



Short communication

Synthesis of supramolecular solid polymer electrolytes via self-assembly of diborylated ionic liquid

Noriyoshi Matsumi*, Akihito Kagata, Keigo Aoi

Graduate School of Bioagricultural Sciences, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan

ARTICLE INFO

Article history:

Received 29 September 2009

Received in revised form

11 November 2009

Accepted 11 November 2009

Available online 18 November 2009

Keywords:

Solid polymer electrolytes

Organoboron polymers

Self-assembly, lithium ion conductors

Coordination polymers

ABSTRACT

Novel supramolecular type solid polymer electrolytes were prepared by self-assembly of diborylated ionic liquid in the presence of bifunctional ligands. The polymers obtained were well soluble in methanol, and their structures were supported by ^1H and ^{11}B NMR spectra. The ionic conductivity of the polymers was evaluated by ac-impedance method after the samples were dried thoroughly. The ionic conductivity observed was 8.8×10^{-6} to $5.4 \times 10^{-6} \text{ S cm}^{-1}$ at 51°C in the presence of equimolar amount of LiTFSA to ionic liquid unit. The temperature dependence of ionic conductivity was successfully fitted to VFT (Vogel–Fulcher–Tamman) plots, indicating that ionic conduction is taking place according to typical ion transport model in viscous matrix.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

After ionic liquids [1] emerged as a novel class of electrolytes, polymer homologues of ionic liquids [2] have also been vigorously studied as solid polymer electrolytes, microwave absorption materials and so forth. Since ionic liquids generally show unique characteristics such as non-volatility, non-flammability and high ionic conductivity, preparation of polymer homologue of ionic liquids is also a promising approach to design novel class of polymer materials possessing such properties. Particularly, in the field of ionic devices such as lithium ion secondary batteries and fuel cells, there has been growing interest toward polymerized ionic liquids because non-flammable property of ionic liquids is desirable to improve the safety problems of battery devices.

As a typical approach for solidification of ionic liquids, Ohno et al. first reported radical polymerization of vinylimidazolium type ionic liquids [2a]. Although ionic conductivity of the resulting polymer electrolytes decreased after polymerization, the polymerized ionic liquids still showed ionic conductivity of over $10^{-6} \text{ S cm}^{-1}$ at ambient temperature. It was also shown that design of comb like polymer electrolytes having spacer units between main chain and ionic liquid unit [2b] shows significantly improved ionic conductivity. As extension of these methodologies, variety of polymer electrolytes such as polycation type electrolytes, polyanion type electrolytes, cation/anion mixed polymer electrolytes have been

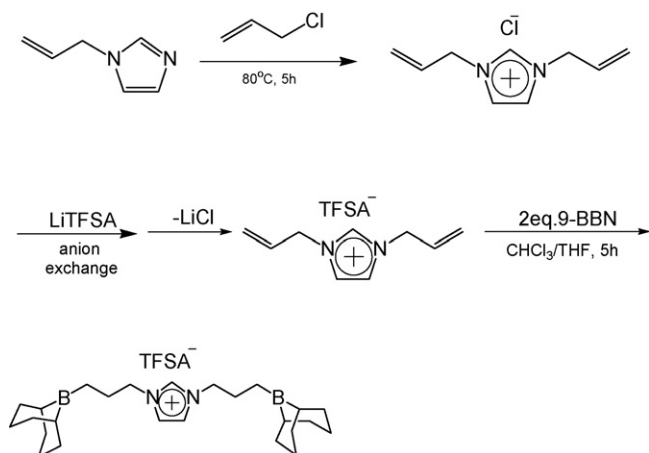
successfully developed so far. At the same time, one of the problems in these radical polymerization method is the difficulty in controlling of nano-structure of ionic conduction path. One approach to regulate the nano-structure of ion conductive path has been incorporation of liquid crystalline structures into ion conductive matrix. Kato and Ohno et al. reported that dimensional control of ion conductive path constituted by Smectic A phase resulted in significantly enhanced ionic conductivity [3].

In the present study, another possible approach for the control of nano-structure of ion conductive path was undertaken by self-assembly process of ionic liquid monomer.

A number of coordination polymer [4] matrix via self-assembly between various metals and ligands are known so far. Such materials having completely regulated nano-structure has been earnestly studied for the application of gas separation or gas storage. The utilization of self-assembly process for the design of polymer electrolytes might lead to precise control of distance between ion hopping sites and pore size of nano-structure.

