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Hydroboration Polymerization. 1. Synthesis of Organoboron Polymers by Polyaddition between Diene and Monoalkylborane

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ABSTRACT: We report here a polyaddition between diene and monoalkylborane, that is, "Hydroboration Polymerization". The reaction of thexylborane with 1,7-octadiene was carried out in tetrahydrofuran at 0 °C under nitrogen atmosphere to produce an organoboron polymer. The molecular weight of the polymer obtained increased as the feed ratio to unity was approached. As a diene component, 1,9-decadiene, *p*-divinylbenzene, *p*-diallylbenzene, bis(allyl ether)s of ethylene glycol, 1,4-butanediol, triethylene glycol, hydroquinone, and bisphenol A were used in this hydroboration polymerization to give the corresponding organoboron polymers. The thermal and oxidative stabilities of the obtained polymers were examined. These polymers were a little more stable toward air in comparison with conventional "trialkylboranes".

Introduction

Hydroboration is a well-known methodology in organic synthesis, which takes place under mild conditions to produce various alkylborane compounds almost quantitatively. For these several decades, Brown et al. have established the chemistry of hydroboration.[1,2] However, the direct use of this reaction in polymer synthesis has been very limited so far. Among numerous studies reported by Brown and his group, the formation of polymeric materials has been described in their papers on the reaction of thexylborane and 1,3-butadiene[3] or of monochloroborane and 1,7-octadiene.[4] However, no detail was reported about the yield, molecular weights, and characterization (structure) of the resulting polymers. These polymers were formed as intermediates to obtain boron heterocycles by the so-called "thermal depolymerization".

Previously, Urry et al. mentioned that the organoboron polymer was formed by the pyrolysis of 2,5-dimethyl-2,5-diborahexane.[5] Mikhailov et al. also reported the formation of organoboron polymer by thermal isomerization of triallylborane and triisobutylborane.[6] However, these reactions required severe conditions, and the obtained polymers have not been characterized. Recently, Pinazzi has described the modification of polybutadiene by the hydroboration method.[7] Chung also reported the polymers having organoboron branches for the preparation of polymers with alcohol functionalities.[8-10] Very recently, we reported a novel method (haloboration polymerization) for the preparation of organoboron polymers, which consisted of C–B bonds in the main chains.[11]

Here we report a polyaddition between diene and monoalkylborane, which we term "Hydroboration Polymerization".[12] This is the first example to study the nature of polymerization and to characterize the structure and the molecular weight of organoboron polymers. The resulting organoboron polymer can be regarded as a polymer homologue of trialkylborane and can be used as a novel type of polymer having unique reactivities and properties.

Experimental Section

Materials and Instruments. Borane–tetrahydrofuran (THF) complex and borane–dimethylsulfide were obtained from Merck Co. 2,3-Dimethyl-2-butene, allyl bromide, 1,7-octadiene, 1,9-decadiene, p-divinylbenzene, and all solvents were dried and distilled under nitrogen. Various diols were purified by distillation or by recrystallization. Thexylborane (1,1,2-trimethylpropylborane) (1) was prepared by the reaction of borane–THF complex[3] or of borane–dimethylsulfide[13] with 2,3-dimethyl-2-butene as reported earlier and was purified by distillation [48–49 °C (0.1 mmHg)]. Hydrogen titration by hydrolysis of 1 showed that the isolated sample was pure enough for the following hydroboration polymerization.

IR spectra were obtained on a Hitachi 260-50 grating spectrophotometer. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 (60-MHz) instrument. Gas chromatographic analysis (GC) was made on a Shimadzu GC-6A instrument. Gel permeation chromatographic analysis (GPC) was carried out on a Toyo-Soda HLC-8020 (Toyo-Soda G3000) by using dried THF as an eluent with nitrogen bubbling after calibration with standard polystyrene samples. Thermogravimetric analysis (TGA) was made on a Shimadzu DT-30 instrument (15 °C/min) under an air or a nitrogen stream. Cryoscopic experiment was carried out under nitrogen atmosphere by using benzene as a solvent.

