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Alternating boration copolymerization between diyne and bisallene

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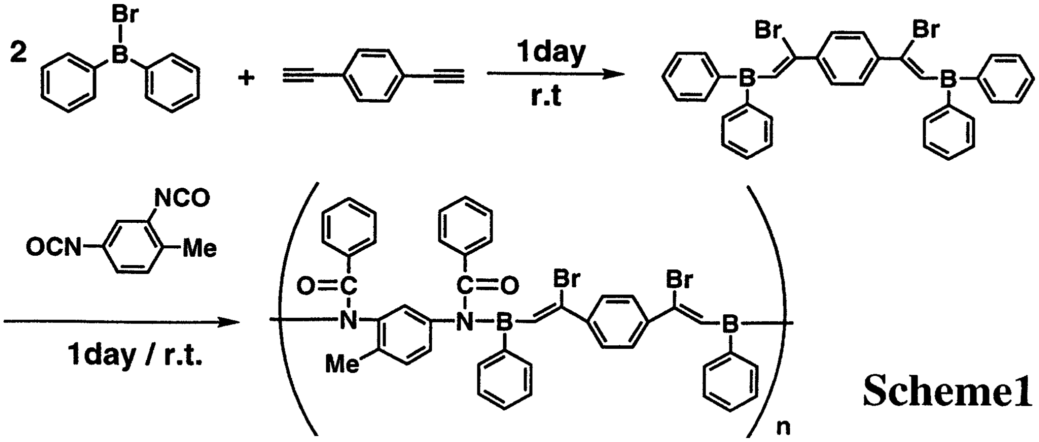
Summary

Alternating boration copolymerization between 1,4-diallenylbenzene (2) and 2,7-diethynylfluorene (3) was examined using diphenylbromoborane (1) to give the corresponding copolymer (4). The organoboron copolymer obtained was characterized by ^{1}H-, ^{11}B-NMR, IR, and UV-vis absorption spectra.

Results and Discussions

Recently, organoboron materials [1] have begun to attract a growing interest because some of them exhibit sufficient stability and their unknown characteristics are stimulating. Especially, synthesis of π-conjugated organoboron polymers [2] is an attractive subject since they might show fairly unique electric or optical behavior arising from their unknown electronic states.

As a way to obtain a new class of π-conjugated polymers, for instance, we have explored an alternating boration copolymerization strategy [3] making use of different boration reactivity between haloboration and phenylboration reactions toward acetylene or isocyanate [4]. The resulting polymers bearing monomeric iminoborane in their mainchain can be regarded as a novel π-conjugated polymer via B-N bond that possesses double bond like nature due to pπ-pπ interaction [5]. As depicted in Scheme 1, after the treatment of 1,4-diethynylbenzene with 2 equiv. of diphenylbromoborane at room temperature (selective haloboration reaction), the phenylboration polymerization with 1 equiv. of tolylene-2,4-diisocyanate gave the alternating copolymer whose *M*n was several thousands [3]. The ^{11}B-NMR spectra of the obtained polymer demonstrated a highly alternating nature of the polymerization.



