Polymer Bulletin 42, 33–40 (1999)

Polymer Bulletin

Synthesis of hydroboration copolymer of TCNQ and formation of polymer charge transfer complex therefrom

Noriyoshi Matsumi, Kensuke Naka, Yoshiki Chujo[*]

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University,
Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

Received: 29 September 1998/Revised version: 17 November 1998/Accepted: 24 November 1998

Summary

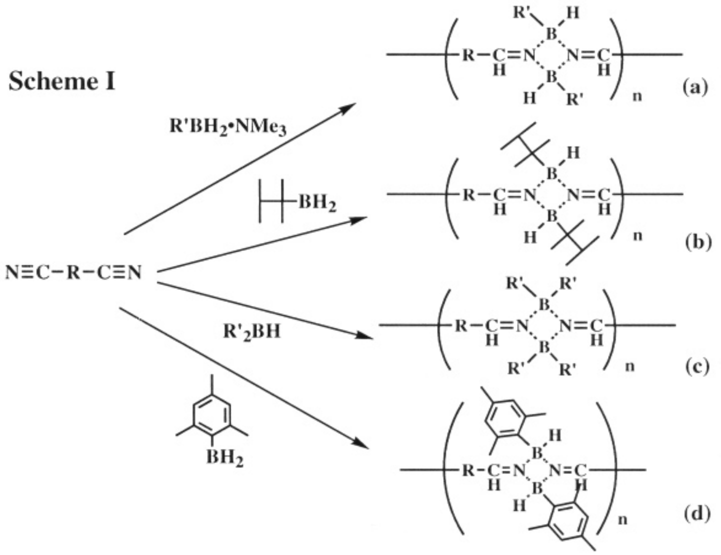
Novel TCNQ copolymers were prepared by hydroboration copolymerization of TCNQ with mesitylborane. The polymers obtained exhibited characteristics as a new class of polymer electron acceptors. When these polymers were treated with p-phenylenediamine at 80°C - 140°C in diglyme solutions, charge transfer complex formation was observed in UV-vis spectra. Hydroboration polymerization of p-, m-dicyanotetrafluorobenzene also proceeded to give the corresponding polymer electron acceptors.

Introduction

Synthesis of polymeric charge transfer complex is one of the attractive approaches for the preparation of processable organic conductors. A number of conductive or photoconductive polymer matrices have been prepared by doping the insulating polymer matrix with charge transfer salts additive [reticulate-doped polymers (RDPs)] [1-8] or addition of the electron acceptor such as TCNQ to the polymers having electron donor groups [9-11]. Here, we report a novel approach to produce polymeric electron acceptors by "TCNQ as a monomer" method, together with the formation of polymeric charge transfer complex.

We have recently developed a new method for the polymerization of dicyano compounds by hydroboration polymerization to give the air-moisture stable poly(cyclodiborazane)s in excellent yields [12-16] (Scheme I). In this polymerization system, electron accepting property of cyano group would be retained to some extent even after polymerization.

Scheme I



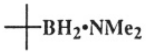
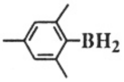
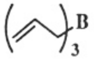
---