Synthesis of *p*-Diallylbenzene (2d). To a benzene solution of *p*-dibromobenzene (7.94 g, 33.7 mmol) and $PdCl_2(PPh_3)_2$ (0.45

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Table I
Dependence of MW on the Feed Ratio of 1/2a[a]

run	1, mmol	2a, mmol	1/2a	$\bar{M}_n$[b]	$\bar{M}_w$[b]
1	0.64	0.95	0.68	540	840
2	0.73	0.96	0.76	850	1 710
3	0.91	0.93	0.98	1 770	6 540
4	0.98	0.92	1.05	19 000	27 700
5	1.10	0.98	1.12	18 000	27 000
6	1.11	0.92	1.22	14 000	21 600
7	1.24	0.98	1.27	11 900	19 100
8	1.43	1.01	1.42	13 300	21 800

[a] Reactions were carried out by adding 1 to a THF 1 M solution of **2a** using a microfeeder at 0 °C under nitrogen. [b] GPC (dry THF), polystyrene standard.

Table II
Dependence of MW on the Feed Ratio of 2a/1[a]

run	1, mmol	2a, mmol	2a/1	$\bar{M}_n$[b]	$\bar{M}_w$[b]
1	1.00	0.63	0.63	940	2 270
2	1.05	0.77	0.73	1150	3 040
3	1.03	0.92	0.89	2830	8 910
4	1.00	0.98	0.98	3470	12 200
5	0.97	1.02	1.05	4370	14 600
6	0.98	1.19	1.21	2900	14 000
7	0.97	1.29	1.33	1850	13 400

[a] Reactions were carried out by adding **2a** to a THF 1 M solution of 1 using a microfeeder at 0 °C under nitrogen. [b] GPC (dry THF), polystyrene standard.

g, 0.64 mmol) were added allyltributyltin (0.48 g, 1.45 mmol) and a THF solution of allylmagnesium chloride (1.0 M, 80 mL) under nitrogen. The mixture was stirred for 1 day at a reflux temperature. The obtained **2d** was purified by SiO_2 column chromatography (*n*-hexane) and then by distillation. Yield: 1.58 g (9.98 mmol, 30%).

Bis(allyl ether)s of Ethylene Glycol (2e), 1,4-Butanediol (2f), and Triethylene Glycol (2g). To a 100-mL THF suspension of *n*-hexane-washed sodium hydride (4.3 g, 180 mmol) were added ethylene glycol (5.6 g, 90 mmol) and then allyl bromide (22 g, 180 mmol) slowly at 0 °C. After 1 day of refluxing, 100 mL of water was added to the reaction mixture. The organic layer was extracted with three portions (100 mL) of diethyl ether and dried over magnesium sulfate. After evaporation of solvent, **2e** was dried over sodium and distilled [72–73 °C (26 mmHg)]. Yield: 6.5 g (46 mmol, 51%). **2f** and **2g** were obtained similarly in 67% [83–84 °C (10 mmHg)] and 56% [108–110 °C (0.65 mmHg)] yield, respectively.

Bis(allyl ether)s of Hydroquinone (2h) and Bisphenol A (2i). To a 40-mL acetone suspension of potassium carbonate (5.5 g, 40 mmol) were added hydroquinone (2.3 g, 21 mmol) and allyl bromide (5.6 g, 46 mmol) at ambient temperature. After 15 h of refluxing, 50 mL of diluted aqueous sodium hydroxide was added to the reaction mixture. The organic layer was extracted with three portions (100 mL) of diethyl ether and dried over magnesium sulfate. The purification with SiO_2 column chromatography (*n*-hexane) gave 3.6 g (19 mmol, 90%) of **2h** as a white crystal (mp 31.9–32.4°C). In a similar manner, **2i** was obtained as a colorless oil in 81% yield.

Polyaddition between 1,7-Octadiene (2a) and Thexylborane (1). The dependence of the molecular weight of the polymer obtained on the feed ratio was examined as follows. 1 was added slowly (45 μmol/min) to a 1.0 M THF solution of **2a** by using a microfeeder at 0 °C under nitrogen. After 1 h of stirring at 0 °C, GPC analysis was subjected directly. Amounts of 1 and **2a** used are summarized in Table I. On the other hand, **2a** was added slowly (40 μmol/min) to a THF solution of 1 by a procedure similar to that described above. These experiments are summarized in Table II.

