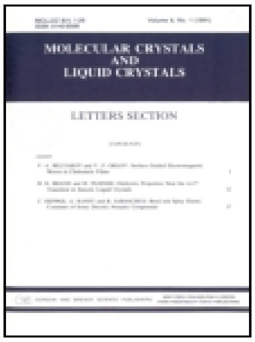


Taylor & Francis
Taylor & Francis Group

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Challenges for Unique Application of Ionic Liquids as a Novel Initiator of Radical Polymerization

Shuichi Kanno

To cite this article: Shuichi Kanno (2014) Challenges for Unique Application of Ionic Liquids as a Novel Initiator of Radical Polymerization, Molecular Crystals and Liquid Crystals, 603:1, 3-19, DOI: 10.1080/15421406.2014.966234

To link to this article: http://dx.doi.org/10.1080/15421406.2014.966234

Published online: 15 Dec 2014.

Submit your article to this journal

Article views: 22

View related articles

View Crossmark data

Full Terms & Conditions of access and use can be found at
http://www.tandfonline.com/action/journalInformation?journalCode=gmcl20

Download by: [University Town Library of Shenzhen] **Date:** 02 January 2016, At: 00:40

Mol. Cryst. Liq. Cryst., Vol. 603: pp. 3–19, 2014
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.966234

Downloaded by [University Town Library of Shenzhen] at 00:40 02 January 2016

Challenges for Unique Application of Ionic Liquids as a Novel Initiator of Radical Polymerization

SHUICHI KANNO*

Polymer Chemistry Laboratory, Tohoku Seikatsu Bunka University, Izumi-ku, Sendai-shi, Miyagi, Japan

In this study, the author has investigated the polymerization of styrene (St), methyl methacrylate, and methyl acrylate initiated with guanidinium-based ionic liquids such as guanidinium tris(pentafluoroethyl)trifluorophosphate ([gua]e3fap), guanidinium trifluoromethanesulfonate, N,N,N′N′-tetramethyl-N′′-ethylguanidinium tris(pentafluoroethyl)trifluorophosphate, and N,N,N′N′-tetramethyl-N′′-ethylguanidinium trifluoromethanesulfonate to elucidate the new possibility of ionic liquids as an initiator of radical polymerization. For example, the polymerization of St initiated with [gua]e3fap proceeded at 70°C under air and under argon. It was strongly suggested that the St-polymerization initiated with [gua]e3fap proceeds via a radical pathway, because the inhibitory effects of 2,6-di-tert-butyl-p-cresol and hydroquinone as a radical inhibitor and 1-dodecanethiol as a radical chain transfer agent were observed.

Keywords Ionic liquids; radical polymerization; initiator; methyl acrylate; methyl methacrylate; styrene

Introduction

Ionic liquids are low-melting-point salts with virtually no vapor pressure. In other words, they consist of cations and anions and, owing to the very strong ion-ion interactions, they exhibit high boiling points and low vapor pressures. About thirty years ago, research on ionic liquids was a relatively unknown backwater of chemistry. However, research in the field of ionic liquids has grown exponentially and ionic liquids became more familiar to a broad public in recent years. The major advantage with using ionic liquids is their ability to dissolve a wide range of organic and ionic compounds to an appreciable extent. In addition, their polarity, high thermal stability, and lack of volatility are also important features. These features of ionic liquids are the important driving force in quest for novel applications. In the beginning, research and development on ionic liquids concentrated mainly on electrochemical applications [1–4]. On the other hand, it is generally known that free radical polymerization processes are extremely important for manufacturing of polymers. The use of ionic liquids as solvents in polymerization reactions has been reported for free radical polymerization [5–7]. For example, some kinds of ionic liquids are expected as green solvents for free radical polymerization by virtue of their negligible vapor pressure, non-flammability, temperature stability, and chemical stability [8, 9]. However, to the author's

---

*Address correspondence to Shuichi Kanno, Polymer Chemistry Laboratory, Tohoku Seikatsu Bunka University, 18-2, Nijinooka 1-chome, Izumi-ku, Sendai-shi, Miyagi 981-8585, Japan. E-mail: skanno@mishima.ac.jp best knowledge, it must be mentioned that aspects of environmental and safety problems through the use of ionic liquids, namely, their disposal and their toxicity have not been enough explored yet. In the meantime, until now, the author reported an radical initiating ability of some kinds of ionic liquids. Although the polymerization mechanism initiated with ionic liquids is not clear, it was indicated that the appropriate selection of the polymerization solvent is very important for ionic liquids to reveal the radical initiating ability. Furthermore the author recognizes that there may be no research on the radical polymerization initiated with ionic liquid except for the author's investidations [10–14]. In other words, the use of ionic liquids as an initiator of radical polymerization has been still in its infancy. For example, the relationship between the radical initiating ability of ionic liquids and their molecular structure is still obscure. Additionally, interactions between the cations and the anions of ionic liquids may also influence the radical initiating ability. Hence, a lot of work is necessary to understand the initiating ability of ionic liquids on free radical polymerization process. In other words, the author believes that the author's investigations about the radical initiating ability of ionic liquids will significantly improve the general understanding of ionic liquids. On the other hand, a general advantage of ionic liquids is their systematic variation of ionic structure. And furthermore, the variability of the ionic liquid structure opens numerous possibilities of designing ionic liquids for additional advantages. In a word, the structure of ionic liquids can be varied infinitely by the combination of cations and anions, and in practice, the properties of ionic liquids can be tailor made for the appropriate demands of specific applications. Therefore, a systematic variation of the ionic liquid structure is an efficient approach to understand the initiating ability of ionic liquids on radical polymerization, and to make a useful selection of ionic liquids for these applications. In this work, in order to further understand the nature of the ionic liquid-initiated polymerization, the author discusses fundamental features of the polymerization of styrene (St), methyl methacrylate (MMA), and methyl acrylate (MA) initiated with guanidinium-based ionic liquids such as guanidinium tris(pentafluoroethyl)trifluorophosphate ([gua]e3fap), guanidinium trifluoromethanesulfonate ([gua]otf), *N,N,N′N′*-tetramethyl-*N″*-ethylguanidinium tris(pentafluoroethyl)trifluorophosphate ([ewtmg]e3fap), and *N,N,N′N′*-tetramethyl-*N″*-ethylguanidinium trifluoromethanesulfonate ([ewtmg]otf). The chemical structures of these guanidinium-based ionic liquids are shown schematically in Scheme 1.