[*] Corresponding author

Results and Discussion

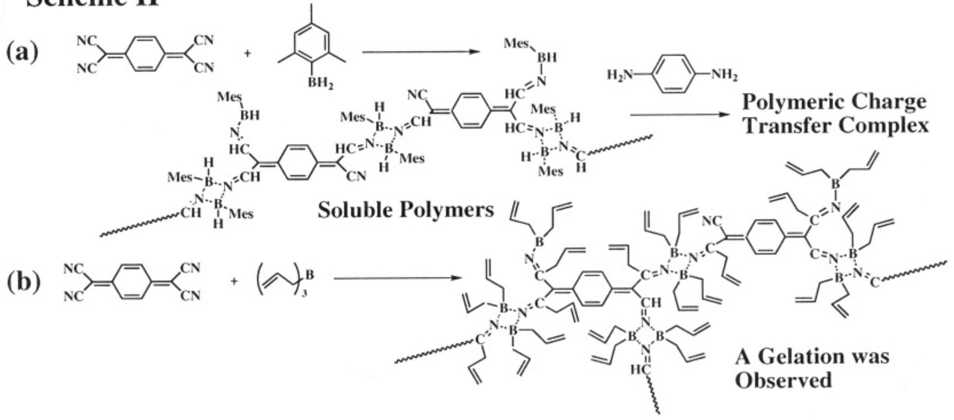
The results of boration polymerization of TCNQ with various boron monomers are summarized in Table I. The hydroboration polymerization of TCNQ using mesitylborane was first examined [Scheme II a)]. The reaction was carried out by adding a 1.0 M THF solution of mesitylborane to a suspension of TCNQ in THF under nitrogen at room temperature [feed ratio (mmol); $MesBH_2$/TCNQ = 2.56]. During the addition of mesitylborane, the heterogeneous reaction mixture became gradually homogeneous orange solution. After stirring for 12h and evaporation of the solvent, the obtained orange gum was purified by reprecipitation into H2O/MeOH = 1/1 (v/v) (yield 66%). Gel permeation chromatographic analysis (THF as an eluent, polystyrene standards) showed ***Mn*** of the oligomer was 1500 (***Mw***/***Mn*** = 1.4). The hydroboration polymerization of TCNQ using *tert*-butylborane-amine complex was also examined. However, no polymerization took place probably due to the complexation of the two monomers. We also tried an allylboration polymerization using triallylborane, but in this case a gelation was observed. This result can be elucidated as follows. In the polymerization using mesitylborane, formation of two cyclodiborazanes in one side of TCNQ might be difficult due to the steric hindrance of bulky mesityl group. However, when triallylborane [Scheme II b)] was employed, steric hindrance might not be so large as to disturb the crosslinking.

Table I. Boration Polymerization of TCNQ with Various Borane Reagents [a)]

run	Borane Reagents	Borane / TCNQ	*Mw* [b)]	*Mn* [b)]	*Mw/Mn* [b)]	yield (%) [c)]
1		3.67	No Polymerization			
2		2.56	2100	1500	1.4	66
3		3.36	7700	2200	3.5	- [d)]
4	$PhBCl_2$	2.89	No Polymerization			
5	BBr_3	2.47	No Polymerization			

a) Reactions were carried out in diglyme at 100°C (run 1) in THF at r.t. (runs 2-3) in dichloromethane at 0°C~r.t. (run 4) -78°C~r.t. (run 5) b) GPC (THF), polystyrene standards.
c) Isolated yields after reprecipitation into H_2O/MeOH = 1/1(v/v)
d) Gelation was also observed.

Scheme II



To obtain higher molecular weight polymers, hydroboration copolymerization among TCNQ, adiponitrile and mesitylborane was carried out in various feed ratios of monomers. When [Mesitylborane/(Adiponitrile+TCNQ) = x] was changed in a fixed feed ratio of cyano compounds (Adiponitrile/TCNQ = y = 7.7), a slightly excess amount of mesitylborane was required to produce relatively high molecular weight polymers (***Mn*** was 4900 when x = 2.69).

Incorporation of the TCNQ unit was comfirmed by UV-vis spectra (in $CHCl_3$ at r.t.) (Figure 1). The UV spectrum of the copolymer prepared in the feed ratio of x = 2.06 and y = 7.7 (***Mn*** = 1700) had its λ_{max} at 327 nm, although it is relatively blue-shifted in comparison with that of actual TCNQ (λ_{max} = 390 nm). When the feed ratio of mesitylborane increased (x = 2.69, ***Mn*** = 4900), further blue-shift was observed (λ_{max} = 318 nm) possibly due to hydroboration of cyano groups in side-chain to form monomeric iminoborane. In the ^{11}B-NMR spectra, relative intensity of the peak at 31 ppm [monomeric iminoborane; compared with one at 0.9 ppm (cyclodiborazane)] increased as x increased.

