Alternating Boration Copolymerization between Diynes and Diisocyanates. Organoboron Polymers Bearing Monomeric Iminoborane in Their Main Chain

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ABSTRACT: An alternating boration copolymerization methodology was explored by making use of different boration reactivities between diynes and diisocyanates. This method affords a synthetic route for novel type of organoboron polymers having monomeric iminoborane units in their main chain. The polymers obtained were soluble in commom organic solvents such as tetrahydrofuran, chloroform, and benzene. Gel permeation chromatographic analysis showed that their number-average molecular weights were several thousands. The treatment of 1,4-diethynylbenzene with two equimolar amounts of diphenylbromoborane (in $CHCl_3$ at room temperature; selective haloboration) followed by reaction with diisocyanates (in $CHCl_3$ at room temperature; phenylboration polymerization) gave the corresponding polymers in moderate yields. Particularly, the polymer prepared from aromatic monomers showed high air stability. In addition, fully aromatic organoboron polymers can be regarded as a novel type of conjugated polymer via B−N bonds having a double bond nature due to a well-established pπ−pπ interaction.

Introduction

Polymeric inorganic materials have attracted much attention during the past few decades as represented by polysiloxanes,[1] polyphosphazenes,[2] polysilanes,[3] metallocene-based polymers,[4] and rigid rod polymers.[5] Despite the diversity of these materials and their unique mechanical, electrical, and optical properties, only a limited number of organoboron materials have been reported until recently, possibly because these polymers have been believed to be too unstable for practical use.

Recently, we have developed novel methodologies for the preparation of organoboron main chain polymers by means of hydroboration polymerization.[6] Although most of these reactive organoboron polymers were unstable toward air, they served as polymeric precursors that underwent a wide variety of chain transformation reactions to give functionalized carbon-backbone polymers.[7] Furthermore, some organoboron polymers were found to be stable enough to be expected as a new class of boron-containing materials whose properties are unknown. For instance, poly(cyclodiborazane)s prepared by hydroboration polymerization of dicyano compounds (Figure 1 a)[8] and the polymers prepared by phenylboration polymerization of diynes[9] (Figure 1b) exhibit relatively high stabilities against air and thermal oxidation. Moreover, haloboration polymerization of diynes or haloboration−phenylboration polymerization of diisocyanates also afforded the corresponding organoboron polymers having di(β-haloalkenyl)borane units[10] or diamidoborane units[11] respectively (Figure 1c,d). Very recently, it was found that hydroboration polymerization of aromatic diynes with mesitylborane gave relatively air-stable organoboron polymers which showed the characteristics as a novel type of π-conjugated polymer via empty p-orbital of the boron atom.[12]

Here we report a novel alternating boration copolymerization strategy to obtain organoboron polymers having monomeric iminoborane units in their main chain,[13]

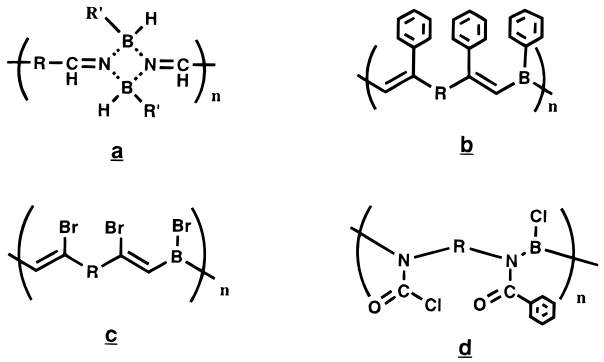

Figure 1. Examples of organoboron polymers produced by boration polymerization.

in which a boron−nitrogen bond can be incorporated in the conjugation path. The fully aromatic polymers prepared from aromatic monomers can be regarded as a new class of π-conjugated polymers via monomeric iminoborane, whose optical or electric properties are of quite a bit of interest because of their unknown electronic structure. To obtain the organoboron polymers bearing amidoalkenylborane units according to this concept, a boration polymerization using stepwise boration reaction should be requisite. Alternating boration copolymerization was achieved by utilizing the different boration reactivity between acetylene and isocyanate. Haloboration of aromatic acetylene bonds takes place under mild reaction conditions (∼−78 °C), while the phenylboration reaction requires more forcing reaction conditions (∼70 °C).[14] On the other hand, both haloboration and phenylboration of isocyanates proceed smoothly at room temperature.[11] Accordingly, the treatment of an aromatic diyne monomer with two molar equivalents of diphenylbromoborane (1b) (selective haloboration reaction toward acetylene bond) and subsequent reaction with an equimolar amount of diisocyanate would give a polymer having the alternating unit structure (Scheme 1b).