Recently, liquid imidazole-borane complexes [5] were found to show low melting point, high polarity, low viscosity and moderate ionic conductivity. Therefore, construction of boron–nitrogen based framework via self-assembly process is an attractive approach to design matrices that are well-regulated and moderately conductive at the same time. These days, increasing number of papers have been published on functional organoboron polymers such as π -conjugated polymers [6], polymer electrolytes [7], ceramics precursors [8] and so forth. The boron containing coordination polymers can also be one such material that are moderately stable to allow versatile applications. Jäkle et al. recently

* Corresponding author. Tel.: +81 52 789 4138; fax: +81 52 789 4141.
E-mail address: matsumi@agr.nagoya-u.ac.jp (N. Matsumi).



Scheme 1.

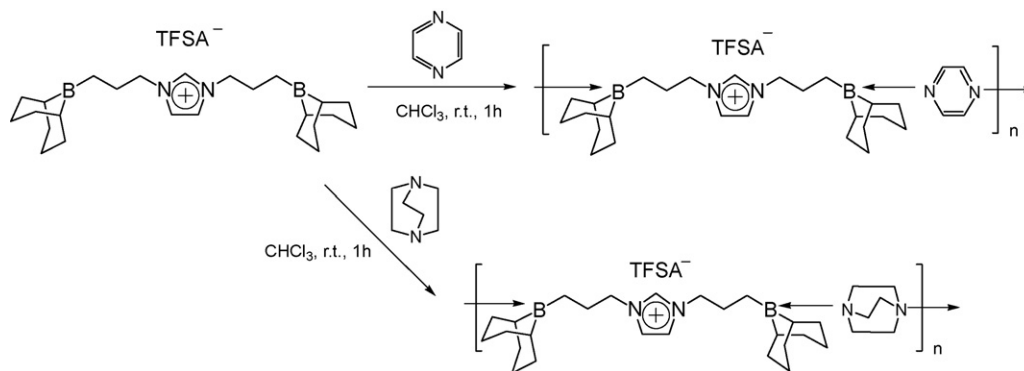
reported an organoboron coordination polymer via self-assembly of boron-terminated polystyrene that were finely designed via ATRP method [9]. In the present work, self-assembly was examined for diborylated ionic liquid which was prepared by hydroboration of diallylimidazolium type ionic liquids (Scheme 1). The ion conductive properties of the resulting solid polymer electrolytes were investigated in detail.

2. Results and discussions

The organoboron coordination polymer electrolytes were prepared according to Scheme 2. Diborylated ionic liquid was prepared by hydroboration of 1,3-diallylimidazolium TFSA (TF_2N) with

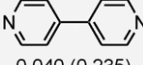
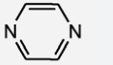
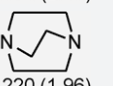
2 equiv. of 9-BBN (9-bora [2.2.1] bicyclononane) in $\text{CHCl}_3/\text{THF} = 1/5$ (v/v) at 0°C (Scheme 1). From ^1H NMR spectrum, complete conversion of allyl group was implied. The self-assembly of diborylated ionic liquid was examined by adding equimolar amount of bifunctional ligands to chloroform solution of diborylated ionic liquid (Scheme 2). After the reaction mixtures were stirred for 1 h at r.t., evaporation of the solvent gave crude solids, which were washed with diethyl ether to give the desired coordination polymers in moderate yields. The results of the self-assembly reactions are listed in Table 1. When 4,4'-bipyridyl was employed as bifunctional ligand, coordination polymer was not obtained possibly because of low solubility of resulting oligomer. On the other hand, the polymerization using pyrazine or 1,4-diazabicyclo[2.2.2]octane resulted in satisfactory solidification of the resulting matrices. The polymers obtained were soluble in methanol, and the structures of the polymers were supported by ^1H and ^{11}B NMR spectra measured in CD_3OD . In the ^1H NMR spectrum of the polymer prepared using 1,4-diazabicyclo[2.2.2]octane (polymer 1), the peak due to 1,4-diazabicyclo[2.2.2]octane was observed at 3.0 ppm in addition to the peaks due to diborylated ionic liquid. The ^{11}B NMR spectrum (Fig. 1) showed the main peak at 12.2 ppm, suggesting that borane was coordinated with the nitrogen atom. A small peak around 0.26 ppm can be ascribed for terminal group of the polymer.