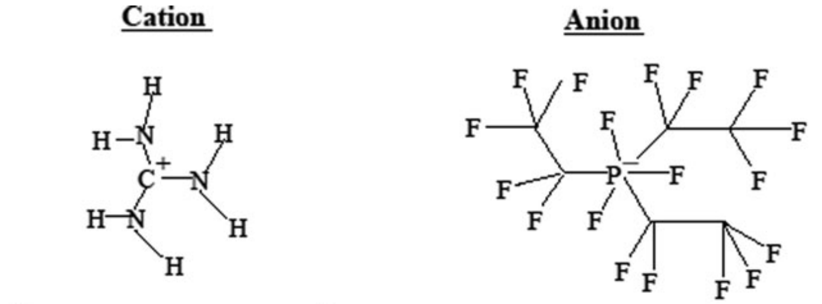
Experimental

Materials

Commercially available St, MMA, and MA (Wako Pure Chemical Industries, Ltd.) were purified by distillation according to conventional methods. These distilled vinyl monomers were bubbled with argon and stored in a freezer at −20°C. Tetrahydrofuran (THF), dioxane, toluene, benzene, *N,N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) used as polymerization media were ultra-pure grade for spectroscopic analysis (Kanto Chemical Co., Inc.), which were used without further purification. Only diglyme used as polymerization media from Wako Pure Chemical Industries, Ltd. was distilled by conventional method. [gua]e3fap, [gua]otf, [ewtmg]e3fap and [ewtmg]otf were supplied by Merk Ltd and used without further purification. 2,6-Di-*tert*-butyl-*p*-cresol (BHT) was purchased from Wako Pure Chemical Industries, Ltd. and purified by recrystallization using ethyl alcohol. Commercially obtained hydroquinone (HQ) (Wako Pure Chemical Industries, Ltd.) was recrystallized from distilled water. 1-Dodecanethiol (1-DT) was purchased from Wako Pure

Downloaded by [University Town Library of Shenzhen] at 00:40 02 January 2016

Downloaded by [University Town Library of Shenzhen] at 00:40 02 January 2016



① Guanidinium Cation ([gua]$^+$).

③ Tris(pentafluoroethyl)trifluorophosphate Aniion ([e3fap$^-$).

② N,N,N′N′-Tetramethyl-N″-ethylguanidinium Cation ([ewtmg]$^+$).

④ Trifluoromethanesulfonate Anion (otf$^-$).

Scheme 1. Combination of cation and anion of ionic liquids. ① + ③ Guanidinium Tris(pentafluoroethyl)trifluorophosphate ([gua]e3fap). ① + ④ Guanidinium Trifluoromethanesulfonate ([gua]otf). ② + ③ *N,N,N′N′*-Tetramethyl-*N″*-ethylguanidinium Tris(pentafluoroethyl)trifluorophosphate ([ewtmg]e3fap). ② + ④ *N,N,N′N′*-Tetramethyl-*N′′′′*-ethylguanidinium Trifluoromethanesulfonate ([ewtmg]otf).

Chemical Industries, Ltd., and was used as received. Research-grade quality argon (oxygen <0.2 ppm) was purchased from Toho Acetylene Co., Ltd. and used as received.

Polymerization

The polymerization was carried out in a brown glass tube. The tube was charged with vinyl monomer, ionic liquid and solvent, stoppered with a rubber septum. The polymerization was carried out after purging with research-grade argon for 10 minutes (250–350 ml/min) using two injection needles through the septum of the brown glass tube which was cooled in a Dewar vessel at 0°C. In order to compare the result, parallel experiment under the same condition was carried out under air. The tube was maintained at a constant temperature in a thermostatic water bath. At certain time intervals, the reaction mixture was poured into a large amount of miscible nonsolvent to precipitate the product polymer. The obtained polymer was washed by the nonsolvent and dried under vacuum at 50°C–80°C overnight. The conversion was determined gravimetrically.

Instrumentation

Gel-permeation chromatography (GPC) was used to measure molecular weights and molecular weight distributions, $\overline{Mw}/\overline{Mn}$, with respect to linear polystyrenes of known molecular weights and of narrow polydispersity factors (SHOWA DENKO K. K.). The GPC experiments were carried out at 40°C in THF using a SHIMADZU CLASS-VP GPC series high-speed liquid chromatography system with refractive index detector (flow rate: 0.8 mL/mim, column: TSK gel column, GMH_{HR}-N).

Results and Discussion

Polymerization of St, MMA, and MA Initiated with [gua]e3fap

The catalytic ability of ionic liquids for organic and bioorganic synthesis has long been revealed [15–19], but the initiating ability of ionic liquids for radical initiating ability has not been recognized until the author's paper presented unambiguous evidence [10–14]. On the other hand, from the commercial standpoint, vinyl polymers are the most important of all polymer types. Consequently, a lot more investigation has been accomplished in the field of vinyl polymerization than with most other polymerization types. For these reasons, further research in this field will focus on testing polymerizations of different vinyl monomers initiated with many kinds of ionic liquids. [gua]e3fap initiated the polymerization of St and poly(St) was obtained. The characterization data for the effect of solvents on the polymerization of St initiated with [gua]e3fap at 70°C under air and under argon are presented in Tables 1 and 2, respectively. As shown in these tables, the behavior of the St-polymerization initiated with [gua]e3fap under air resembles that under argon very closely. In other words, as the common behavior of the polymerization, the bulk polymerization and the solution polymerization in benzene, toluene and carbon tetrachloride proceeded smoothly, whereas the solution polymerization in diglyme, dioxane, DMF, DMSO and THF scarcely proceeded. From the results described later, it was suggested that the St-polymerization initiated with [gua]e3fap proceeds via radical mechanism. Consequently, the experimental results obtained here in which the solution polymerization proceeds in limited solvents and the polymerization proceeds similarly under air and under argon are important data to shed light on the mechanism of this novel radical polymerization. In addition, the most striking characteristic of this polymerization is that the molecular weights of obtained

Table 1. Effect of solvents on the polymerization of St initiated with [gua]e3fap[a]

Entry	Time (hr)	Solvent	Conversion (%)	Mn^c	Mw/Mn^c
1	4	(Nil)	59.4	7000	1.94
2	4	Benzene	56.0	4000	2.00
3	4	Toluene	58.7	2000	2.12
4	4	Diglyme	5.9	—	—
5	4	Dioxane	3.8	—	—
6	4	Carbon tetrachloride	51.7	3000	1.96
7	4	DMF	4.2	—	—
8	4	DMSO	2.4	—	—
9[b]	4	THF	3.0	—	—

[a] St 4.4 mmol, [gua]e3fap 0.044 mmol, solvent 1.0 ml, under air, 70°C.
[b] 60°C.
[c] Determined by GPC with standard polystyrenes (eluent:THF).