As a typical example of the polymerization, 1 (0.096 g, 0.98 mmol) was added to a 1.0 M THF solution of **2a** (0.102 g, 0.92 mmol) by using a microfeeder (45 μmol/min) at 0 °C under nitrogen. The evaporation of solvent gave colorless gum in a quantitative yield. The obtained organoboron polymer (**3a**) was soluble in common organic solvents such as THF, chloroform, benzene, and *n*-hexane. All the spectroscopic analyses and GPC measurements were performed without further purification. **3a**: ^{1}H NMR (δ, $CDCl_3$) 0.52–1.02 (–CH_3, 12 H), 1.02–2.20 (–CH, –CH_2–, 17 H); IR (neat) 2940, 1470 cm^{-1}. **3a** can be further purified by reprecipitation from THF into dried DMF under nitrogen and isolated in 54% yield.

Hydroboration Polymerizations of Various Dienes with 1. The following organoboron polymers were obtained in quantitative yields by using a procedure similar to that described for **3a**.

3b from 1 (0.091 g, 0.93 mmol) and **2b** (0.109 g, 0.79 mmol): ^{1}H NMR (δ, $CDCl_3$) 0.58–1.02 (–CH_3, 12 H), 1.02–2.20 (–CH, –CH_2–, 21 H); IR (in $CHCl_3$) 2840, 1460, 1350 cm^{-1}.

3c from 1 (0.095 g, 0.96 mmol) and **2c** (0.117 g, 0.90 mmol): ^{1}H NMR (δ, $CDCl_3$) 0.54–1.02 (–CH_3, 12 H), 1.09–2.04 (–CH, –CH_2–, 5 H), 2.35–2.98 ($ArCH_2$–, 4 H), 7.14 (C_6H_4, s, 4 H); IR (in $CHCl_3$) 2960, 1455, 1340 cm^{-1}.

3d from 1 (0.097 g, 0.99 mmol) and **2d** (0.136 g, 0.86 mmol): ^{1}H NMR (δ, $CDCl_3$) 0.49–0.92 (–CH_3, 12 H), 1.02–2.21 (–CH, –CH_2–, 9 H), 2.60 ($ArCH_2$–, m, 4 H), 7.10 (C_6H_4, s, 4 H); IR (in $CHCl_3$) 2950, 1512, 1458 cm^{-1}.

3e from 1 (0.116 g, 1.19 mmol) and **2e** (0.154 g, 1.08 mmol): ^{1}H NMR (δ, $CDCl_3$) 0.58–1.03 (–CH_3, 12 H), 1.03–2.12 (–CH, –CH_2–, 9 H), 3.28–3.91 (OCH_2–, 8 H); IR (neat) 2940, 1465, 1320, 1100 cm^{-1}.

3f from 1 (0.099 g, 1.01 mmol) and **2f** (0.160 g, 0.94 mmol): ^{1}H NMR (δ, $CDCl_3$) 0.53–0.98 (–CH_3, 12 H), 0.98–2.36 (–CH, –CH_2–, 13 H), 3.13–3.66 (OCH_2–, 8 H); IR (in $CHCl_3$) 2950, 1466, 1366, 1244, 1103 cm^{-1}.

3g from 1 (0.113 g, 1.15 mmol) and **2g** (0.237 g, 1.03 mmol): ^{1}H NMR (δ, $CDCl_3$) 0.55–1.12 (–CH_3, 12 H), 1.12–2.21 (–CH, –CH_2–, 9 H), 3.24–4.16 (OCH_2–, 16 H); IR (neat) 2950, 1460, 1350, 1085 cm^{-1}.

3h from 1 (0.108 g, 1.11 mmol) and **2h** (0.182 g, 0.95 mmol): ^{1}H NMR (δ, $CDCl_3$) 0.53–1.02 (–CH_3, 12 H), 1.02–2.40 (–CH, –CH_2–, 9 H), 3.89 (OCH_2–, m, 4 H), 6.81 (C_6H_4, s, 4 H); IR (in $CHCl_3$) 2957, 1505, 1468, 1238, 1061, 1030, 826 cm^{-1}.

3i from 1 (0.089 g, 0.91 mmol) and **2i** (0.247 g, 0.78 mmol): ^{1}H NMR (δ, $CDCl_3$) 0.62–1.05 (–CH_3, 12 H), 1.08–2.46 (–CH, –CH_2–, –CH_3, 15 H), 3.60–4.35 (OCH_2–, m, 4 H), 6.62–7.34 (C_6H_4, m, 8 H); IR (in $CHCl_3$) 2959, 1608, 1510, 1469, 1248, 1011, 832 cm^{-1}.

