2.21 (9H, Ar−$\mathrm{CH_3}$), 2.87 (1H, N−CH), 3.47 (2H, N−$\mathrm{CH_2}$), 3.66 (6H, $\mathrm{OCH_3}$), 6.65 (2H, Ar−H).

Polyaddition between Mesityldimethoxyborane and 2,4-Tolylene Diisocyanate. As a typical example of polymerization, **1** (196.6 mg, 1.02 mmol) was added to **2e** (164.4 mg, 0.944 mmol) at room temperature under a nitrogen atmosphere. Then the resulting mixture was heated to 150 °C and stirred for 12 h. After the crude product was dissolved in THF, reprecipitation was carried out into *n*-pentane. The polymer was obtained as a yellow gum, but after reprecipitation as a brown solid. Yield: 133.0 mg, 37%. ^{1}H NMR (δ, ppm): 2.20 (12H, Ar−$\mathrm{CH_3}$), 3.62 (6H, $\mathrm{OCH_3}$), 6.86 (2H, B−C−C−CH), 7.05 (3H, N−C−CH−CH).

Polymerization between Various Aromatic Diisocyanates and Mesityldimethoxyborane. The following organoboron polymers were prepared by using the procedure similar to that described for **3e**. Polymer prepared from 1,3-phenylene diisocyanate (**3f**): yield 42%; ^{1}H NMR (δ, ppm) 2.22 (9H, Ar−$\mathrm{CH_3}$), 3.58 (6H, OMe), 6.76 (2H, B−C−C−CH), 7.03 (1H, N−C−C−CH), 7.21 (3H, N−C−CH). Polymer prepared from diphenylmethane diisocyanate (**3g**): yield 49%; ^{1}H NMR (δ, ppm) 2.25 (9H, Ar−$\mathrm{CH_3}$), 3.58 (6H, $\mathrm{OCH_3}$), 3.80 (2H, $\mathrm{CH_2}$), 6.80 (2H, B−C−C−CH), 7.07 (4H, N−C−CH−CH).

Stability of Organoboron Polymers. The stability of organoboron polymers toward air oxidation was examined by monitoring the change of the molecular weights by the GPC curve during an oxidation experiment, in which a stream of air was bubbled into a THF solution of organoboron polymer. After the designated time, the resulting polymer was characterized by GPC.

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