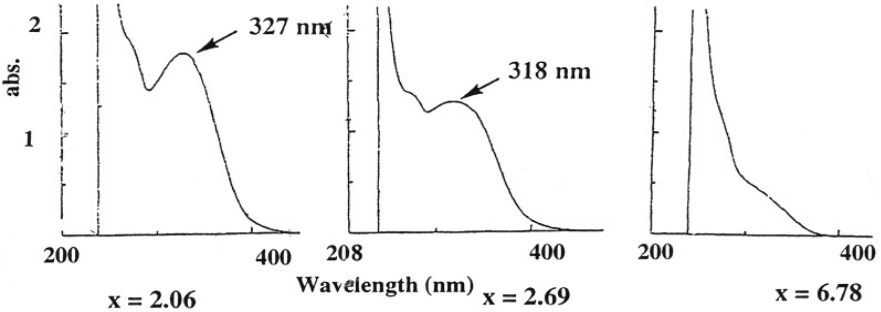
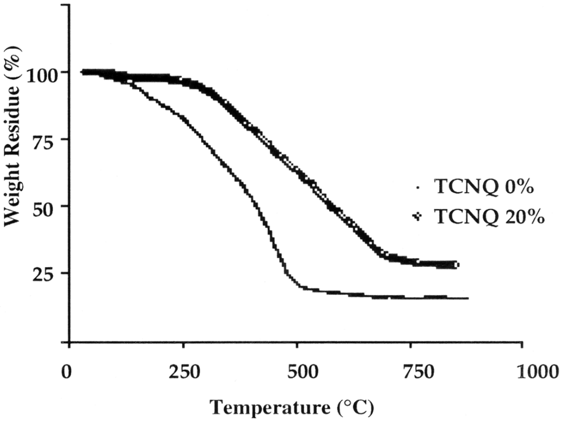


Figure 1. UV spectra of TCNQ copolymers prepared in various feed ratios of monomers.

Air stability of the copolymer was checked by air-bubbling experiment in a THF solution. The change of ***Mw*** was traced by GPC measurement, however, no significant decomposition was observed after the air-bubbling for 12h.

Thermogravimetric analysis (TGA, 10°C/min) was recorded for each copolymer [feed ratio of monomers; x = 2.42 and y = 4.33, ***M n*** = 2700] and poly-(cyclodiborazane) produced from adiponitrile. The results of the measurement under nitrogen are represented in Figure 2. The weight loss curve of the copolymer was shifted to higher temperature region, which showed fairly higher stability of the copolymer. The temperature at which 10% weight loss was observed was 328°C in the case of TCNQ copolymer, while it was 184°C in homopolymer. This difference might be attributed to π-π stacking of TCNQ unit in the copolymer which would retard oxidative degradation.

Figure 2.TGA traces of poly (cyclodiborazane) prepared from adiponitrile and TCNQ copolymer under nitrogen.



The charge transfer complexation ability of TCNQ copolymer [feed ratio of monomers; x = 2.42 and y = 4.33, ***Mn*** = 2700] was studied by treatment with an excess amount of p-phenylenediamine in diglyme solution. The complexation was monitored by UV-vis spectra (Figure 3; the measurements were carried out in $CHCl_3$ at r.t., after treatment with p-phenylenediamine). At 80°C, the charge transfer band appeared at 380 nm in addition to the peak at 320 nm corresponding to non-complex TCNQ units. As raising the temperature, the relative intensity of the peak at 320 nm decreased. On the other hand, that of the peak at 380 nm increased dramatically to form strong charge transfer band. These results show the majority of the TCNQ units had formed charge transfer complex at 140°C. However, no complexation between the copolymer and TTF has been observed so far. This also indicates that the structure of TCNQ unit is fairly modified compared with TCNQ itself.