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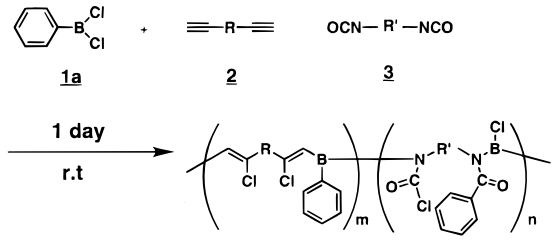
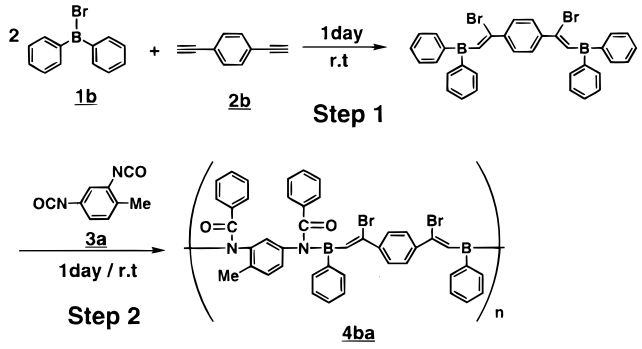
Scheme 1

a) Simultaneous Feeding Method



b) Stepwise Feeding Method



Results and Discussion

Haloboration−Phenylboration Copolymerization Using Phenyldichloroborane (1a). Initially, haloboration−phenylboration copolymerization among diynes (**2**), diisocyanates (**3**) and phenyldichloroborane (**1a**) was examined by simultaneous feeding of these monomers (Scheme 1a). A typical procedure was as follows. Half molar amounts of tolylene-2,4-diisocyanate (**3a**) and 1,9-decadiyne (**2a**) were added to a 1.0 M solution of **1a** in chloroform at room temperature under nitrogen. After stirring the reaction mixture for 24 h, the resulting polymer was purified by reprecipitation into *n*-hexane to give a brown powder. The results of polymerization using various combinations of monomers are listed in Table 1. Although the polymerization using 1,4-diethynylbenzene (**2b**) was unsuccessful, the corresponding copolymers were obtained by using **2a**. However, the content of the unit (estimated from ^{1}H NMR) originating from the diyne monomer was much lower than expected from the feed ratio, probably due to relatively low reactivity of the diyne monomers.

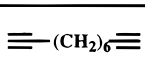
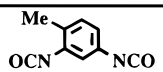
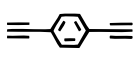
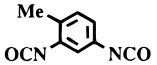
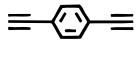
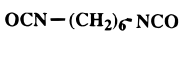
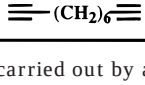
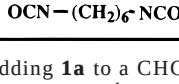
Alternating Boration Copolymerization Using Diphenylbromoborane (1b). The stepwise polymerization method was examined next, to obtain a copolymer having a higher content of the alkenylborane unit and alternating unit structure (Scheme 1b). In the first step, 2 equiv of **1b** was added to a 1.0 M chloroform solution of **2b** at room temperature under nitrogen atmosphere, and then the reaction mixture was stirred for 24 h. The disappearance of the acetylene proton (3.22 ppm) was observed in the ^{1}H NMR spectrum. In the second step, 1 equiv of **3** was added very slowly, and the reaction mixture was stirred for another 24 h. After the solvent was removed, the resulting brown gum was purified by reprecipitation from chloroform into *n*-hexane. The obtained polymers were soluble in common organic solvents such as THF, chloroform, DMSO and DMF. However, when too much **3** was fed, or **3** was fed too rapidly, sometimes gelation was also observed. Alternating boration copolymerization using various diisocyanates are examined. The results are listed in Table 2. Except in the case of run 2, the corresponding polymers (**4**) were obtained. The reason for the relatively high estimated molecular weight of the polymer prepared in run 1 might be the rigid backbone structure compared with those prepared in runs 3 and 4.