Stability of Organoboron Polymer 3a toward Air. The oxidation stability of **3a** toward air was examined by monitoring the change of the GPC curve during an oxidation experiment, in which a stream of air was bubbled (at a rate of 120 mL/min) into a THF (1 mL) solution of **3a** (0.25 g). After the designated time, the resulting polymer was characterized by GPC analysis.

Results and Discussion

According to the previous reports, some monoalkylboranes such as thexylborane,[14] (S–B) 3-(methylthio)propylborane,[15] and monoalkylborane–amine complexes[16] are known to be stable enough as bifunctional B–H compounds. Among them, thexylborane (1) is gradually decomposed in a THF solution.[14] However, 1 is known to be stable enough after distillation (in the bulk).[17] Thus, distilled 1 was employed as a bifunctional monoalkylborane component in the present hydroboration polymerization. In reference to the previous studies, the cyclized products were formed by the reactions of 1 with 1,3-butadiene,[3] 1,4-pentadiene,[3] 1,5-hexadiene,[3] diallylamines,[18] divinylsilanes,[19] diallylsilanes,[19] and so on. To avoid this competitive cyclization reaction, relatively longer chain dienes were used here.

The reaction condition in this study was fixed at the temperature of 0 °C, and a monomer was added to a 1.0 M THF solution of another monomer by using a microfeeder. Similar to the conventional "trialkylboranes", the organoboron polymer may be unstable under air. This instability requires the careful GPC measurement to avoid the decomposition of the obtained organoboron polymers. Thus, GPC analysis should be carried out by using air- and peroxide-free THF as an eluent. In addition, con-

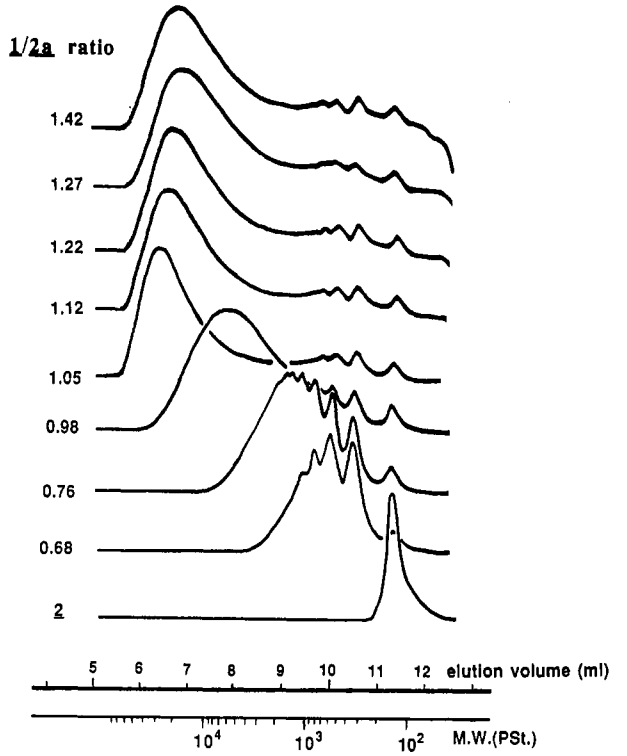


Figure 1. GPC traces for the product polymers by hydroboration polymerization by changing the feed ratio of 1 to **2a**.

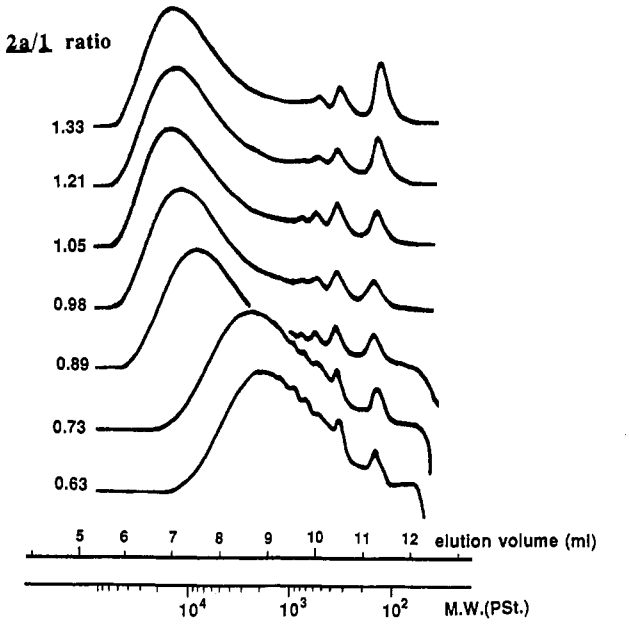
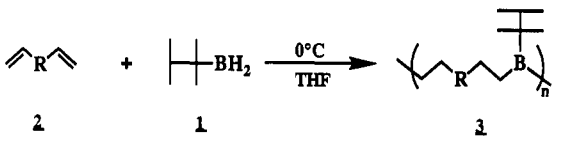