When TCNQ is used in hydroboration polymerization, the hydroboration of the remained cyano groups degraded the ability of TCNQ unit as electron acceptor, as shown in blue-shifted UV spectrum absorbance in the presence of excess boron monomer. To overcome this problem and to synthesize polymer electron acceptor with definite structure, boration polymerization of bifunctional electron acceptor, p-tetrafluorodicyanobenzene was examined (Table II). First, hydroboration polymerization with mesitylborane was carried out (run 2, Scheme III). To p-tetrafluorodicyanobenzene suspended in THF, THF solution of mesitylborane was added at room temperature. After the addition, the reaction mixture became homogeneous. The reaction mixture was directly subjected to GPC measurement and ***Mn*** of the polymer was 4700. Hydroboration polymerization with *tert*-butylborane amine complex was also performed in diglyme at 100°C (run 1). The GPC measurement showed ***Mn*** of the obtained polymer was 2000, however, purification by reprecipitation was unsuccessful probably due to complexation of amine with the resulting polymer. Allylboration polymerization with triallylborane also gave the corresponding polymer (run 3). But in this case, the yield of the obtained polymer was much lower than that in run 2. This might be due to high viscosity of the reaction mixture in the bulk reaction system.

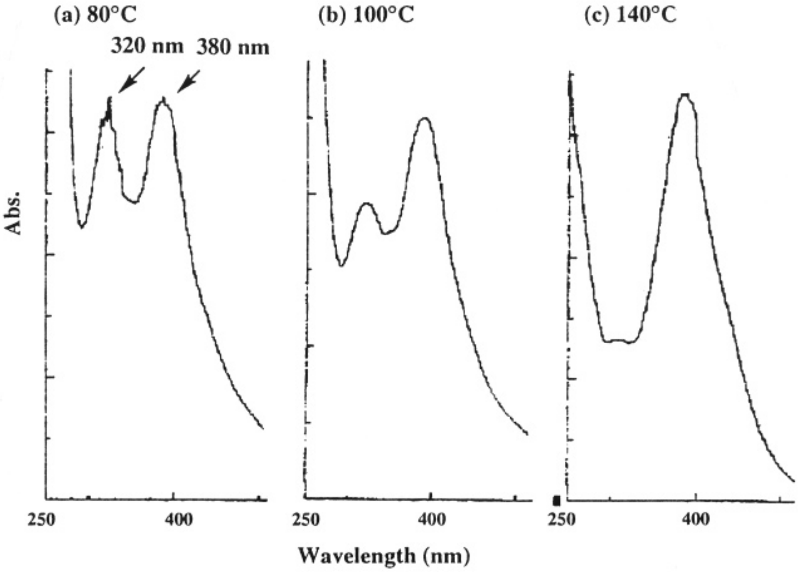
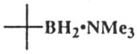
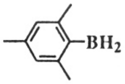
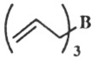
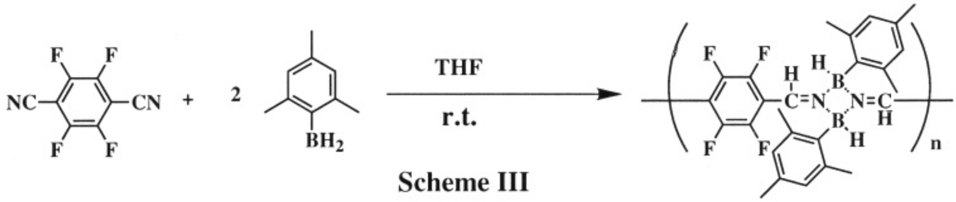


Figure 3. UV spectra of polymeric complexes prepared by the treatment of TCNQ copolymer with p-phenylenediamine.