Downloaded by [University Town Library of Shenzhen] at 00:40 02 January 2016

Downloaded by [University Town Library of Shenzhen] at 00:40 02 January 2016

Table 2. Effect of solvents on the polymerization of St initiated with [gua]e3fap[a]

Entry	Time (hr)	Solvent	Conversion (%)	$\overline{Mn}^c$	$\overline{Mw}/\overline{Mn}^c$
1	4	(Nil)	56.7	6000	1.74
2	4	Benzene	61.1	4000	1.74
3	4	Toluene	61.1	3000	1.83
4	4	Diglyme	2.1	—	—
5	4	Dioxane	1.6	—	—
6	4	Carbon tetrachloride	61.5	3000	1.94
7	4	DMF	0.0	—	—
8	4	DMSO	1.6	—	—
9[b]	4	THF	2.5	—	—

[a] St 4.4 mmol, [gua]e3fap 0.044 mmol, solvent 1.0 ml, under argon, 70°C.
[b] 60°C.
[c] Determined by GPC with standard polystyrenes (eluent:THF).

polymers are very small in spite of their relatively high percentages of conversion. This phenomenon can not be observed with conventional radical polymerization. Further, in order to compare the results of the St-polymerization, polymerizations of MMA and MA were carried out under the same reaction condition. The characterization data were summarized in Tables 3 and 4, respectively. In contrast to the St-polymerization (see Tables 1 and 2), it can be noted that the polymerizations of MMA and MA were completely inhibited or scarcely proceeded. For example, only a 13.3% conversion of MMA as the maximum value was observed in THF at 60°C under argon after 4 h, and only a 9.3% conversion as the maximum value was obtained in the case of the MA-polymerization in diglyme at 70°C under argon after 4 h. These experimental observations obtained here are suggestive of excellent initiating ability of [gua]e3fap on the vinyl polymerization for a limited kind of vinyl monomer. The facts that [gua]e3fap-initiated polymerization of St proceeds via

Table 3. Effect of solvents on the polymerization of MMA initiated with [gua]e3fap[a]

Entry	Time (hr)	Solvent	Conversion[c] (%)	Conversion[d] (%)
1	4	(Nil)	(Trace)	0.0
2	4	Benzene	0.0	0.0
3	4	Toluene	0.0	0.0
4	4	Diglyme	10.7	1.7
5	4	Dioxane	5.4	2.7
6	4	Carbon tetrachloride	0.0	0.0
7	4	DMF	1.0	0.0
8	4	DMSO	1.1	0.0
9[b]	4	THF	2.7	13.3

[a] MMA 4.7 mmol, [gua]e3fap 0.047 mmol, solvent 1.0 ml, 70°C.
[b] 60°C.
[c] under air. [d] under argon.

Downloaded by [University Town Library of Shenzhen] at 00:40 02 January 2016

Table 4. Effect of solvents on the polymerization of MA initiated with [gua]e3fap[a]

Entry	Time (hr)	Solvent	Conversion[c] (%)	Conversion[d] (%)
1	4	(Nil)	(Trace)	0.0
2	4	Benzene	1.2	0.0
3	4	Toluene	0.0	0.0
4	4	Diglyme	(Trace)	9.3
5	4	Dioxane	0.0	5.0
6	4	Carbon tetrachloride	1.8	0.3
7	4	DMF	0.9	(Trace)
8	4	DMSO	0.0	8.4
9[b]	4	THF	0.0	6.3

[a] MA 5.6 mmol, [gua]e3fap 0.056 mmol, solvent 1.0 ml, 70°C.
[b] 60°C.
[c] under air. [d] under argon.

radical mechanism, as described later, and that only a limited kind of vinyl monomer can be polymerized by [gua]e3fap suggest the attractive possibility of novel radical polymerization reaction.

St-Polymerizations Initiated with [gua]otf, [ewtmg]e3fap, and [ewtmg]otf

In order to shed light on the reaction mechanism of [gua]e3fap-initiated polymerization, the polymerizations of St, which was most smoothly polymerized by [gua]e3fap as described in the preceding section, initiated with other guanidinium-based ionic liquids such as [gua]otf, [ewtmg]e3fap, and [ewtmg]otf were examined next. Needless to say, the structural characteristic of these guanidinium-based ionic liquids can be explained as follows. The chemical structure of the cation of [gua]otf is same as that of [gua]e3fap, and the chemical structure of the anion of [ewtmg]e3fap is same as that of [gua]e3fap. [ewtmg]otf was formed

Table 5. Effect of solvents on the polymerization of St initiated with [gua]otf[a]

Entry	Time (hr)	Solvent	Conversion[c] (%)	Conversion[d] (%)
1	4	(Nil)	(Trace)	2.3
2	4	Benzene	(Trace)	2.0
3	4	Toluene (trace)	1.5	
4	4	Diglyme	2.1	2.1
5	4	Dioxane	1.5	3.5
6	4	Carbon tetrachloride	1.6	1.7
7	4	DMF	2.5	2.4
8	4	DMSO	2.5	4.1
9[b]	4	THF	2.0	4.1

[a] St 4.4 mmol, [gua]otf 0.044 mmol, solvent 1.0 ml, 70°C.
[b] 60°C.
[c] under air. [d] under argon.

Table 6. Effect of solvents on the polymerization of St initiated with [ewtmg]e3fap[a]

Entry	Time (hr)	Solvent	Conversion[c] (%)	Conversion[d] (%)
1	4	(Nil)	9.3	3.1
2	4	Benzene	2.2	2.2
3	4	Toluene (trace)	2.5	
4	4	Diglyme	4.2	2.3
5	4	Dioxane	4.0	3.3
6	4	Carbon tetrachloride	2.4	1.7
7	4	DMF	5.2	1.9
8	4	DMSO	3.0	1.6
9[b]	4	THF	0.0	1.8

[a] St 4.4 mmol, [ewtmg]e3fap 0.044 mmol, solvent 1.0 ml, 70°C.
[b] 60°C.
[c] under air.
[d] under argon.