Alternating Boration Copolymerization between 3a and Various Aromatic Diynes. The alternating boration copolymerization between **3a** and various aromatic diynes was also carried out (Table 3). Instead of **2b**, every monomer (**2c**−**2e**) gave the corresponding polymer in good yield. The polymerization with 4,4′-diethynylbiphenyl (**2c**) resulted in a slight decrease of the molecular weight due to the relatively poor solubility of **2c**. 2,5-Diethynylthiophene (**2e**) also gave a polymer with lower M_n, possibly due to some interaction between the sulfur and the boron atom.

Alternating Boration Copolymerization Using 1,2-Diethynyl-1,1,2,2-tetramethyldisilane. Introduction of the disilanylene unit in the conjugated system generally leads to a formation of materials that exhibits unique optical properties owing to their intramolecular charge transferred structure in their excited states. Here, 1,2-diethynyl-1,1,2,2-tetramethyldisilane (**2f**) was also employed for the alternating boration copolymerization to give the corresponding copolymer in a moderate yield (Scheme 2, Table 4). The number-average molecular weight of the polymer was 1700. This polymer as well showed good solubility in common organic solvents such as THF, chloroform, and benzene.

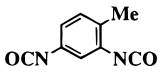
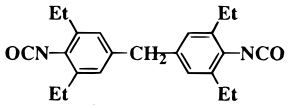
Polymer Structure. The structures of the series of organoboron copolymers were comfirmed by ^{1}H NMR,

Table 1. Boration Copolymerization of Diyne (2) and Various Diisocyanates (3) with $PhBCl_2$ (1a)[a]

run	2	3	Feed Ratio (1a / 3 / 2)	Mw[b]	Mn[b]	Mw/Mn[b]	Polymer Content[c] (3 / 2)	Yield[d] (%)
1			1.0 / 0.58 / 0.52	2600	2000	1.83	79 / 21	75.3
2			1.0 / 0.50 / 0.50	No Polymerization				
3			1.0 / 0.52/ 0.51	6000	3600	1.68	100 / 0	—
4			1.0 / 0.51/ 0.51	5200	4100	1.27	87 / 13	74.9

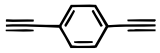
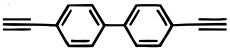
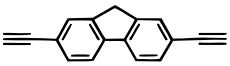
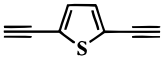
[a] Reactions were carried out by adding **1a** to a $CHCl_3$ solution of **2** and **3** at room temperature. [b] GPC (THF). Polystyrene standards. [c] All the polymer contents were determined by ^{1}H NMR spectra. [d] Isolated yields after reprecipitation into *n*-hexane.

Table 2. Alternating Boration Copolymerization of 1,4-Diethynylbenzene (2b) and Various Diisocyanates (3) with Ph_2BBr (1b)[a]

run	3		Feed Ratio (1b / 3 / 2b)	*Mw*[b]	*Mn*[b]	*Mw/Mn*[b]	Yield(%)[c]
1		(3a)	1.0 / 0.51/ 0.48	13600	4300	3.17	74.5
2		(3b)	1.0 / 0.48 / 0.50	No Polymerization			
3	NCO−$(CH_2)_6$−NCO	(3c)	1.0 / 0.58 / 0.52	4600	2600	1.78	71.9
4	NCO−$(CH_2)_{12}$−NCO	(3d)	1.0 / 0.54 / 0.51	4600	2500	1.86	68.2

[a] Step 1 was carried out by adding **1b** to a $CHCl_3$ solution of **2b** at room temperature. Step 2 was performed by adding **3** to the resulting solution from step 1. [b] GPC (THF). Polystyrene standards. [c] Isolated yields after reprecipitation into *n*-hexane.

Table 3. Alternating Boration Copolymerization of Various Aromatic Diynes (2) with Tolylene-2,4-diisocyanate (3a)[a]

Run	Diynes		Feed Ratio (mmol) 1b/2/3a	*Mn* [b]	*Mw* [b]	*Mw/Mn* [b]	Yield (%) [c]
1		(2b)	1/0.482/0.509	4300	13600	3.2	75
2		(2c)	1/0.461/0.486	2200	3600	1.7	87
3		(2d)	1/0.428/0.480	3000	5900	1.9	83
4		(2e)	1/0.449/0.467	2100	4300	2.0	68

[a] Reaction was carried out in $CHCl_3$ at room temperature. [b] GPC (THF). Polystyrene standards. [c] Isolated yields after the reprecipitation into *n*-hexane.