Table II. Boration Polymerization of p-Tetrafluoroterephthalonitrile with Various Borane Reagents [a)]

run	Borane Reagents	Borane / CN	*Mw* [b)]	*Mn* [b)]	*Mw/Mn* [b)]	yield (%) [c)]
1		2.62	3500	2000	1.7	- [d)]
2		2.31	10200	4700	2.2	90
3		2.56	7000	3800	1.9	19

a) Reactions were carried out in diglyme at 100°C (run 1) in THF at r.t. (run 2) in bulk at r.t. (run 3)
b) GPC (THF), polystyrene standards. c) Isolated yields after reprecipitation into H_2O/MeOH = 1/1(v/v) d) Amine could not be eliminated.

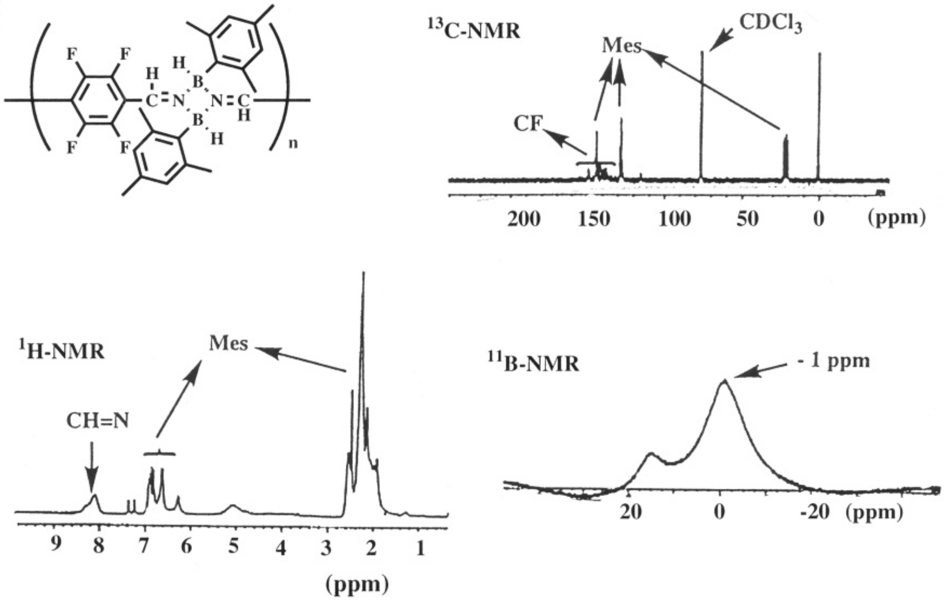

Scheme III

^{1}H-, ^{13}C- and ^{11}B-NMR spectra of the polymer prepared in run 2 are shown in Figure 4. These spectra were in good agreement with the expected structures.

Air stability of the polymer prepared from p-tetrafluorodicyanobenzene and mesitylborane was examined. Air bubbling was performed in THF solution of polymer and the degradation was followed by the GPC measurement. Stability of the polymer toward water was also investigated. The GPC curve of the polymer after air-bubbling was almost identical to that of the starting polymer, which shows the polymer has high air stability. However, GPC curve of the polymer after the treatment with water was significantly shifted to lower molecular weight region. This indicates the polymer obtained here was not completely stable toward hydrolysis. The relative instability of the obtained polymer is attributable to electron-withdrawing effect of fluoro groups that might weaken the coordination of nitrogen to boron atom.

Hydroboration polymerization between mesitylborane and various tetrafluorodicyanobenzene was performed. Although m- or o-tetrafluorodicyanobenzene has better solubility in comparison with p-tetrafluorodicyanobenzene, the molecular weight of the polymer prepared from m-tetrafluorodicyanobenzene was relatively lower (***Mn*** 2000) and no polymerization was observed when o-tetrafluorodicyanobenzene was employed. This is probably because of steric hindrance between cyclodiborazane units in the case of o- and m- monomers.

Figure 4. ^{1}H-,^{13}C and ^{11}B-NMR spectra of the polymer prepared from p-tetrafluorodicyanobenzene and mesitylborane.



