Synthesis of Poly(organoboron halide)s by Hydroboration Polymerization between Diene and Monobromoborane

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Hydroboration polymerization between various dienes and monobromoborane–dimethyl sulfide complex produces poly(organoboron halide)s consisting of C–B bonds in the main chain and having B–Br bonds, which show characteristic properties as a polymeric Lewis acid.

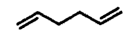
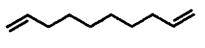
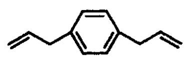
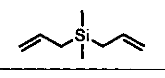
Recently, we have explored new methodologies for the preparation of organoboron polymers, *i.e.* hydroboration polymerization of dienes,[1] diynes,[2] or dicyano compounds[3] with monoalkylborane. The obtained organoboron polymers can be used as a novel type of reactive polymer.[4] For example, these polymers can be transformed into polyalcohols or polyketones by treatment with carbon monoxide or cyanide anion, respectively, followed by oxidative treatment.[5] We have also reported haloboration polymerization[6] between boron tribromide and terminal diynes to give poly(organoboron halide)s as a polymeric Lewis acid, which has scarcely ever been known.

We describe here the synthesis of poly(organoboron halide)s by hydroboration polymerization of various dienes with monobromoborane–dimethyl sulfide complex (Scheme 1). The produced polymers consist of C–B bonds in the main chain. In addition, poly(organoboron halide)s have B–Br bonds showing the characteristic properties as a polymeric Lewis acid.

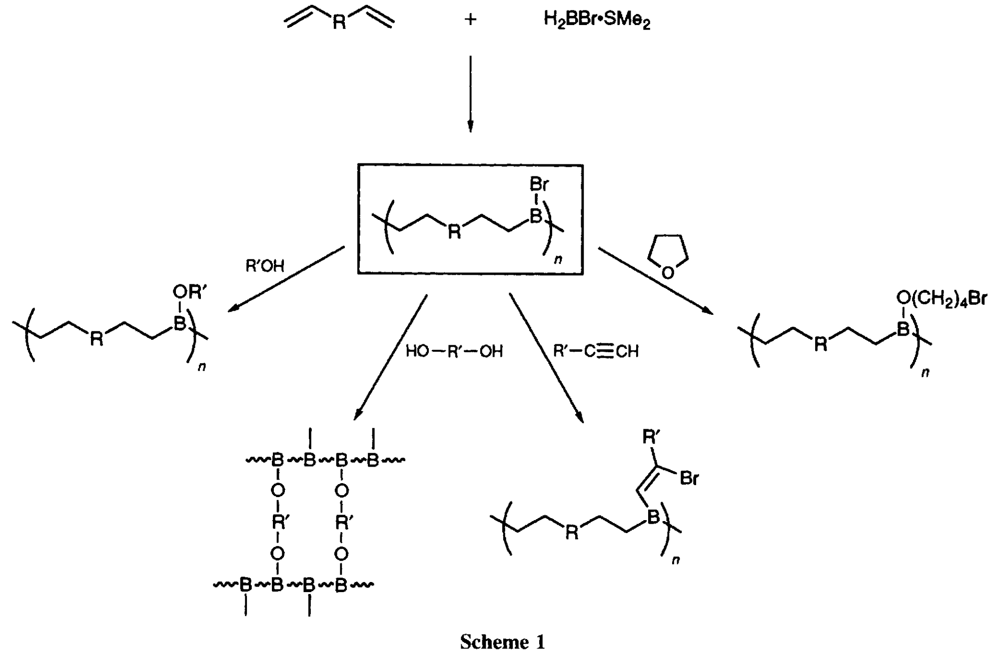
As a typical example of hydroboration polymerization, octa-1,7-diene was added to a 1.0 mol dm^{-3} dichloromethane solution of the monobromoborane–dimethyl sulfide complex with stirring at 0 °C under nitrogen. The reaction mixture was warmed gradually to room temperature and the reaction was completed within several hours; the reaction mixture was directly subjected to GPC measurement. The molecular mass of the polymer obtained was increased when the feed ratio of monobromoborane to diene approached or slightly exceeded unity.

The produced poly(organoboron halide) was very reactive toward moisture under air. Thus, the polymer was isolated after coagulation with dry methanol under nitrogen, by which the B–Br bonds were replaced by the B–OMe bonds. The isolated yield of the polymer was thus calculated after washing with *n*-pentane and drying *in vacuo*. After the treatment with methanol, no change in the molecular mass was observed. This result indicates that no side-reactions such as chain scission took place during the transformation reaction. The B–OMe bonds were also introduced quantitatively into the polymer by the reaction of B–Br bonds with sodium methoxide in methanol. The structure of the B–OMe substituted polymer was confirmed by ^{1}H and ^{11}B NMR spectra. The results of hydroboration polymerization of various dienes with monobromoborane–dimethyl sulfide complex are sum-

Table 1 Hydroboration polymerization of various dienes with $H_2BBr{\cdot}SMe_2$

Run	Diene	Yield (%)[a]	$\bar{M}_n$[b]	$\bar{M}_w$[b]
1		75	6 600	10 300
2		78	23 500	31 500
3		88	16 400	23 500
4		86	8 800	14 800
5		85	5 400	7 900

[a] After treatment with MeOH. [b] Determined by GPC ($CHCl_3$, polystyrene standards).



Scheme 1

marized in Table 1. In all cases, the corresponding poly(organoboron halide)s were obtained effectively.

The poly(organoboron halide) was reacted with water or diol compounds such as ethylene glycol to produce the corresponding gel by the intermolecular substitution reactions. The B–Br group in the polymer chain has a potential to be subjected to haloboration reaction toward terminal acetylene. Thus, haloboration reaction with phenylacetylene or hex-1-yne was carried out by adding an equimolar amount of boron tribromide, which removed dimethyl sulfide from the polymer to generate *in situ* the free B–Br group. As a result, the alkenyl-branched organoboron polymer was obtained. The poly(organoboron halide) was also reacted with THF *via* ether cleavage reaction to give 4-bromobutoxy-substituted organoboron polymer. These reactions are summarized in Scheme 1, which demonstrates the characteristic property of the polymer as a polymeric Lewis acid.

Received, 3rd September 1993; Com. 3/05296F

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