Table 7. Effect of solvents on the polymerization of St initiated with [ewtmg]otf[a]

Entry	Time (hr)	Solvent	Conversion[c] (%)	Conversion[d] (%)
1	4	(Nil)	2.8	3.0
2	4	Benzene	0.0	1.7
3	4	Toluene	0.0	2.3
4	4	Diglyme	4.4	1.4
5	4	Dioxane	3.4	3.4
6	4	Carbon tetrachloride	0.0	2.1
7	4	DMF	1.5	2.3
8	4	DMSO	2.4	2.6
9[b]	4	THF (trace)	7.9	

[a] St 4.4 mmol, [ewtmg]otf 0.044 mmol, solvent 1.0 ml, 70°C.
[b] 60°C. [c] under air. [d] under argon.

from a combination of the anion of [gua]otf and the cation of [ewtmg]e3fap. Tables 5, 6, and 7 present the percent conversion and GPC results about the effect of solvents on the St-polymerizations initiated with [gua]otf, [ewtmg]e3fap, and [ewtmg]otf under air and argon, respectively. These St-polymerizations scarcely proceeded, compared with the St-polymerization initiated with [gua]e3fap under the same reaction conditions. On the basis of the experimental results, polymerization of St initiated with [gua]e3fap was investigated in detail as described below.

Bulk Polymerization of St Initiated with [gua]e3fap

The author's previous investigations provided a marked tendency for the radical polymerization initiated with other ionic liquids to proceed smoothly in limited solvents but to be depressed in bulk [10, 11]. In contrast to the fact, the remarkable feature of the St-polymerization initiated with [gua]e3fap is that the bulk polymerization proceeded

Downloaded by [University Town Library of Shenzhen] at 00:40 02 January 2016

Table 8. Polymerization of St initiated with [gua]e3fap in bulk[a]

Entry	Time (hr)	Atmosphere	Conversion (%)	$\overline{Mn}^b$	$\overline{Mw}/\overline{Mn}^b$
1	1	Air	2.7	—	—
2	2	Air	3.0	—	—
3	8	Air	10.9	7000	1.45
4	24	Air	25.1	9000	1.46
5	48	Air	34.5	8000	1.52
6	1	Argon	2.1	—	—
7	2	Argon	2.1	—	—
8	8	Argon	7.5	9000	1.43
9	24	Argon	15.3	9000	1.46
10	48	Argon	32.1	9000	1.51

[a] St 4.4 mmol, [gua]e3fap 0.044 mmol, 0°C.
[b] Determined by GPC with standard polystyrenes (eluent:THF).

smoothly, in which the conversion was 59.4% under air and the conversion was 56.7% under argon at 70°C in 4 hours, respectively (see Tables 1 and 2) In essence, the phenomenon that thermal self-initiated polymerizations of St at 70°C under air and under argon scarcely proceed was actually confirmed in the author's laboratory. The information provided conclusive proof that [gua]e3fap is the initiator of St polymerization. On the other hand, Table 8 shows the GPC results and the time-conversion data of the bulk polymerization of St initiated with [gua]e3fap under air and under argon at 0°C. In spite of the slow rate of polymerization, the bulk polymerization of St at 0°C proceeded gradually, and similar behavior of the polymerization was observed under air and under argon. Importantly, Table 8 clearly shows that the molecular weight of obtained polymer was constancy and relatively small during the entire polymerization process, in which the number-average molecular weight ($\overline{Mn}$) was 8000–9000. Table 8 further shows that the molecular weight distribution remains very constant with the polydispersity index (PDI = $\overline{Mw}/\overline{Mn}$) about 1.5. Whilst the polymerization was run at a temperature high, 30°C, to evaluate the effect of temperature on the bulk polymerization of St initiated with [gua]e3fap, and the results

Table 9. Polymerization of St initiated with [gua] e3fap in bulk[a]

Entry	Time (min)	Atmosphere	Conversion (%)	Mn^b	Mw/Mn^b
1	5	Air	3.8	12000	1.41
2	10	Air	5.1	11000	1.46
3	30	Air	8.6	11000	1.35
4	60	Air	25.4	10000	1.58
5	5	Argon	1.2	9000	1.46
6	10	Argon	5.9	11000	1.42
7	30	Argon	13.2	12000	1.46
8	60	Argon	24.7	11000	1.61

[a] St 4.4 mmol, [gua]e3fap 0.022 mmol, 30°C.
[b] Determined by GPC with standard polystyrenes (eluent:THF).

Downloaded by [University Town Library of Shenzhen] at 00:40 02 January 2016

Downloaded by [University Town Library of Shenzhen] at 00:40 02 January 2016

are summarized in Table 9. As seen in this table, the behavior of the polymerization at 30°C under air resembles that under argon very closely in a similar manner as the polymerization at 0°C mentioned above. However, contrary to the polymerization at 0°C, it can be noted that the polymerization at 30°C exhibited the rapid rate of polymerization. As a concrete example, about a 25% conversion of St under air was observed after 24 h at 0°C. The same conversion under air was obtained only after 1 h at 30°C. Anyhow, the obtained result that the bulk polymerization of St initiated with [gua]e3fap proceeds similarly regardless of its reaction temperature under air and under argon is particularly interesting, because the phenomenon was first found in my laboratory.

Effect of Radical Inhibitor and Radical Chain Transfer Agent on the Bulk Polymerization of St Initiated with [gua]e3fap

As reported previously [10–14], using other ionic liquids as an initiator of vinyl polymerization, it was strongly suggested that the polymerization proceeds via radical pathways in which the initiating radical is generated from the reaction mixture of monomer, solvent, and ionic liquid. In these meaning, it is noteworthy that [gua]e3fap-initiated polymerization of St proceeds in bulk as discussed above section. Consequently, in order to gain a better understanding of the St-polymerization initiated with [gua]e3fap in bulk, the effects of a radical inhibitor and a radical chain transfer agent were investigated on this polymerization.

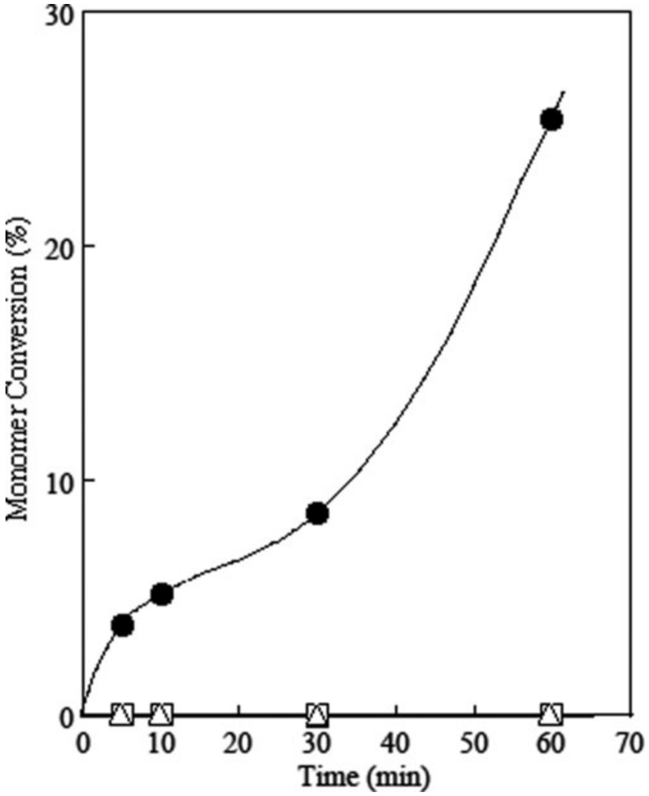


Figure 1. Polymerization of St initiated with [gua]e3fap in bulk. St 4.4 mmol, [gua]e3fap, 0.022 mmol, under air, 30°C, (•) control, (□) BHT 0.13 mmol, (△) 1-DT 0.13 mmol.