The complexation ability of the polymer prepared from tetrafluorodicyanobenzene with p-phenylenediamine was investigated. To a diglyme solution of the polymer, p-phenylenediamine was added and complexation was examined. When complexation was examined at 60°C, the corresponding polymer complex was readily produced (λ_{max}=382, Figure 5). The complexation of the polymer prepared from m-tetrafluorodicyanobenzene was also examined. However, the polymer did not show obvious complexation, although shoulder peak was observed around 350 nm. This might be due to the difference in the structural symmetry of unit structures. The polymer prepared by allylboration polymerization of p-tetrafluorodicyanobenzene was also treated with p-phenylenediamine in diglyme at 100°C. In the UV spectrum, a CT band was observed at 383 nm. This shows not only hydroboration polymerization but also allylboration polymerization is available for the preparation of polymer electron acceptor.

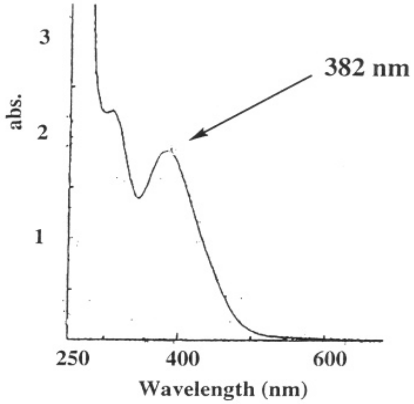


Figure 5. UV spectrum of the polymer prepared from p-tetrafluorodicyanobenzene and mesitylborane doped with p-phenylenediamine at 60°C in diglyme.

In conclusion, a novel type of polymeric electron acceptors was prepared by hydroboration copolymerization using *TCNQ as a monomer* or hydroboration polymerization of tetrafluorodicyanobenzene. The polymers obtained here were soluble in common organic solvents such as THF, dichloromethane and chloroform. They were also found to form charge transfer complexes with p-phenylenediamine. Further investigation for conductivity or photoconductivity of these polymers is now under study.

Experimental Section

Materials and Instruments Tetrahydrofuran was dried over sodium and distilled before use. Commercially available tetracyanoquinodimethane, tetrafluorodicyanobenzene and p-phenylenediamine were used without further purification. Mesitylborane was prepared by a modified procedure [17] of the reported method [18]. Commercially available adiponitrile was distilled.

^{1}H-, ^{13}C- 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 $G3000_{XI}$ by using THF as an eluent after calibration with standard polystyrene samples. Thermogravimetric analysis (TGA) was made on a Shimadzu DT-30 instrument (10°C/min). UV-vis spectra were recorded on a JASCO V-530 spectrophotometer. DSC measurement was carried out on a Seiko DCS 200 instrument.

Hydroboration Copolymerization between TCNQ and Adiponitrile by Using Mesitylborane A typical procedure is as follows. To TCNQ (12.8 mg, 0.0627 mmol) and adiponitrile (52.2 mg, 0.483 mmol) suspended in THF (2 ml), THF solution (1 ml) of mesitylborane (195.5 mg, 1.48 mmol) was added dropwise under nitrogen at room temperature. When the addition was completed, the reaction mixture became homogeneous. After stirring for 24h, the reaction mixture was directly subjected to GPC measurement. Evaporation of the solvent gave an orange gum, which was further purified by reprecipitation from THF into $MeOH/H_2O$= 1/1 (v/v) to give an orange powder (135.5 mg). ^{11}B-NMR (δ, ppm) 0.9 (cyclodiborazane), 31 (monomeric iminoborane). UV (Vis) (nm) 318 (originated from TCNQ).