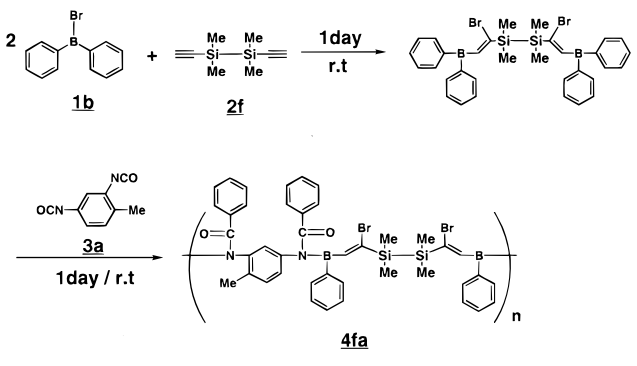
Table 4. Alternating Boration Copolymerization of 1,2-Diethynyl-1,1,2,2-tetramethyldisilane (2f) with Tolylene-2,4-diisocyanate (3a)[a]

Run	Diyne		Feed Ratio (mmol) 1b/2f/3a	*Mn* [b]	*Mw* [b]	*Mw/Mn* [b]	Yield (%) [c]
1		(2f)	1/0.432/0.440	1700	2300	1.4	21

[a] Reaction was carried out in $CHCl_3$ at room temperature. [b] GPC (THF). Polystyrene standards. [c] Isolated yields after the reprecipitation into *n*-hexane.

^{11}B NMR, and IR spectra. As represented in Figure 2a, measurement of ^{11}B NMR spectra is a very convenient way to monitor the extent of unit alternation. In the ^{11}B NMR spectrum of the polymer prepared from 1,6-hexamethylene diisocyanate (**3c**) and **1a**, the main peak is observed at 4.7 ppm (diamidoborane) and that of the polymer prepared from **2b** and **1a** appears at 60.5 ppm (di(*β*-haloalkenyl)borane). On the other hand, that of polymer **4ba** (produced from **2b** and **3a**) is located almost in the midpoint of those two polymers, at 29.2 ppm (*β*-haloalkenylamidoborane). This result indicates a considerably alternating nature of the present polymerization system. The small peak at 0.55 ppm is assignable to diamidoalkenylborane that was formed by further phenylboration reaction of the B−Ph moiety with isocyanate (cross-linking reaction).

Scheme 2



On the other hand, the structure of the polymer **4ea** obtained from 2,5-diethynylthiophene (**2e**) was not as