Scheme1

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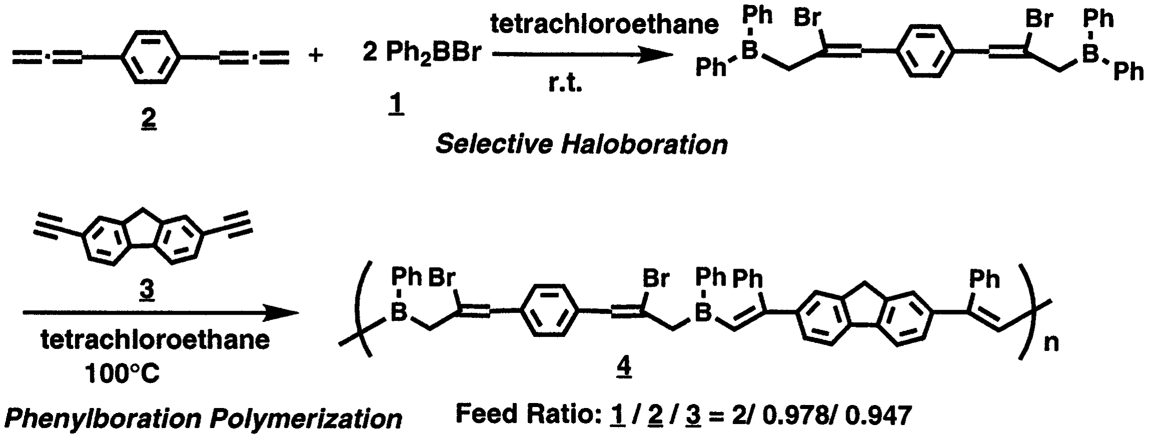
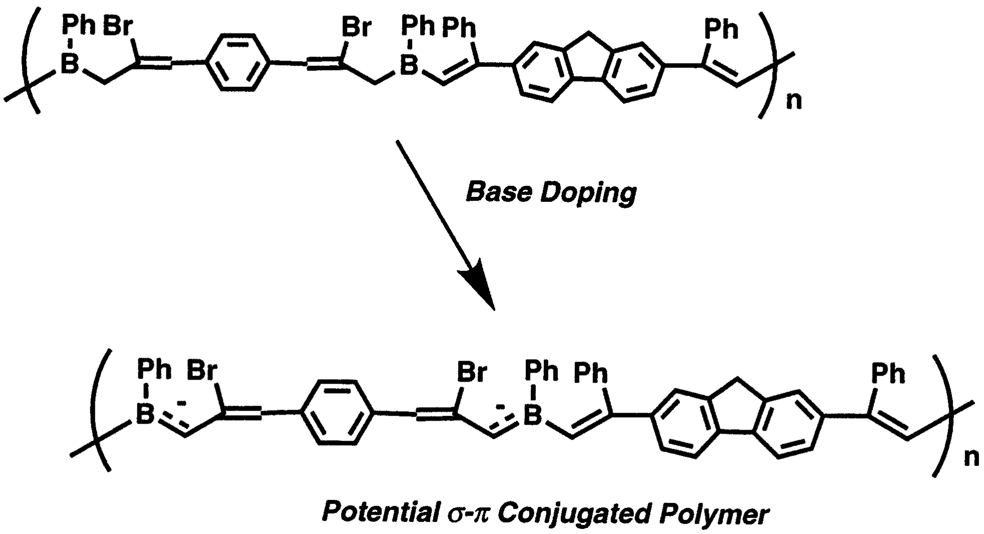
Here, alternating boration copolymerization between bisallene (1,4-allenylbenzene; 2) and diyne (2,7-diethynylfluorene; 3) was carried out to afford the corresponding alternating copolymer 4 (Scheme 2). Previously, we have reported that boration polymerization of bisallene compounds proceeded to give poly(diallylborane)s [6] due to the regio selective boration reaction toward terminal allenes [7]. Therefore, the alternating boration copolymerization would give the polymer having alkenylallylborane unit, in which B-C bond could be incorporated in the conjugation path. Since B^--C bond interacts conjugatively with the adjacant vinyl group similarly with Si-Si bond [8], the polymer produced in the present system is expected as a polymeric precursor for novel σ-π conjugated polymer (Scheme 3)



Scheme 2



Scheme 3

The alternating boration copolymerization between 2 and 3 was performed as follows. Under nitrogen atmosphere, 2 equiv. of 1 was added to 1 equiv. of 2 in tetrachloroethane at room temperature, and the reaction mixture was stirred for 24h (selective haloboration). Then 1 equiv. of 3 in tetrachloroethane was added and phenylboration polymerization was carried out at 100°C. The resulting polymer was purified by reprecipitation into *n*-hexane to afford 4 as a brown powder in 17% yield. 4 was soluble in common organic solvents such as THF, chloroform and benzene. The structure of 4 was comfirmed by 1H-, 11B-NMR and IR spectra.

The ^{11}B-NMR spectrum of 4 recorded in $CDCl_3$ is represented in Figure 1, in which the main peak corresponding to alkenylallylborane was observed at 30.1 ppm. The smaller peak at 46.1 ppm is assignable to the crosslinked structure formed by further phenylboration. In the IR spectrum of 4 (Figure 2), the characteristic peak for double bond was observed at 1608 cm^{-1}.

The UV-vis absorption spectrum of 4 was recorded in chloroform at room temperature, as shown in Figure 3. The absorption maximum was observed at 324 nm possibly owing to some hyperconjugation via allyl group and extension of π-conjugation via the vacant p-orbital of the boron atom. The polymer 4 was slightly fluorescent. In the fluorescence emission spectrum of 4 (Figure 4; in chloroform at room temperature; excitation wavelength at 320 nm), the emission maximum was observed at 506 nm in the visible green region.