Hydroboration Polymerization of p-Tetrafluorodicyanobenzene by Using Mesitylborane To p-tetrafluorodicyanobenzene (94.5 mg, 0.472 mmol) suspended in THF (2 ml), THF solution (1 ml) of mesitylborane (143.7 mg, 1.09 mmol) was added dropwise at room temperature. After the addition was completed, the reaction mixture became homogeneous. After stirring for 24h, the reaction mixture was directly subjected to GPC measurement. Evaporation of the solvent gave a yellow gum. Further purification by reprecipitation from THF into $MeOH/H_2O$=1/1 (v/v) gave an orange powder (196.7 mg). Yield 90%. ^{1}H-NMR (δ, ppm) 2.30 (18H, CH_3), 6.64-6.93 (4H, Ar-H), 8.11 (2H, CH=N). ^{13}C-NMR (δ, ppm) 23 (CH_3), 128, 143 [benzene ring (mesityl)], 137-142 (C-F), 149 (C=N). ^{11}B-NMR (δ, ppm) -1 (cyclodiborazane).

Allylboration Polymerization of p-Tetrafluorodicyanobenzene by Using Triallylborane To bulk p-tetrafluorodicyanobenzene (80.2 mg, 0.401 mmol), triallylborane (137.7 mg, 1.03 mmol) was added under nitrogen at 0°C. The reaction mixture was gradually warmed up to room temperature. After stirring for 24h, the reaction mixture was dissolved in THF and subjected to GPC measurement. Evaporation of the solvent gave a yellow gum. Further purification was carried out by reprecipitation from THF into $MeOH/H_2O$=1/1 (v/v). The resulting polymer was obtained as an orange powder (36.2 mg). Yield 19%. ^{1}H-NMR (δ, ppm) 1.35-1.86 ($B-CH_2-C=C$), 3.41 ($N=C-CH_2-C=C$), 4.82-5.94 ($-CH=CH_2$).

Formation of Polymer Charge Transfer Complex Complexation ability of organoboron polymers was examined as follows. About 10 mg of organoboron polymer was dissolved in diglyme and an excess amount of p-phenylenediamine (about 5 mg) was added to the solution and the reaction mixture was stirred at designated temperature. Complexation was monitored by UV-vis measurement.

Stability of Polymers under Air The air stability of organoboron polymers toward air oxidation was examined by monitoring the change of the molecular weights by GPC curve during an oxidation experiment, in which a stream of air was bubbled into a THF solution of organoboron polymers. After the designated time, the resulting polymer was characterized by GPC measurement.

References

1 Jeszka J K, Ulanski J, Kryszewski M (1981) Nature 289:390
2 Watanabe M, Kamiya T, Goto K, Matsubara N, Tsuchikura A, Shinohara I (1981) Makromol. Chem. 182:2659
3 Kryszewski M, Jeszka J K, Ulanski J, Tracz A (1984) Pure&Appl. Chem 56(3):355
4 Pecherz J, Kryszewski M (1989) Makromol. Chem 190:865
5 Jeszka J K, Tracz A, Kryszewski M, Ulanski J, Kobayashi T, Yamamoto N (1990) Synth Met 35: 215
6 Pechers J, Firlej L, Jeszka J K, Ulanski J, Kryszewski M (1990) Synth Met 37:189
7 Tracz A, Jeszka J K (1991) Synth Met 41-43: 1831
8 Ulanski J (1991), Synth Met 41-43:923
9 Hallensleben M L (1971) Eur Polym J 7:1197
10 Lupinski J H, Kopple K D, Hertz J J (1967) J Polym Sci (C) 16:1561
11 Nugay N, Kücükyavuz Z, Kücükyavuz S (1993) Polymer 34 (22):4649
12 Chujo Y, Tomita I, Murata N, Mauermann H, Saegusa T (1992) Macromolecules 25:27
13 Chujo Y, Tomita I, Saegusa T (1993) Polym Bull 31:553
14 Chujo Y, Tomita I, Saegusa T (1993) Polym Bull 31:547
15 Chujo Y, Tomita I, Saegusa T (1994) Macromolecules 27:6714
16 Matsumi N, Naka K, Chujo Y (1998), Polym. J in press
17 Matsumi N, Chujo Y (1997) Polym Bull 38:531
18 Smith K, Pelter A, Jin Z (1994) Angew Chem Int Ed Engl 33:851