Figure 2. GPC traces for the product polymers by hydroboration polymerization by changing the feed ratio of **2a** to 1.

tinuous nitrogen bubbling in THF during the analysis made a success of the measurement of the molecular weights of organoboron polymers.

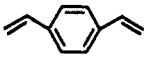
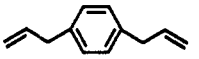
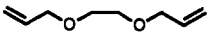
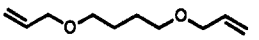
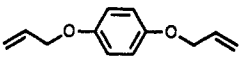
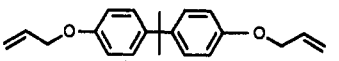
Dependence of Molecular Weight on the Feed Ratio of Monomers. Generally, the stoichiometry of the employed two monomers is quite important in polyaddition reaction. Thus, the dependence of the feed ratio of monomers was examined in the hydroboration polymerization between thexylborane (1) and 1,7-octadiene (**2a**). When 1 was added to a THF solution of **2a** (method A), the molecular weight of the polymer obtained increased with the approach of the feed ratio to unity (Table I; Figure 1). The number-average molecular weight of the polymer obtained was up to 19 000 from the result of GPC using

Scheme I



2 1 3

Table III
Hydroboration Polymerization between Thexylborane and Various Dienes[a]

run	diene	no.	$\bar{M}_n$[b]	$\bar{M}_w$[b]
1		**2a**	19000	27 700
2		**2b**	18400	27 400
3		**2c**	19000	29 200
4		**2d**	9400	16 900
5		**2e**	1200	2 600
6		**2f**	1900	4 500
7		**2g**	1900	3 200
8		**2h**	5100	11 200
9		**2i**	7600	15 400

[a] Polymerizations were carried out by adding a small excess of thexylborane to the 1 M THF solution of diene at 0 °C. [b] GPC (dry THF), polystrene standard.

polystyrene calibration curves.[20] The rate of the addition of 1 was 10 μmol/min. In the case of fast addition (400 μmol/min) of 1, no change of the molecular weight was observed. This result shows that the polymerization was completed during the addition of the monomer. In other words, an excess amount of 1 remained when the feed ratio was higher than unity. Accordingly, the decrease of molecular weight in this case might be caused by the so-called back-biting reaction (disproportionation between the polymer chain and 1).[21] This is not clear at the present time because the contribution of this reaction should be too small to be detected. However, it is confirmed at least that the molecular weight reached a maximum when the feed ratio of two monomers came to unity or slight excess.

Another method, in which **2a** was added to a THF solution of 1 (method B) also showed similar results and is summarized in Table II and in Figure 2. The molecular weight of the obtained polymer was increased when the feed ratio reached unity. Thus, method A was used for hydroboration polymerization of various dienes. In all cases, a slight excess of 1 was employed.

Hydroboration Polymerization of Various Dienes. The general scheme of hydroboration polymerization is shown in Scheme I. Similar to **2a**, various hydrocarbon diolefins such as 1,9-decadiene (**2b**), *p*-divinylbenzene (**2c**), and *p*-diallylbenzene (**2d**) were used for this polymerization. Diolefins containing oxygen atoms (**2e–2i**) also produced the corresponding organoboron polymers. In all cases, the obtained polymers were colorless gum and soluble in common organic solvents such as THF, chloroform, and benzene. These results are summarized in Table III. The molecular weights of the polymers from ethers were somewhat lower than those from hydrocarbon olefins. This might be the result of intramolecular coordination of an oxygen atom to boron.