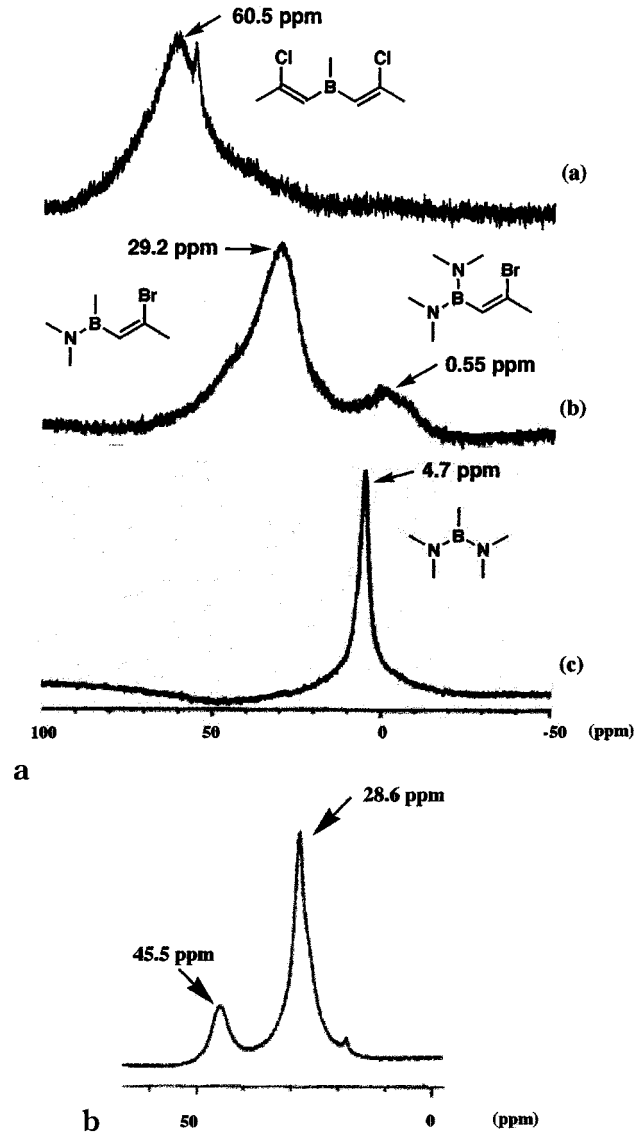


Figure 2. (a) ^{11}B NMR spectra of organoboron polymers prepared by boration polymerization: (a) haloboration polymerization between **1a** and **2b**; (b) haloboration phenylboration alternating copolymerization between **2b** and **3a** using **1b**; (c) haloboration phenylboration polymerization between **1a** and **3c**. (b) ^{11}B NMR spectrum of **4ea**.

regular as that of polymer **4ba**, although **4ea** as well consists mainly of alternating units (Figure 2b). In the ^{11}B NMR spectrum of **4ea**, the peak assignable to the dialkenylborane unit was also observed, due to incomplete selectivity between haloboration and phenylboration, which is considered to arise from less aromaticity (lack of the thermodynamic advantage of phenylboration by extension of conjugation) of **2e** compared with **2b**. The alternating boration copolymerization using 1,2-diethynyl-1,1,2,2-tetramethyldisilane (**2f**) also resulted in the formation of a structural defect, possibly due to similar reasons.

In the IR spectra of the alternating polymers, the peak due to N=C=O stretching disappeared while C=O stretching of the amide group appeared. As an example, the IR spectrum of **4ba** is represented in Figure 3, in which C=O stretching was observed at 1715 cm^{-1}. The relatively high wavenumber of C=O stretching might be due to the coordination of the carbonyl group to the boron atom.

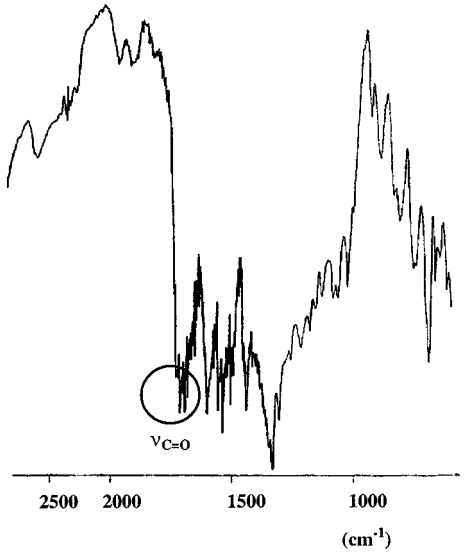


Figure 3. IR spectrum of **4ba**.

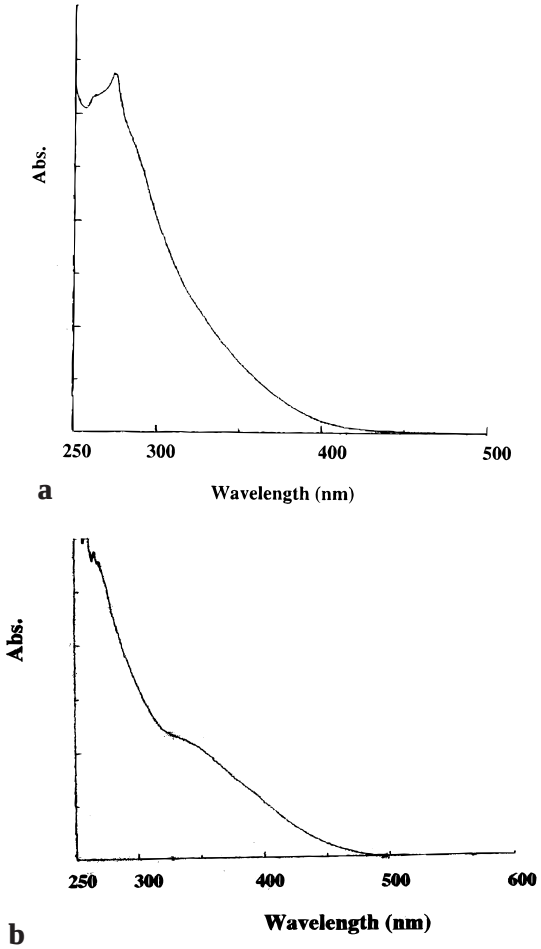


Figure 4. (a) UV−vis absorption spectrum of **4ba** in $CHCl_3$ at room temperature. (b) UV−vis absorption spectrum of **4ea** in $CHCl_3$ at room temperature.

