# Silver(I)-Induced Coupling Polymerization of Bifunctional Organoboron Compounds

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*Received December 21, 1992*

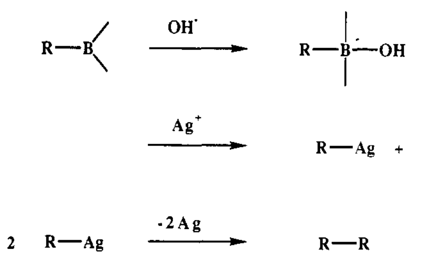
*Revised Manuscript Received March 8, 1993*

Homocoupling reaction of organoboron compounds induced by silver nitrate has been used as an important synthetic tool for carbon–carbon bond formation in organic chemistry.[3] This reaction is believed to proceed via migration of alkyl groups on a boron atom to silver, which breaks homolytically to form alkyl radicals.[4] These radicals formed here readily react with each other to give a coupling product (Scheme I). Bifunctional organoboron compounds prepared from dienes or internal acetylenes were subjected to this reaction to give cyclic hydrocarbons[5] or olefins,[6] respectively. These reactions include the so-called intramolecular coupling. Consequently, if intermolecular coupling takes place, the formation of linear polymers can be expected. We describe here the first example of the polymerization via a Ag(I)-induced coupling reaction of bifunctional organoboron compounds. Since the discovery of the hydroboration method,[7] organoboron compounds are readily available from the corresponding olefins. Thus, the expected bifunctional (telechelic) organoboron compounds can be prepared from dienes for the present study. The general idea of the present Ag(I)-induced coupling polymerization of telechelic organoboron compounds is shown in Scheme II.

Bifunctional boranes were prepared from 1,7-octadiene[8] (**1a**) or *p*-divinylbenzene (**1b**) by reaction with a large excess amount[9] of borane–tetrahydrofuran ($BH_3$/THF). However, these organoboron compounds gave only low molecular weight (several hundreds) oligomers after reaction with silver(I) nitrate. From the results of the $^1H$ NMR spectra of the oligomers obtained, the protons assignable to the terminal methyl groups were detected. The observed intensity of this peak was larger than that of the methyl groups of secondary borane species (6%),[7c] which were formed by the Markovnikov addition of borane to C=C. This result must be caused by the disproportionation of two radicals formed. The coupling reaction of the radicals is known to play an important role as a termination in radical polymerization. Thus, in the present system, it seems to be important to increase the proportion of recombination of two radicals to avoid undesirable disproportionation.

It is well-known that the recombination mainly takes place as a termination in the radical polymerization of styrene.[10] Accordingly, if starting dienes can be designed as to favor the formation of benzylic borane at the hydroboration stage, the following coupling polymerization comes closer to the model of termination of the radical polymerization system of styrene. For this purpose, β,β′-dimethyl-*p*-divinylbenzene (**1c**) and β,β,β′,β′-tetramethyl-*p*-divinylbenzene (**1d**) were prepared respectively by the Wittig reaction of terephthalaldehyde with the corresponding phosphonium salts and were examined for the present coupling polymerization.

**Scheme I**



**Scheme II**

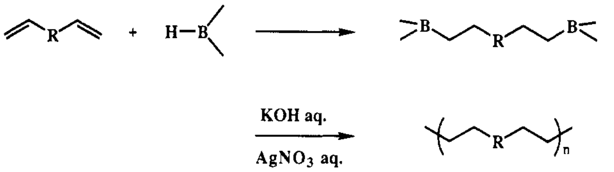
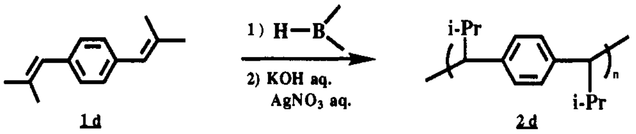
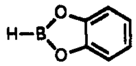


**Table I. Ag(I)-Induced Coupling Polymerization of 1d Using Various Boranes**



| run | borane | 2d yield[a] (%) | 2d $\bar{M}_n$[b] | 2d $\bar{M}_w$[b] |
|---|---|---|---|---|
| 1 | $BH_3$/THF | 63 | 2630 | 5880 |
| 2 | $Me_2S{\cdot}BH_2Br$ | 81 | 42200 | 116500 |
| 3 | $Me_2S{\cdot}BH_2Cl$ | 61 | 121400 | 199000 |
| 4 |  | 63 | 800 | 1060 |
| 5 | 9-BBN | | 1360 | 2770 |

[a] Isolated yields after reprecipitation into MeOH. [b] GPC (THF), polystyrene standard.