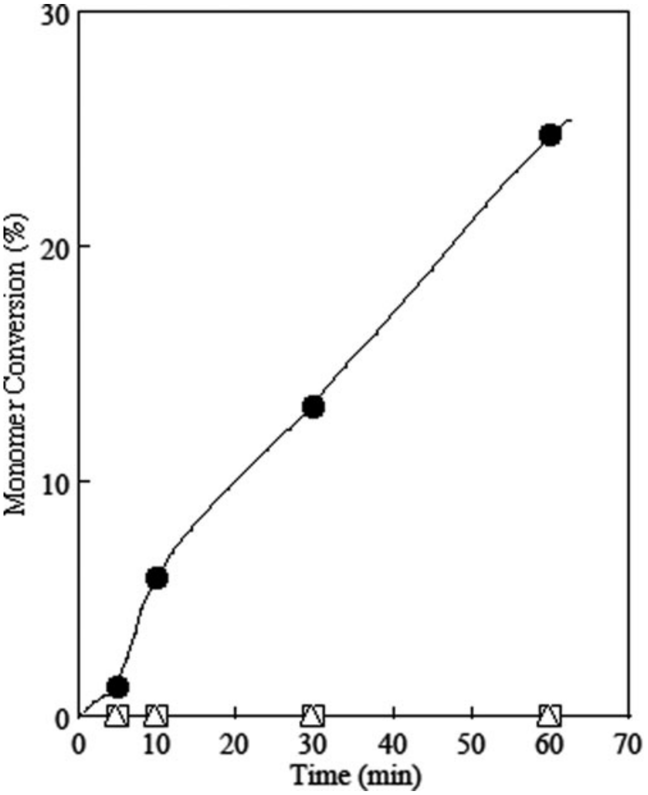


Figure 2. Polymerization of St initiated with [gua]e3fap in bulk. St 4.4 mmol, [gua]e3fap, 0.022 mmol, under argon, 30°C, (●) control, (□) BHT 0.13 mmol, (△) 1-DT 0.13 mmol.

Figs. 1 and 2 present the time-conversion plots about the effects of BHT as a radical inhibitor and 1-DT as a radical chain transfer agent on the bulk polymerization of St initiated with [gua]e3fap at 30°C under air and under argon, respectively. As shown in these figures, both polymerizations under air and under argon were perfectly inhibited in the presence of BHT and 1-DT. These experimental results strongly suggest that the [gua]e3fap-initiated polymerization of St in bulk at 30°C under air and under argon proceeds via radical pathway in a similar manner as the solution polymerization initiated with other ionic liquids as described before [10–14]. However, it can be presumed that the producing mechanism of initiating radical on the [gua]e3fap-initiated polymerization of St in bulk is different from that on the solution polymerization initiated with other ionic liquids. In other words, these mean that [gua]e3fap is a specific radical initiator compared with some other ionic liquid which was investigated as an novel radical initiator in my laboratory.

Polymerization of St Initiated with [gua]e3fap in Toluene

The fact that the bulk polymerization of St initiated with [gua]e3fap proceeds smoothly as described through preceding section is worthy of remark, whilst the [gua]e3fap-initiated polymerization of St proceeds in limited solvents (see Tables 1 and 2) in a similar manner as the polymerization initiated with other ionic liquids as investigated before [10–14].

Downloaded by [University Town Library of Shenzhen] at 00:40 02 January 2016

Downloaded by [University Town Library of Shenzhen] at 00:40 02 January 2016

Table 10. Effect of temperature on the polymerization of St initiated with [gua]e3fap in bulk[a]

Entry	Time (min)	Temperature (°C)	Conversion (%)	Mn^b	Mw/Mn^b
1	60	40	11.4	—	—
2	120	40	40.6	4000	1.67
3	240	40	57.4	3000	1.96
4	480	40	60.0	3000	2.11
5	30	50	18.7	4000	1.84
6	60	50	21.7	4000	1.69
7	120	50	54.5	3000	1.93
8	240	50	62.1	3000	2.05
9	10	60	3.5	3000	1.54
10	30	60	7.5	3000	1.75
11	90	60	40.6	2000	1.91
12	120	60	60.7	2000	2.07

[a] St 4.4 mmol, [gua]e3fap 0.022 mmol, toluene 1.0 ml, under air.
[b] Determined by GPC with standard polystyrenes (eluent:THF).

Consequently, in order to compare the results of the 'bulk' polymerization, solution polymerization of St initiated with [gua]e3fap in toluene was investigated in detail. Tables 10 and 11 show the GPC results and the time-conversion data of the effect of temperature on the polymerization of St initiated with [gua]e3fap in toluene under air and under argon,

Table 11. Effect of temperature on the polymerization of St initiated with [gua]e3fap in toluene[a]

Entry	Time (min)	Temperature (°C)	Conversion (%)	$\overline{Mn}^b$	$\overline{Mw}/\overline{Mn}^b$
1	60	40	33.5	—	—
2	120	40	56.1	4000	1.91
3	240	40	57.6	3000	1.94
4	480	40	57.1	3000	1.85
5	30	50	33.8	5000	1.64
6	60	50	47.7	3000	1.84
7	120	50	58.1	2000	2.52
8	240	50	59.7	3000	2.73
9	10	60	1.7	4000	1.40
10	30	60	16.1	4000	1.67
11	60	60	52.5	3000	2.03
12	90	60	60.9	3000	2.07

[a] St 4.4 mmol, [gua]e3fap 0.022 mmol, toluene 1.0 ml, under argon.
[b] Determined by GPC with standard polystyrenes (eluent:THF).