Optical Properties of Polymers. As mentioned above, the polymers prepared from aromatic monomers in the present polymerization can be regarded as a novel type of conjugated polymers that have monomeric B−N bond in their main chain. However, in the UV−vis spectrum of **4ba** (Figure 4a), poorly extended conjugation was implied from the observation of an absorption maximum at 274 nm. This result is presumably because

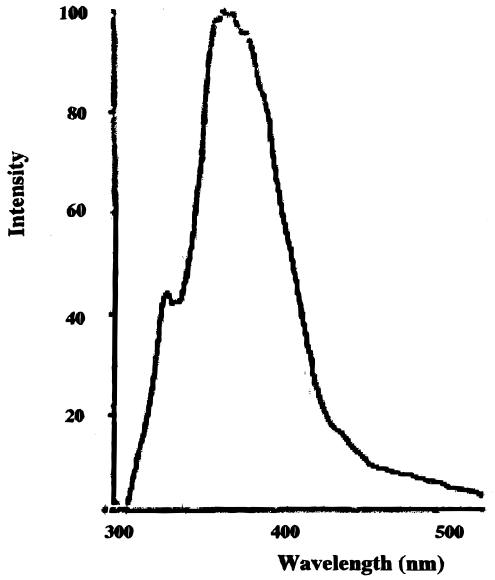


Figure 5. Fluorescence emisson spectrum of **4fa** in $CHCl_3$ at room temperature.

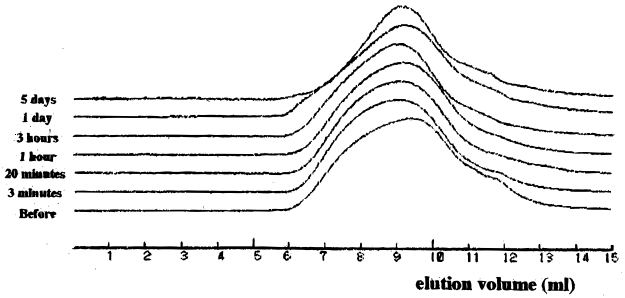


Figure 6. GPC curves of **4ba** during the air-bubbling experiment.

of the effectively interrupted conjugation by the presence of cross-linked moiety, diamidoborane units.

On the other hand, **4ea** showed a relatively bathochromic shifted absorption edge (Figure 4b), although an absorption maximum was not clearly observed. The irradiation of a dilute chloroform solution of **4ea** with ultraviolet light resulted in an observation of visible green light emission. However, considering the presence of structural defect in **4ea**, these characteristics might not originate from conjugation, but from the dialkenylborane structure.

The polymer bearing disilanylene units showed an intense visible violet emission (Figure 5) when a dilute chloroform solution was irradiated by ultraviolet light, despite its insufficiently $\sigma-\pi$ conjugated structure interrupted with cross-linking diamidoborane units. Since the polymer produced by alternating boration copolymerization between 1,4-diethynylbenzene (**2b**) and 1,2-diethynyl-1,1,2,2-tetramethyldisilane (**2f**) showed only a weak emission,[15] the observed intense emission does not appear to be from the structural defect (dialkenylborane), but it likely comes from the local $\sigma-\pi$ conjugated unit, including a B−N bond.

Stability of Polymer 4ba. To investigate the air stability of the polymer **4ba**, an air bubbling experiment was carried out in THF solution (Figure 6). From the GPC traces, significant degradation of the polymer was not observed even after air bubbling for 5 days. Interestingly, this result shows improved air stability of **4ba** compared with poly(boronic amide)s. It is likely that the boronic amide unit in **4ba** is stabilized by the presence of an adjacent alkenyl group by some conjugative effect. The measurement of thermogravimetric analysis (TGA) was also carried out (Figure 7) for **4ba** under nitrogen. As the temperature rose, thermal decomposition of **4ba** had gradually taken place due to a retroboration reaction. The temperature at which 10% weight loss was observed was 180 °C. After the measurement, a considerable amount of ceramics remained in the cell, possibly owing to formation of a highly closs-linked material as a result of disproportionation of the main chain.