The ionic conductivity of the polymers was evaluated by impedance method after the addition of lithium salts. In the presence of LiTFSA equimolar to ionic liquid unit, the polymer bearing pyrazine unit (polymer 2) showed ionic conductivity of $8.8 \times 10^{-6} \text{ Scm}^{-1}$ at 51°C , which was slightly higher than that of polymer bearing 1,4-diazabicyclo[2.2.2]octane unit (polymer 1) [Fig. 2(i)]. When lithium salt additive was LiCF_3SO_3 , the ionic conductivity of polymer 2 decreased by two orders of magnitude [Fig. 2(ii)]. Moreover, ionic conductivity of polymer 1 was unmeasurable because of too low ionic conductivity. Dependence of salt



Scheme 2.

Table 1
Synthesis of organoboron coordination polymers.^a

Entry	Diborylated IL, g (mmol)	Ligand, g (mmol)	CHCl_3 , ml	Temp., $^\circ\text{C}$	Yield, ^b g (%)
1	0.172 (0.235)	 0.040 (0.235)	10	r.t.	– ^c
2	1.46 (2.17)	 0.174 (2.17)	10	r.t.	0.883 (54)
3	1.32 (1.96)	 0.220 (1.96)	10	r.t.	0.917 (60)

^a The reactions were carried out under nitrogen atmosphere for 1 h.

^b Isolated yields after washing with diethyl ether.

^c Not determined.

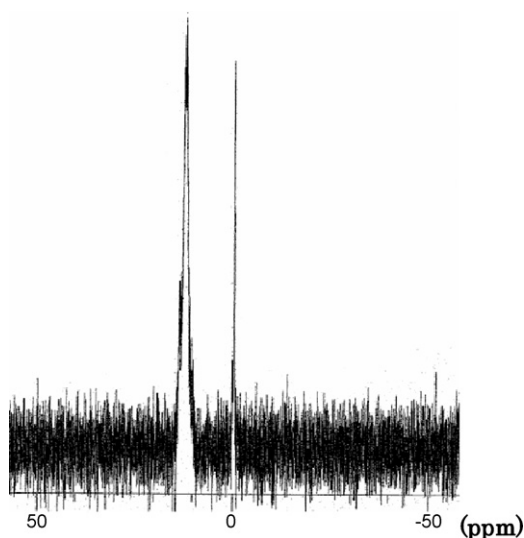


Fig. 1. ^{11}B NMR spectrum of polymer 1 measured in CD_3OD .

concentration on ionic conductivity was also studied as shown in Fig. 2(iii) and (iv). In both polymers, higher ionic conductivity was observed for systems where ligand:LiTFSA = 1:1 in comparison with systems where ligand:LiTFSA = 2:1.

In order to obtain further information on ionic conduction, the temperature dependence of ionic conductivity was fitted to Vogel–Fulcher–Tamman (VFT) plots [10] (Fig. 3). All the Arrhenius plots were successfully converted to VFT plots, implying that ionic conduction in these systems follows typical ion conductive mechanism in viscous solution. Since, Arrhenius plots are also well fitted in the present systems, it should be noted that there is limitation to discuss the subject of VFT vs. Arrhenius behavior under the

Table 2

VFT parameters for organoboron coordination polymers in the presence of LiTFSA.

Sample	A ($\text{S cm}^{-1} \text{K}^{1/2}$)	B (K)	T_0 (K)	R^2
●	3.88	1427	183	0.9997
○	38101	3451	150	0.9993
△	736747	4024	150	0.9991

observed temperature range. From the VFT parameters (Table 2), the parameters corresponding to activation energy (B) was higher for polymer 1 than that was observed for polymer 2. This might be due to relatively weaker coordination of pyrazine in which electrical communication between two neighboring nitrogen atoms might retard the efficient electron donation to the boron atom. The lower carrier ion number (A) for 2 can also be explained by considering the weaker electron donation of nitrogen atoms in 2, which would lower the polarity of the matrices. As for dependence of salt concentration on VFT parameters, lower concentration of LiTFSA led to significantly higher activation energy of matrices. This should be due to the plasticizing effect of LiTFSA. Under high concentration of LiTFSA, strong electrostatic interactions restricted further dissociation of LiTFSA. Lower concentration of LiTFSA led to increased number of separated ion pair, which resulted in larger value of parameter A corresponding to carrier ion number. However, plasticizing effect of LiTFSA was predominant factor that governs the ionic conductivity.