respectively. The solution polymerization of St initiated with [gua]e3fap in toluene, as well as the 'bulk' polymerization, proceeds similarly under air and under argon. Furthermore, the rate of the solution polymerization was almost same at temperatures of 40°C to 60°C, and suffice it to say that a decaying rate type curve was identified. The fact that rate curve of polymerization is the decaying rate type gives a clue to shed light on the polymerization mechanism. Because, in general, rate decay is attributed to reduce the number or activity of active centers. On the other hand, the tendency that the molecular weight of resulting polymer is very small in spite of its relatively high percentage of conversion becomes greater by comparison of its tendency of the 'bulk' polymerization, in which the reaction product was an oligomer. Since St and poly(St) are both soluble in toluene, initiation and propagation occur in a homogeneous environment of the polymerization media. Under such reaction condition of the radical polymerization, it is generally accepted that the molecular weight of the resulting polymer is lower than in bulk [20]. However, as to the solution polymerization of St initiated with [gua]e3fap in toluene, the tendency was progressively great. Therefore, this result is to be expected for the application about the synthesis of St-oligomer in good yield. Whilst Figs. 3 and 4 report the time-conversion plots about the effects of radical inhibitors and a radical chain transfer agent at 50°C as typical examples

Downloaded by [University Town Library of Shenzhen] at 00:40 02 January 2016

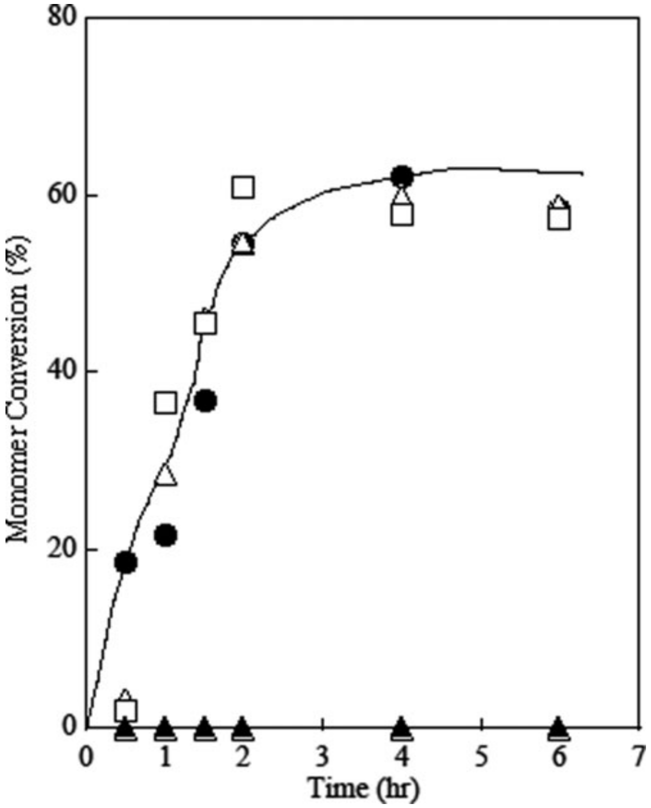


Figure 3. Polymerization of St initiated with [gua]e3fap in toluene. St 4.4 mmol, toluene 1.0 ml, [gua]e3fap 0.022 mmol, under air, 50°C, (●) control, (□) HQ 0.13 mmol, (△) BHT 0.13 mmol, (▲) 1-DT 0.13 mmol.

Downloaded by [University Town Library of Shenzhen] at 00:40 02 January 2016

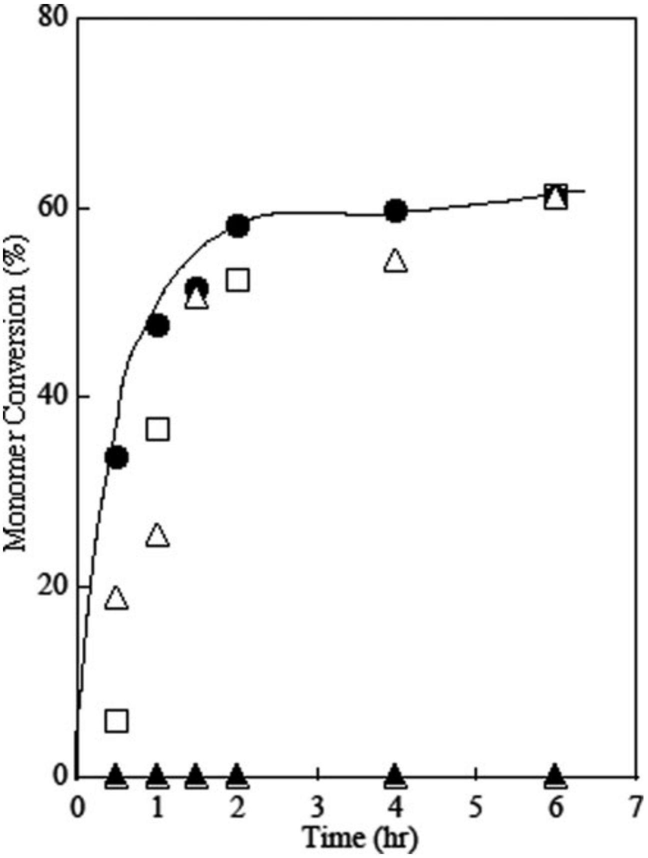


Figure 4. Polymerization of St initiated with [gua]e3fap in toluene. St 4.4 mmol, toluene 1.0 ml, [gua]e3fap, 0.022 mmol, under argon, 50°C, (•) control, (□) HQ 0.13 mmol, (△) BHT 0.13 mmol, (▲) 1-DT 0.13 mmol.

of the solution polymerization of St initiated with [gua]e3fap in toluene under air and argon, respectively. The effects of radical inhibitors and a radical chain transfer agent on the [gua]e3fap-initiated polymerization of St in toluene were similar under air and under argon as well as those on the 'bulk' polymerization of St initiated with [gua]e3fap as described in the proceeding section. In other words, 1-DT as a radical chain transfer agent completely inhibited the solution polymerization of St in toluene under air and under argon. Furthermore, as to the St-polymerization in toluene under air and under argon, induction period was observed by the addition of HQ and BHT as radical inhibitors. Needless to say, the radical inhibitor reacts quickly with every initiating free radical in the process. Therefore, the radical inhibitor prevents any polymerization reaction from taking place until it is perfectly consumed in the polymerization media. As a result, well-defined induction periods exist. Tables 12 and 13 show the effect of HQ and BHT on the solution polymerization of St initiated with [gua]e3fap at 50°C in toluene under air and under argon, respectively. The values of number-average molecular weights and polydispersities of both polymer obtained with the additives, Tables 12 and 13, and that without the additives, entry 6–11 of Tables 10 and 11, are similar, e.g., number-average molecular weight = 2000–5000 against 2000–5000, $\overline{Mw}/\overline{Mn} = 1.42$–$2.43$ against 1.59–2.74. That is to say, the fact suggests that