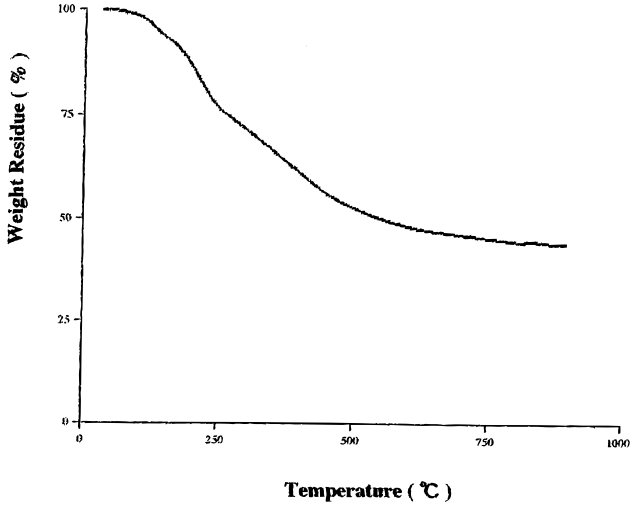


Figure 7. TGA trace of **4ba** (10 °C/min) under nitrogen.

Conclusion

In conclusion, an alternating haloboration−phenylboration copolymerization methodology was explored, taking advantage of different boration reactivity between diynes and diisocyanates. The polymers obtained possess monomeric iminoborane in their main chain and those prepared from aromatic monomers showed high air stability. It is likely that aromaticity of the diyne monomers is important for the structural regularity of the resulting polymers. Interestingly, **4ba**−**4fa** can be regarded as a novel type of conjugated polymer, since the B−N bonds have some double bond nature due to the well-established $p\pi-p\pi$ interaction.[16] However, these polymers did not show particularly red shifted λ_{max} in their UV−vis absorption spectra, because of the prevention of π-conjugation at the closslinking point. This seems to be unavoidable as long as diphenylborane is employed as a boron monomer. Nevertheless, to overcome this problem and develop the conjugated polymer through a B−N bond, extension of this method would still continue to be an attractive approach. For example, control of migratory aptitude or reactivity for both monomers might be also possible by utilizing alkoxyboration or aminoboration, which is fairly active toward isocyanate and inactive to acetylene, or by introducing a mesityl or tripyl group into the boron monomer to restrict the cross-linking. Thus, the potential utility of this system is stimulating enough to let us continue working on this research.

Experimental Section

Instruments and Materials. Chloroform was dried over calcium chloride and distilled before use. Dichlorophenylborane was purchased from Aldrich and distilled. Diphenylbromoborane was prepared according to the reported method.[17]

Aliphatic diynes and all diisocyanates were purchased from Aldrich and purified by distillation. Aromatic diynes were prepared by the reported method.[18] 1,2-Diethynyl-1,1,2,2-tetramethyldisilane was prepared as reported.[19]

^{1}H and ^{11}B NMR spectra were recorded in $CDCl_3$ 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. IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. UV−vis spectra were recorded on a JASCO V-530 spectrophotometer. Thermogravimetric analysis (TGA) was made on a Shimadzu DT-30 instrument (10 °C/min).

Boration Copolymerization between Diyne and Diisocyanate Using Dichlorophenylborane. Under nitrogen atmosphere, dichlorophenylborane (**1a**) (0.1314 g, 0.827 mmol) was added to a mixture of 1,9-decadiyne (**2a**) (0.0579 g, 0.431 mmol) and tolylene-2,4-diisocyanate (**3a**) (0.831 g, 0.477 mol) in chloroform (1 mL) at room temperature. After stirring for 12 h, the reaction mixture was poured into *n*-hexane, and the precipitates were collected and then dried in *vacuo*. From ^{1}H NMR spectrum, the ratio of units originated from diyne and diisocyanate was 1/3.3. The yield was 75%. ^{1}H NMR (δ, ppm): 1.44−1.54 (−CH_2−), 1.95 (−CH_2−C═), 2.19 (−CH_3), 7.48 (−CH═C, C_6H_5, C_6H_3). ^{11}B NMR (δ, ppm): 7.50, 30.9. IR (cm^{-1}): 1715 ($\nu_{C=O}$).

The copolymerizations using other combinations of monomers were similarly carried out. The results are summarized in Table 1.