In conclusion, novel supramolecular type solid polymer electrolytes were prepared via self-assembly of diborylated ionic liquids. The structures of the polymers were confirmed from ^1H and ^{11}B NMR spectra. In the presence of lithium salts, the obtained solid polymer matrices showed ionic conductivity of 8.8×10^{-6} to $5.4 \times 10^{-6} \text{ S cm}^{-1}$. Although the coordination polymers reported herein are one-dimensional systems, further design for three-dimensional control of structure is also currently underway.

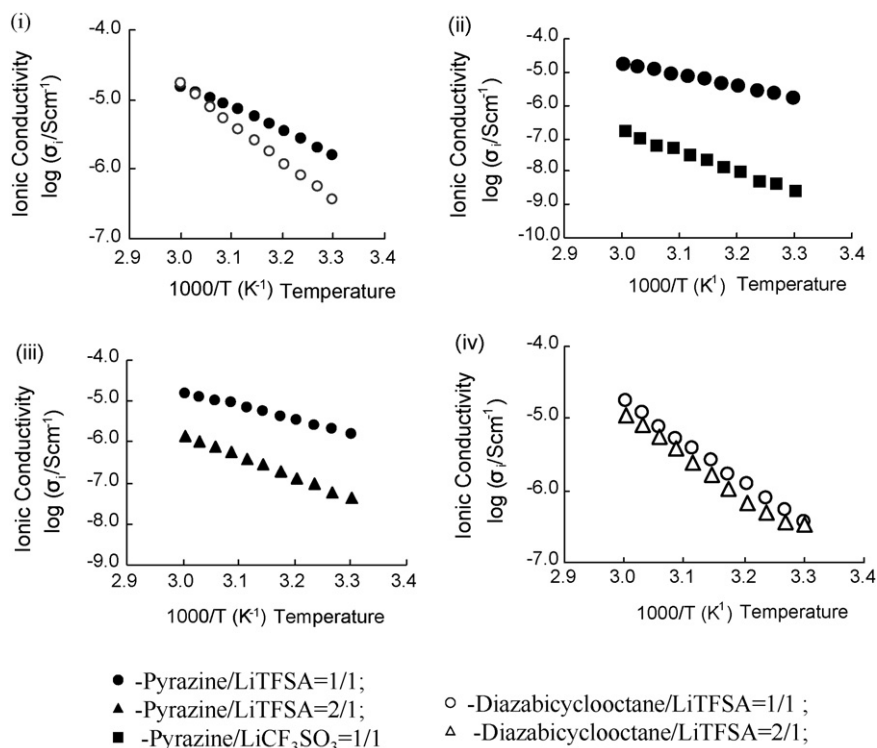


Fig. 2. Temperature dependence of ionic conductivity for organoboron coordination polymers in the presence of various lithium salts.

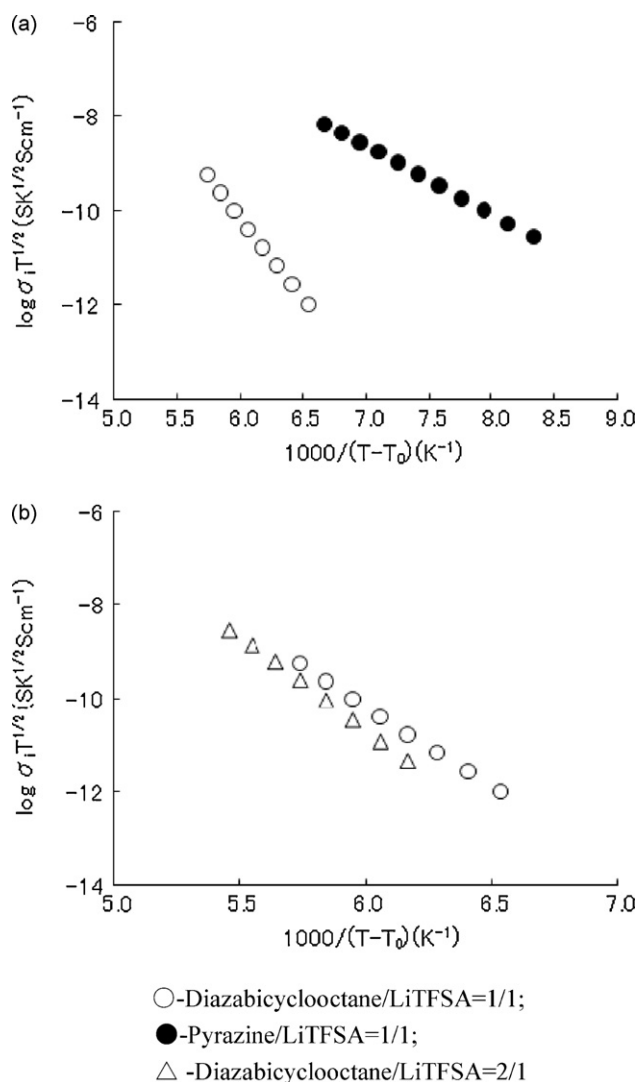


Fig. 3. VFT plots for organoboron coordination polymers in the presence of various lithium salts.