Stability of Organoboron Polymer. The organoboron polymers obtained by hydroboration polymerization were stable enough against protic solvents such as water

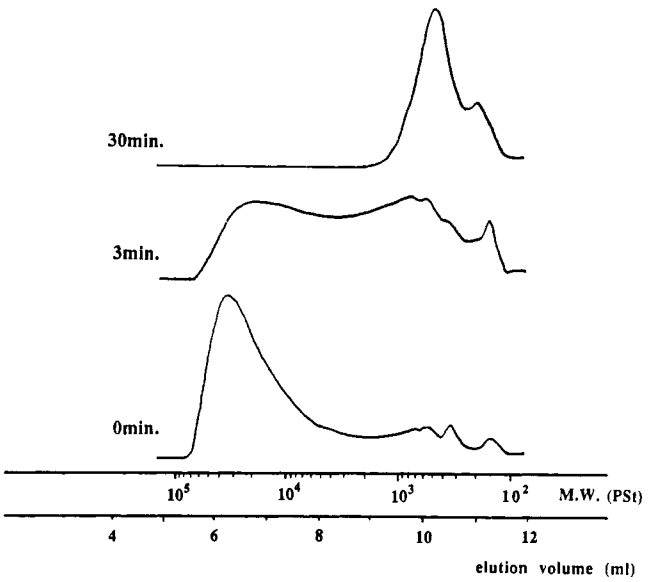


Figure 3. GPC traces for **3a** (0 min), the product after 3 min of air-bubbling in THF solution of **3a** (3 min), and the product after 30 min of air-bubbling (30 min).

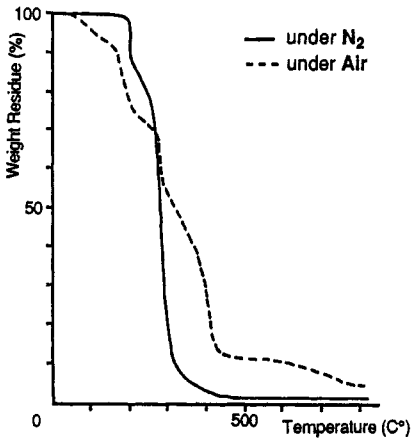


Figure 4. TGA (10 °C/min) traces for **3a** under nitrogen or under air.

and alcohol under nitrogen.[2] However, under air, these polymers were unstable as usual for organoboron compounds.[22,23] This decomposition was monitored by GPC after the air bubbling in THF solution of **3a** at room temperature. The results are illustrated in Figure 3. After 3 min of air-bubbling, the peak became broader and moved to the low molecular weight region. At 30 min, the molecular weight decreased to almost several hundreds. However, in comparison with conventional "trialkylboranes", it should be noted here that the present organoboron polymer was a little more stable toward air.

A THF solution of organoboron polymer (**3a**) was refluxed under nitrogen to form a gel. This gelation might be caused by hydroborane (B–H) species, which were formed by thermal β-elimination (retrohydroboration) of the thexylborane group to evolve 2,3-dimethyl-2-butene. It can be considered that the hydroboration reaction of this B–H group with the terminal double bond in the polymer produced a boron-containing gel.

From the results of thermogravimetric analysis of **3a** (Figure 4), the weight loss of the polymer started at 130 °C and completed at 480 °C under a nitrogen stream. On the other hand, under air, **3a** began to lose its weight at 110 °C. The weight was kept to be nearly 10% above 450 °C. After thermal analysis, a black solid remained in a cell under air.

The polymers obtained in the present hydroboration polymerization have a structure consisting of C–B bonds in the main chain. Generally, these organoboron polymers can be regarded as a polymer homologue of trialkylborane, which is known to be a very versatile compound in organic synthesis. Thus, the polymers obtained by hydroboration polymerization can be expected as a novel type of reactive polymers, which is a next target of our group and will be demonstrated in the forthcoming paper.

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Registry No. (1)(**2a**) (copolymer), 128967-04-4; (1)(**2b**) (copolymer, 130934-20-2; (1)(**2c**) (copolymer), 130934-21-3; (1)(**2d**) (copolymer), 130934-22-4; (1)(**2e**) (copolymer), 130934-23-5; (1)(**2f**) (copolymer), 130934-24-6; (1)(**2g**) (copolymer), 130934-25-7; (1)(**2h**) (copolymer), 130934-26-8; (1)(**2i**) (copolymer), 130934-27-9; **2d**, 2664-28-0; **2e**, 7529-27-3; **2f**, 1471-16-5; **2g**, 90736-68-8; **2h**, 37592-20-4; **2i**, 3739-67-1; BrC_6H_4-*p*-Br, 106-37-6; allyltributyltin, 24850-33-7; ethylene glycol, 107-21-1; allyl bromide, 106-95-6; hydroquinone, 123-31-9.