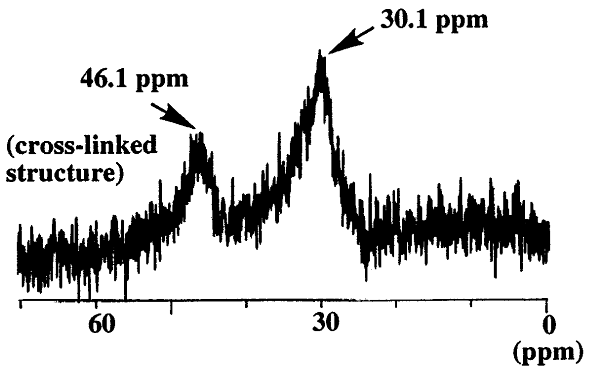


Figure 1. ^{11}B-NMR Spectrum of 4 in $CDCl_3$

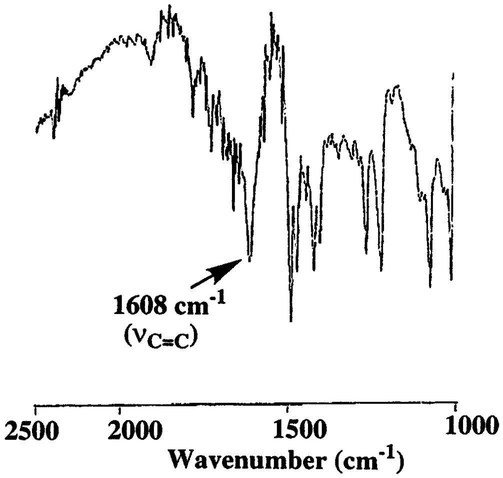


Figure 2. IR Spectrum of 4

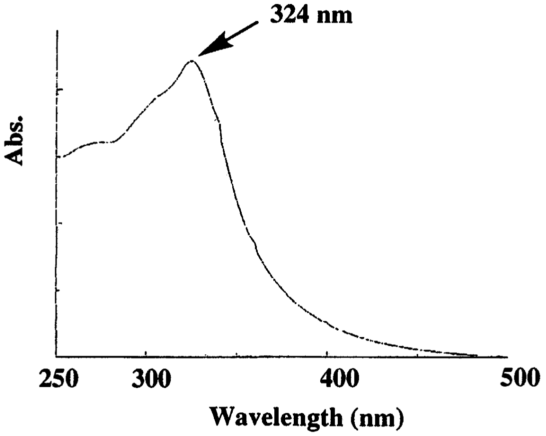


Figure 3. UV-vis Absorption Spectrum of 4 in $CHCl_3$ at r.t.

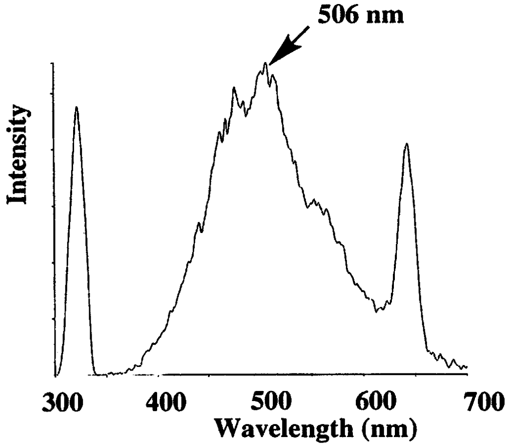


Figure 4. Fluorescence Emission Spectrum of 4 in $CHCl_3$ at r.t. (Excited at 320 nm)

In conclusion, alternating boration copolymerization between 2 and 3 gave the corresponding copolymer 4 having alkenylallylborane unit in the mainchain. The obtained polymer is expected to act as a new class of σ-π conjugated polymer after anion doping because of its structure having the B-C bond in the conjugation path. This should be our next research target.

Experimental Section

Materials and Instruments. 2 was prepared by organometallic coupling between 1,4-dibromobenzene and methyl propargyl ether in the presence of copper bromide [9]. **3** was prepared by Sonogashira-coupling of 2,7-dibromofluorene with trimethylsilylacetylene and subsequent hydrolysis [10]. **1** was prepared according to the reported method [11]. Tetrachloroethane was dried over calcium hydride and distilled. ^{1}H-NMR 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 G3000H$_{XI}$ by using THF as an eluent after calibration with standard polystyrene samples. IR spectrum was obtained on a Perkin Elmer 1600 spectrometer. UV-vis spectrum was recorded on a JASCO V-530 spectrophotometer. Fluorescence emission spectrum was recorded on a Perkin-Elmer LS50B luminescence spectrometer.

Alternating Boration Copolymerization between 2 and 3. Under nitrogen atmosphere, 2 equiv. of **1** (235.0 mg, 0.959 mmol) was added to 1 equiv. of **2** (72.4 mg, 0.469 mmol) in tetrachloroethane (1 ml) at room temperature. After stirring the reaction mixture for 24h, 1 equiv. of **3** (97.5 mg, 0.454 mmol) in tetrachloroethane (1ml) was added, and then the resulting solution was warmed up to 100°C and stirred for additional 5h. The obtained crude polymer was purified by reprecipitating into *n*-hexane to afford the polymer **4** as a brown powder in 17% yield (66.2 mg, 0.077 mmol). ^{1}H-NMR (δ, ppm) 1.58 (B-CH_2, 4H), 3.83 (Ar-CH_2-Ar, 2H), 6.23 (CH_2-CBr=C*H*, 2H), 7.19-7.72 (Ar-H, B-CH=C, 32H). ^{11}B-NMR (δ, ppm) 30.1. IR (cm^{-1}) 1608 ($\nu_{c=c}$).

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