Table 12. Effect of additives on the polymerization of St initiated with [gua]e3fap in toluene[a]

Entry	Time (min)	Additive[b]	Conversion (%)	$\overline{Mn}^c$	$\overline{Mw}/\overline{Mn}^c$
1	30	HQ	1.9	—	—
2	60	HQ	36.5	3000	1.67
3	120	HQ	60.9	3000	1.97
4	240	HQ	57.8	2000	2.08
5	30	BHT	3.2	4000	1.43
6	60	BHT	28.7	5000	1.55
7	120	BHT	54.8	3000	1.76
8	240	BHT	60.0	3000	1.79

[a] St 4.4 mmol, [gua]e3fap 0.022 mmol, toluene 1.0 ml, under air, 50°C.
[b] 0.13 mmol.
[c] Determined by GPC with standard polystyrenes (eluent:THF).

the polymerization normally proceeds after the radical inhibitors are consumed in the process. As a result, the experimental data about the effects of radical inhibitors and a radical chain transfer agent strongly indicate that the solution polymerization of St initiated with [gua]e3fap in toluene proceeds via a free-radical mechanism in a similar manner as the 'bulk' polymerization of St.

Kinetic Analysis on the Polymerization of St Initiated with [gua]e3fap in Bulk

From the results described in the preceding sections, without doubt, the polymerization of St initiated with [gua]e3fap proceeds via a radical pathway, but the details of the mechanism of the St-polymerization are still obscure. The polymerization of vinyl monomer initiated

Table 13. Effect of additives on the polymerization of St initiated with [gua]e3fap in toluene[a]

Entry	Time (min)	Additive[b]	Conversion (%)	$\overline{Mn}^c$	$\overline{Mw}/\overline{Mn}^c$
1	30	HQ	5.9	4000	1.42
2	60	HQ	36.8	4000	1.66
3	120	HQ	52.4	3000	2.17
4	360	HQ	61.3	2000	2.43
5	30	BHT	18.9	5000	1.51
6	60	BHT	25.5	4000	1.50
7	90	BHT	50.5	3000	1.71
8	240	BHT	54.5	3000	1.75
9	360	BHT	61.1	3000	1.79

[a] St 4.4 mmol, [gua]e3fap 0.022 mmol, toluene 1.0 ml, under argon, 50°C.
[b] 0.13 mmol.
[c] Determined by GPC with standard polystyrenes (eluent:THF).

Downloaded by [University Town Library of Shenzhen] at 00:40 02 January 2016

Downloaded by [University Town Library of Shenzhen] at 00:40 02 January 2016

with [gua]e3fap reveals a few important features that can be explained as follows: 1) Only the St-polymerization proceeds smoothly, while the polymerizations of MMA and MA do not occur or scarcely proceed. 2) The behavior of the St-polymerization under air is similar to that under argon. In addition, the serious difference between the [gua]e3fap-initiated polymerization of St and the vinyl polymerization initiated with other ionic liquids as investigated before [10–14] was observed. In the former case, the polymerization reaction proceeds in bulk. Consequently, in order to shed more light on the polymerization mechanism, the author evaluated the kinetic order of the ‘bulk’ polymerization of St. Figs. 5 and 6 present the log-log plots of R_p versus [gua]e3fap concentration, .where R_p is the initial rate of polymerization, on the bulk polymerization of St initiated with [gua]e3fap at 30°C under air and under argon, respectively. As seen in Fig. 5, the initial rate of the [gua]e3fap-initiated polymerization of St in bulk under air at 30°C was proportional to the 1.00 power of [gua]e3fap concentration. In addition, from Fig. 6, it can be noted that the initial rate of the bulk polymerization of St initiated with [gua]e3fap under argon at 30°C was proportional to the 2.45 power of [gua]e3fap concentration. It is generally accepted that the initial rate of conventional radical polymerization is proportional to the square root of initiator concentration, because of bimolecular termination with respect to the propagating chain-end. Therefore, regarding the experimental results described above, the kinetic order of [gua]e3fap-initiated polymerization of St in bulk is completely different from that of conventional radical polymerization. On the other hand, in conventional radical polymerization, the kinetic order with respect to initiator concentration exceeded 0.5, suggests a

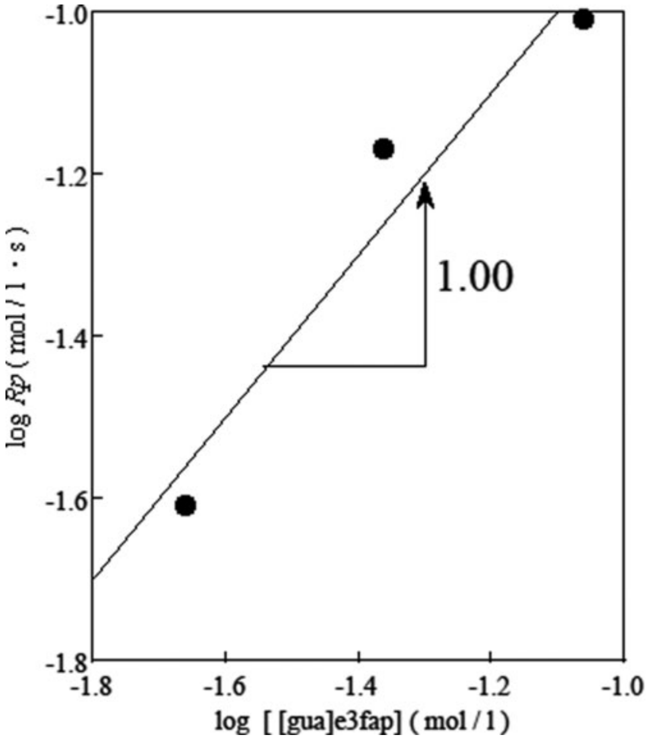


Figure 5. Dependence of the rate of polymerization on [gua]e3fap concentration in bulk. St 4.4 mmol, under air, 30°C.