Alternating Boration Copolymerization between Diynes and Diisocyanates. To a chloroform solution (1 mL) of 1,4-diethynylbenzene (**2b**) (0.063 g, 0.499 mmol) was added 2 equiv of diphenylbromoborane (**1b**) (0.248 g, 1.013 mmol) under nitrogen atmosphere at room temperature. After the reaction mixture was stirred, the disappearance of acetylene proton was observed in the ^{1}H NMR measurement. Then, an equivalent amount of tolylene-2,4-diisocyanate (**3a**) (0.0859 g, 0.493 mmol) was added, and the mixture was stirred for another 24 h. The polymer prepared (**4ba**) was purified by reprecipitation into *n*-hexane to give a brown powder in 71% yield. ^{1}H NMR (δ, ppm): 2.28 (CH_3, 3H), 7.35−7.74 (−CH═C, C_6H_3, C_6H_4, C_6H_5, 27H). ^{11}B NMR (δ, ppm): 0.55, 29.2 (main). IR (cm^{-1}): 1715 ($\nu_{C=O}$).

The polymers **4bc**−**4bd** were similarly prepared by using 1,6-diisocyanatohexane or 1,12-diisocyanatododecane instead of tolylene-2,4-diisocyanate. The polymers **4ca**−**4fa** were prepared by using 4,4′-diethynylbiphenyl, 2,7-diethynylfluorene, 2,5-diethynylthiophene, or 1,2-diethynyl-1,1,2,2-tetramethyldisilane, instead of 1,4-diethynylbenzene.

4bc: from 0.1178 g (0.481 mmol) of **1b**; 0.0319 g (0.253 mmol) of **2b**; 0.0474 g (0.282 mmol) of **3c**. Yield: 72%. ^{1}H NMR (δ, ppm): 1.18 (−CH_2−, 8H), 3.14−3.66 (−CH_2−N, 4H), 7.34−7.74 (−CH═C, C_6H_4, C_6H_5, 24H). ^{11}B NMR (δ, ppm): 30.3.

4bd: from 0.1199 g (0.490 mmol) of **1b**; 0.318 g (0.252 mmol) of **2b**; 0.0667 g (0.264 mmol) of **3d**. Yield: 68%. ^{1}H NMR (δ, ppm): 1.18 (−CH_2−, 20H), 3.32 (−CH_2−N, 4H), 7.29−7.67 (−CH═C, C_6H_4, C_6H_5, 24H). ^{11}B NMR (δ, ppm): 3.08, 30.33 (main).

4ca: from 0.2572 g (1.050 mmol) of **1b**; 0.0978 g (0.483 mmol) of **2c**; 0.0889 g (0.511 mmol) of **3a**. Yield: 87%. ^{1}H NMR (δ, ppm): 2.36 (CH_3, 3H), 7.42 (Ar−H, vinyl, 33H). ^{11}B NMR (δ, ppm): 30.9. IR (cm^{-1}): 1700 ($\nu_{C=O}$).

4da: from 0.2571 g (1.050 mmol) of **1b**; 0.0963 g (0.449 mmol) of **2d**; 0.0878 g (0.504 mmol) of **3a**; Yield: 83%. ^{1}H NMR (δ, ppm): 2.34 (CH_3, 3H), 3.98 (Ar−CH_2−Ar, 2H), 7.40 (Ar−H, vinyl, 33H). ^{11}B NMR (δ, ppm): 31.3. IR (cm^{-1}) 1694 ($\nu_{C=O}$).

4ea: from 0.2528 g (1.032 mmol) of **1b**; 0.0612 g (0.463 mmol) of **2e**; 0.0840 g (0.482 mmol) of **3a**. Yield: 68%. ^{1}H NMR (δ, ppm): 2.17 (CH_3, 3H), 7.36 (Ar−H, Thi−H, vinyl, 27H). ^{11}B NMR (δ, ppm): 28.6 (main), 45.5. IR (cm^{-1}): 1710 ($\nu_{C=O}$).

4fa: from 0.1418 g (0.579 mmol) of **1b**; 0.0445 g (0.255 mmol) of **2f**; 0.0432 g (0.248 mmol) of **3a**. Yield: 21%. ^{1}H NMR (δ, ppm): 0.216 (Si−CH_3, 12H), 2.40 (CH_3, 3H), 7.31 (Ar−H, vinyl, 25H). ^{11}B NMR (δ, ppm): 18.8, 31.9 (main), 46.8. IR (cm^{-1}): 1709 ($\nu_{C=O}$).

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