3. Experimental

3.1. Materials and instruments

1,3-Diallylimidazolium TFSA was prepared according to reported method [11]. 9-Borabicyclo[3.3.1]nonane (0.5 M in THF) was purchased from Aldrich Co. Ltd. and used as received. LiTFSA and LiTf were purchased from TCI Co. Ltd. and Kishida Co. Ltd., respectively, and used without further purification. Pyrazine and 1,4-diazabicyclo[2.2.2]octane purchased from Wako Co. Ltd. were used as received. Tetrahydrofuran, diethyl ether and n-hexane were dried over sodium and distilled before use. All the reactions were carried out under inert atmosphere. 1H and ^{11}B NMR spectra were recorded on Bruker ARX-400 or JEOL-A400 Win Alpha FT-NMR system. Ionic conductivity of the coordination polymers was measured by ac-impedance method using Solartron 1260.

3.2. Synthesis of diborylated ionic liquid

Under nitrogen atmosphere, 15 ml of 0.5 M 9-borabicyclo[3.3.1]nonane in THF was added to chloroform solution (3 ml) of 1,3-diallylimidazolium TFSA (0.840 g, 1.97 mmol) at $0^\circ C$, and the resulting solution was stirred for 5 h. After the solvents were

removed under reduced pressure, the crude compound was washed with n-hexane to remove excess 9-borabicyclo[3.3.1]nonane. The desired compound was highly viscous yellowish liquid (1.31 g, 1.95 mmol, 99% yield).

1H NMR (CD_3OD , δ , ppm) 0.8–2.0 (36H, 9-BBN, CH_2CH_2B), 4.90 (4H, NCH_2CH_2), 7.58 (2H, $NCH=CHN$), 8.92 (1H, $NCHN$).

3.3. Synthesis of polymer 1

Under nitrogen atmosphere, 0.220 g (1.96 mmol) of 1,4-diazabicyclo[2.2.2]octane was dissolved in 10 ml of chloroform. The resulting solution was added to 1.32 g (2.17 mmol) of diborylated ionic liquid, and the reaction mixture was stirred for 1 h. After solvents were removed under reduced pressure, the crude polymer was washed with diethyl ether. The desired polymer was obtained as a white solid (0.917 g, 1.17 mmol, 60% yield).

1H NMR (CD_3OD , δ , ppm) 0.8–2.0 (36H, 9-BBN, BCH_2CH_2), 3.00 (12H, 1,4-diazabicyclooctane), 4.21 (4H, NCH_2CH_2), 7.62 (2H, $NCH=CHN$).

^{11}B NMR (CD_3OD , δ , ppm) 0.26 (end group), 12.2 (main peak)

3.4. Synthesis of polymer 2

Under nitrogen atmosphere, 0.174 g (2.17 mmol) of pyrazine was dissolved in 10 ml of chloroform. The resulting solution was added to 1.46 g (2.17 mmol) of diborylated ionic liquid, and the reaction mixture was stirred for 1 h. After solvents were removed under reduced pressure, the crude polymer was washed with diethyl ether. The desired polymer was obtained as an orange solid (0.883 g, 1.17 mmol, 54% yield).

1H NMR (CD_3OD , δ , ppm) 0.8–2.0 (36H, 9-BBN, BCH_2CH_2), 4.18 (4H, NCH_2CH_2), 7.62 (2H, $NCH=CHN$), 8.64 (4H, pyrazine), 8.91 (1H, $NCHN$).

^{11}B NMR (CD_3OD , δ , ppm) 0.02 (end group), 12.5 (main peak).

Acknowledgements

The present study was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan (#20031013 and #19685018). We also thank financial assistance by New Energy and Industrial Technology Development Organization (NEDO; #09B33004a).