As a typical experimental example, **1d** (0.5 mmol) was reacted with an excess amount of monobromoborane–dimethyl sulfide ($Me_2S{\cdot}BH_2Br$; 5.0 mmol) at room temperature under nitrogen. The resulting material was treated with aqueous KOH and silver(I) nitrate at 0 °C. The produced polymer was isolated by coagulation with methanol.

When **1d** was reacted with various kinds of boranes followed by treatment with silver(I) nitrate under alkaline conditions, the molecular weights of the resulting polymers were quite dependent on the boranes used (Table I). $Me_2S{\cdot}BH_2Br$ was reported to be a more selective hydroboration reagent due to the steric effect of a halogen atom in comparison with $BH_3$/THF.[11] Higher selectivity in hydroboration increased the ratio of benzylic borane species, which is more suitable for the present coupling polymerization. As a result, high molecular weight polymer (**2d**) was produced by using $Me_2S{\cdot}BH_2Br$ (run 2). Similarly, $Me_2S{\cdot}BH_2Cl$ also gave high molecular weight polymer although the yield was relatively lower (run 3). These results support the effectiveness of monohaloboranes for the present polymerization. When catecholborane or 9-borabicyclo[3.3.1]nonane (9-BBN) was used at the hydroboration stage, the resulting polymers had rather low molecular weights (runs 4 and 5). In the case of catecholborane, the dimethyl substituent in **1d** seems to be too large for the complete hydroboration.[12] 9-BBN also did not give high molecular weight polymers because the bicyclic alkyl group in 9-BBN produced radicals, which interrupted the desired polymerization.[13]

Among the boranes examined here, monohaloborane was found to be the best hydroboration reagent. Thus,

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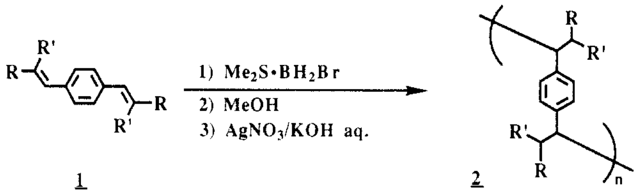
**Table II. Ag(I)-Induced Coupling Polymerization of Various Diolefins Using $Me_2S{\cdot}BH_2Br$**



| run | compd | R | R′ | yield[a] (%) | $\bar{M}_n$[b] | $\bar{M}_w$[b] |
|---|---|---|---|---|---|---|
| 1 | **1b** | H | H | | 360 | 840 |
| 2 | **1c** | Me | H | 47 | 6330 | 27 600 |
| 3 | **1d** | Me | Me | 81 | 42200 | 116 500 |

[a] Isolated yields after reprecipitation into MeOH. [b] GPC (THF), polystyrene standard.

regioselectivity of the hydroboration reaction was examined using $Me_2S{\cdot}BH_2Br$ with a model compound ($\beta,\beta$-dimethylstyrene, **3d**). The boron atom was favorably introduced at the benzylic position (87%) by using **3d**, which possessed a dimethyl substituent at the $\beta$-position. From the results of $^1H$ and $^{13}C$ NMR of the polymer obtained (**2d**),[14] it should be noted here that methylene groups and quaternary carbons were not observed in the structure of the polymer. In other words, the structure of **2d** was formed selectively in the present polymerization.

Table II summarizes the results of the Ag(I)-induced coupling polymerization starting from **1b–d**. The more substituents at the $\beta$-position of diolefins, the higher were the molecular weights of the polymers obtained. This result supports our idea that recombination of radicals should be important in the present Ag(I)-induced coupling polymerization.

## References and Notes

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(8) In ref 5a, it was reported that cyclooctane was produced by a Ag(I)-induced intramolecular coupling reaction.
(9) A large excess amount of borane was used to prevent gelation of dienes.
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(12) Brown, H. C.; Chandrasekharan, J. *J. Org. Chem.* **1983**, *48*, 5080.
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(14) **2d**: $^1H$ NMR ($\delta$, $CDCl_3$) 0.35–1.20 (m, 12 H), 1.45–2.25 (br, 2 H), 4.15–4.75 (m, 2 H), 7.00–7.50 (m, 4 H); $^{13}C$ NMR ($\delta$, $CDCl_3$) 19.3, 19.4, 32.2, 90.0, 91.1, 125.5, 127.0, 140.0, 140.3.