Downloaded by [University Town Library of Shenzhen] at 00:40 02 January 2016

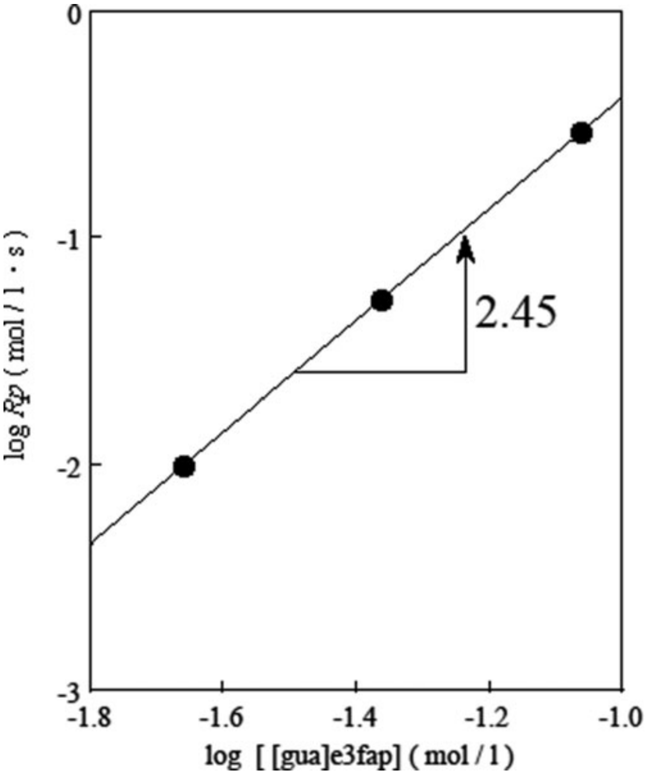


Figure 6. Dependence of the rate of polymerization on [gua]e3fap concentration in bulk. St 4.4 mmol, under argon, 30°C.

unimolecular termination of the propagating radical chain end. That is to say, as to the the bulk polymerization of St initiated with [gua]e3fap, a unimolecular termination may occur, but the detailed reaction mechanism is still unclear. From the results described in this section and in the preceding sections, true catalytic mechanism of [gua]e3fap for the vinyl polymerization is not understood at this time. Therefore, further experiments to determine the catalytic mechanism of [gua]e3fap are underway in the author's laboratory.

Conclusion

The main focus of this study is to find the new possibility of ionic liquids as an initiator for vinyl polymerization. That is to say, the vinyl polymerization initiated with guanidinium-based ionic liquids such as [gua]e3fap, [gua]otf, [ewtmg]e3fap, and [ewtmg]otf has been investigated in detail to find the new application of ionic liquids. As a conclusion, it has been shown for the first time that [gua]e3fap exhibited the initiating ability of vinyl polymerization. The most remarkable feature of the vinyl polymerization initiated with [gua]e3fap is the fact that only the St-polymerization proceeds smoothly at 70°C under air and under argon, but the polymerizations of MMA and MA under same reaction conditions scarcely proceed. The important characteristic of the St-polymerization initiated with [gua]e3fap can be explained as follows: 1) The bulk polymerization and the solution polymerization in benzene, toluene and carbon tetrachloride proceeded smoothly, whereas

Downloaded by [University Town Library of Shenzhen] at 00:40 02 January 2016

the solution polymerization in diglyme, dioxane, DMSO, DMF and THF was strictly inhibited. 2) The molecular weights of obtained poly(St) were very small in spite of their relatively high percentages of conversion. 3) The fact that the inhibitory effects were observed by the addition of BHT or HQ as a radical inhibitor and 1-DT as a radical chain transfer agent in the polymerization media, suggested the polymerization proceeds via a radical pathway. 4) The kinetics about the polymerization was completely different from that of traditional radical polymerization. Whilst, in contrast to the St-polymerization initiated with [gua]e3fap, the St-polymerization initiated with [gua]otf, [ewtmg]e3fap, and [ewtmg]otf scarcely proceeded under same reaction conditions. It is not possible at the present time to give a definitive mechanism for the vinyl polymerization initiated with [gua]e3fap. With the results obtained here, however, it may be possible to employ the system of St-polymerization initiated with [gua]e3fap as the industrial production of St-oligomer. Anyhow, the author believes that the use of ionic liquids as an initiator for radical polymerization opened up a wide field for future investigations about ionic liquids. Therefore, work in this field of the polymerization using ionic liquids as an initiator is currently in progress in the author's laboratory.

References

[1] Scheffler, T. B., Hussey, C. L., Seddon, K. R., Kear, C. M., & Armitage, P. D. (1983). *Inorg. Chem.*, *22*, 2099.
[2] Laher, T. M., & Hussey, C. L. (1983). *Inorg. Chem.*, *22*, 3247.
[3] Scheffler, T. B., & Hussey, C. L. (1984). *Inorg. Chem.*, *23*, 1926.
[4] Hitchcock, P. B., Mohammed, T. J., Seddon, K. R., Zora, J. A., Hussey, C. L., & Ward, E. H. (1986). *Inorg. Chim. Acta*, *113*, L25–L26.
[5] Claude, F. (1997). *European Patent, FP 97-100109.*
[6] Biedron, T., & Kubisa, P. (2002). *J. Polym. Sci. Polym. Chem. Ed.*, *40*(16), 2799.
[7] Ma, H., Wan, X., Chen, X., & Zhou, Q.-F. (2003). *Polymer*, *44*, 5311.
[8] Rogers, R. D., & Brazel, C. S. (Eds.), (2005). *Ionic Liquids in Polymer Systems; ACS Symposium Series 913*, American Chemical Society: Washington, DC.
[9] Wasserscheid, P., & Welton, T. (Eds.), (2003). *Ionic Liquids in Synthesis*, Wiley VCH: Weinheim.
[10] Kanno, S. *Japanese Patent*, Patent Number 4719076.
[11] Kanno, S. *Japanese Patent*, Patent Number 4719080.
[12] Kanno, S. (2010). *BOOK OF ABSTRACTS EUCHEM 2010 Conference on Molten Salts and Ionic Liquids*, 105. Bamberg, Germany.
[13] Kanno S. (2010). Macro2010–*43rd IUPAC World Polymer Congress Polymer Science in the Service of Society–Abstract book and programme, (2010)*, C11–O23. (Scottish Exhibition and Conference Centre/Glasgow, UK)
[14] Kanno, S. (2012). *Molecular Crystals & Liquid Crystals*, *556*, 61.
[15] Welton, T. (1999). *Chem. Rev.*, *99*, 2071.
[16] Holbrey, J. D., & Seddon, K. R. (1999). *Clean Prod. Proc.*, *1*, 223.
[17] Wasserscheid, P., & Keim, W. (2000). *Angew. Chem. Int. Ed.*, *39*, 3772.
[18] Sheldon, R. (2001). *Chem. Commun.*, 2399.
[19] Gordon, C. M. (2002). *Appl. Catal. A*, *222*, 101.
[20] Ravve, A. (1995). *Principles of Polymer Chemistry*, Plenum Press: New York, p. 69.