References

- [1] T. Welton, Chem. Rev. 99 (1999) 2071.
- [2] (a) H. Ohno, K. Ito, Chem. Lett. (1998) 751; (b) M. Yoshizawa, H. Ohno, Chem. Lett. (1999) 889; (c) M. Yoshizawa, H. Ohno, Electrochim. Acta 46 (2001) 1723; (d) J. Tang, M. Radosz, Y. Shen, Macromolecules 41 (2008) 493; (e) J. Tang, H. Tang, W. Sun, M. Radosz, J. Polym. Sci. Part A: Polym. Chem. 43 (2005) 5477; (f) H. Chen, Y.A. Elabd, Macromolecules 42 (2009) 3368.
- [3] (a) K. Hoshino, M. Yoshio, T. Mukai, H. Ohno, T. Kato, J. Polym. Sci. Part A: Polym. Chem. 41 (2003) 3486; (b) M. Yoshio, T. Mukai, K. Kanie, M. Yoshizawa, H. Ohno, T. Kato, Adv. Mater. 14 (2002) 351; (c) K. Kishimoto, M. Yoshio, T. Mukai, M. Yoshizawa, H. Ohno, T. Kato, J. Am. Chem. Soc. 125 (2003) 3196.
- [4] (a) D. Bradshaw, J.B. Claridge, E.J. Cussen, T.J. Prior, M.J. Rosseinsky, Acc. Chem. Res. 38 (2005) 273; (b) O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, Nature 423 (2003) 705; (c) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, Acc. Chem. Res. 38 (2005) 217; (d) S.J. Dalgarno, N.P. Power, J.L. Atwood, Coord. Chem. Rev. 252 (2008) 825; (e) M.P. Suh, Y.E. Cheon, E.Y. Lee, Coord. Chem. Rev. 252 (2008) 1007; (f) J.J. Perry IV, J.A. Perman, M.J. Zaworotko, Chem. Soc. Rev. 38 (2009) 1400; (g) M.J. Rosseinsky, Micropor. Mesopor. Mater. 73 (2004) 15; (h) G. Férey, Chem. Soc. Rev. 37 (2008) 191.
- [5] N. Matsumi, A. Mori, K. Sakamoto, H. Ohno, Chem. Commun. (2005) 4557.

- [6] (a) N. Matsumi, Y. Chujo, *Polym. J.* 40 (2008) 77;
(b) M. Elbing, G.C. Bazan, *Angew. Chem. Int. Ed. Engl.* 41 (2000) 2927;
(c) F. Jäkle, *Coord. Chem. Rev.* 250 (2006) 1107;
(d) C.D. Entwistle, T.B. Marder, *Angew. Chem. Int. Ed. Engl.* 41 (2000) 2927;
(e) C.D. Entwistle, T.B. Marder, *Chem. Mater.* 16 (2004) 4574;
(f) N. Matsumi, K. Naka, Y. Chujo, *J. Am. Chem. Soc.* 120 (1998) 5112;
(g) N. Matsumi, K. Naka, Y. Chujo, *J. Am. Chem. Soc.* 120 (1998) 10776;
(h) N. Matsumi, K. Naka, Y. Chujo, *Macromolecules* 31 (1998) 8047;
(i) N. Matsumi, T. Umeyama, Y. Chujo, *Macromolecules* 33 (2000) 3956.
- [7] (a) N. Matsumi, K. Sugai, H. Ohno, *Macromolecules* 35 (2002) 5731;
(b) N. Matsumi, K. Sugai, H. Ohno, *Macromolecules* 36 (2003) 2321;
(c) N. Matsumi, T. Mizumo, H. Ohno, *Polym. Bull.* 51 (2004) 389;
(d) N. Matsumi, M. Nakashiba, T. Mizumo, H. Ohno, *Macromolecules* 38 (2005) 2040;
(e) N. Matsumi, K. Sugai, K. Sakamoto, T. Mizumo, H. Ohno, *Macromolecules* 38 (2005) 4951;
(f) N. Matsumi, K. Sugai, M. Miyake, H. Ohno, *Macromolecules* 39 (2006) 6924.
- [8] D. Seyferth, R. Smith Jr., William, *Mater. Res. Soc. Symp. Proc.* 121 (1988) 449.
- [9] Y. Qin, F. Jäkle, *Macromolecules* 40 (2007) 1413.
- [10] (a) H. Vogel, *Phys. Z.* 22 (1921) 645;
(b) G.S. Fulcher, *J. Am. Ceram. Soc.* 8 (1925) 339;
(c) G. Tamman, W.Z. Hesse, *Anorg. Allg. Chem.* 156 (1926) 245.
- [11] T. Mizumo, E. Marwanta, N. Matsumi, H. Ohno, *Chem. Lett.* 33 (2004) 1360.